Nuclear Science and Technology

Shunzhong Luo

Nuclear Science and Technology

Isotopes and Radiation

哈爾濱工程大學出版社
Harbin Engineering University Press

Springer

Nuclear Science and Technology

Series Editors

Junchong Yu, Nuclear Power Institute of China, Chengdu, Sichuan, China

Hong Xia, Nuclear Science and Technology, Harbin Engineering University, Harbin, China

Yongping Li, Shanghai Institute of Applied Physics, Shanghai, China

This interdisciplinary book series publishes monographs and edited volumes in all areas of nuclear science and technology, covering developments in theoretical research, experiments, technology and applications. The series attempts to bring together experts and professionals from all over the world, to provide readers with a library on a wide range of topics in physics, engineering, medicine and environmental sciences. Topics include but are not limited to:

Nuclear physics and interdisciplinary research;
Nuclear energy science and engineering;
Nuclear fusion and high temperature plasmas;
Synchrotron radiation applications, beamline technology;
Accelerator, ray technology and applications;
Nuclear chemistry, radiochemistry, radiopharmaceuticals, nuclear medicine; and Nuclear electronics and instrumentation.

The books are intended for researchers, professionals, and students in the field, as well as those interested in staying current with the latest advances.

Shunzhong Luo

Nuclear Science and Technology

Isotopes and Radiation

哈爾濱工程大學出版社
Harbin Engineering University Press

Springer

Shunzhong Luo
Institute of Nuclear Physics and Chemistry,
CAEP
Mianyang, China

ISSN 2948-1856 ISSN 2948-1864 (electronic)
Nuclear Science and Technology
ISBN 978-981-99-3086-9 ISBN 978-981-99-3087-6 (eBook)
https://doi.org/10.1007/978-981-99-3087-6

Jointly published with Harbin Engineering University Press
The print edition is not for sale in China (Mainland). Customers from China (Mainland) please order the print book from: Harbin Engineering University Press.

Translation from the Chinese edition: "He Ji Shu Ying Yong" by Shunzhong Luo, © Harbin Engineering University Press 2021. Published by Harbin Engineering University Press. All Rights Reserved.

© Harbin Engineering University Press 2023

This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publishers, the authors, and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publishers nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publishers remain neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Preface

In 1896, A. H. Becqueral discovered the natural radioactivity of uranium. From then on, major scientific events such as the discovery of artificial radioactivity, the establishment of atomic nuclear models, the construction and operation of accelerators and reactors, and the success of the first atomic bomb explosion laid the scientific foundation for the formation of a new discipline, namely nuclear science and technology.

In 1905, radium was used for internal irradiation for radiation therapy. Subsequently, the emergence of non-destructive testing by X-ray radiography, the application of radioactive tracing in biological research, the acquisition of radiation breeding varieties, the successful development of automatic medical isotope scanners, and the realization of radiation cross-linking of polymer compounds have promoted the formation of a technological foundation in the emerging field of non-power nuclear science and technology applications (referred to as nuclear technology applications or isotope and radiation technology applications).

In 1955, the first International Conference on the Peaceful Uses of Atomic Energy was held in Geneva, which was a milestone in promoting a world consensus on the controllable use of atomic energy for the benefit of mankind and promoting the technological development of nuclear technology applications.

After over a hundred years of development, nuclear technology and its applications have played an irreplaceable role in solving the basic problems faced by mankind, breaking through the bottleneck of modern science and technology, and promoting scientific and technological progress. They have had a tremendous impact on world politics, economy, and society. Through the intersection and integration with scientific disciplines, the application of nuclear technology has enabled people to shift their horizons from macro to micro, trace their understanding from the present to the past, and make it possible to dynamically study changes in matter and observe natural phenomena at the molecular (even atomic, nuclear) level. By radiating and driving into the economic field, nuclear technology has promoted technological innovation in traditional industries, promoted the rapid growth of emerging industries, and ensured the healthy development of the national economy and the harmonious coexistence of society and nature. The International Atomic Energy Agency (IAEA)

once pointed out in a report that only modern electronics and information technology can be compared to isotope and radiation technology in terms of the breadth of application.

The author of this book has been involved in the field of nuclear technology since the early 1980s. He has organized and carried out a large number of systematic studies on the preparation and application of radioisotopes with important application value, as well as the behavioral chemistry of some special nuclides, and has published over 100 papers. This book is compiled based on a "handout" for graduate education formatted according to the accumulation of the above research work and the author's grasp of the development of nuclear technology and its application.

The book is divided into nine chapters, starting with the basic principles, methods, and characteristics, and systematically summarizes the extensive applications, achievements, and development trends of nuclear technology in various fields of the national economy. This book can be used as a textbook for nuclear science and technology majors in colleges and universities, as well as optional teaching materials and references for related majors. It can also be used as a reference book for technical practitioners in nuclear technology research and application.

During the preparation of this book, a large number of documents and materials were consulted, some data and charts were cited, and some ideas (including results and conclusions) were excerpted. The main citation sources have been listed in the references. The writing team expresses its sincere gratitude to the authors of all the literature and materials referred to.

Mianyang, China Shunzhong Luo
March 2023

Acknowledgments

The author would like to express his special and sincere thanks to the following academicians who generously provided directions and concern during the preparation of the Chinese manuscript:

Side Hu
Yibei Fu

The author wishes to thank the following individuals for their hard work and great contributions to the completion of the first version of this book:

Jiaheng He (Institute of Nuclear Physics and Chemistry, CAEP)
Jiarong Lei (Institute of Nuclear Physics and Chemistry, CAEP)
Guoping Liu (Institute of Nuclear Physics and Chemistry, CAEP)
Xiuhua Liu (Institute of Nuclear Physics and Chemistry, CAEP)
Hongtao Song (Institute of Nuclear Physics and Chemistry, CAEP)
Huaming Zhang (Institute of Nuclear Physics and Chemistry, CAEP)
Wenbin Zhong (Institute of Nuclear Physics and Chemistry, CAEP)

During the preparation of the Chinese version, many experts and scholars in the field of nuclear technology applications helped to revise the relevant chapters and provided many valuable comments, the author would like to express his sincere gratitude for their generous help, and by name to:

Dianhua Chen (former Secretary General of the China Isotope and Radiation Association)
Hao Chen (Sichuan Institute of Atomic Energy)
Houfu Deng (Sichuan University)
Manchang Fu (former Chairman of the State Nuclear Power Technology Company)
Ning Liu (Sichuan University)
Bangfa Ni (China Institute of Atomic Energy)
Peixin Zhang (China Institute of Atomic Energy)

The publication of this book has received the support from the Institute of Nuclear Physics and Chemistry of the China Academy of Engineering Physics, and the author hereby expresses his sincere gratitude.

Thanks to **Yingying Zhang** and **Ling Shi** from the editorial department of Harbin Engineering University Press for their hard work.

The author is grateful to his family for their silent support and selfless efforts over the years.

Contributors

Min Huang
Yaodan Jia
Yisong Lei
Xingliang Li
Hu Song
Jing Wang
Hongyuan Wei
Yanqiu Yang
Yuqing Yang

Contents

1 Introduction 1
1.1 History of Nuclear Technology 1
1.2 Definition, Basic Concepts, and Terminology 3
1.2.1 Nuclear Technology 3
1.2.2 Elements, Isotopes, and Nuclides 4
1.2.3 Basic Quantities and Concepts 6
1.2.4 Radiation and Rays 10
1.2.5 Nuclear Decay and Nuclear Reaction 11
1.2.6 Interaction of Alpha Radiation with Matter 12
1.2.7 Interactions of β-Rays with Matter 13
1.2.8 Interaction of Gamma Rays with Matter 14
1.2.9 Interaction of Neutrons with Matter 16
1.2.10 Radioanalytical Technology 18
1.2.11 Radiation Processing Technology 20
1.2.12 Basic Knowledge of Radiation Protection 21
1.3 Applications and Developments of Nuclear Technology 22
1.3.1 Nuclear Technology in Energy 22
1.3.2 Nuclear Technology in the Industry 23
1.3.3 Nuclear Technology in Agriculture 25
1.3.4 Nuclear Technology in Medicine 26
1.3.5 Nuclear Technology in Environmental Protection 28
Bibliography 30

2 Preparation of Radionuclides 31
2.1 Sources of Radionuclides 31
2.1.1 Natural Radionuclides 32
2.1.2 Artificial Radionuclides 35
2.2 Production of Radionuclides in Reactors 36
2.2.1 Neutron Nuclear Reactions and Their Characteristics 37
2.2.2 Production of Radionuclides by Reactor Irradiation 39
2.2.3 Extraction of Radionuclides from Fission Products 52

2.3 Production of Radionuclides by Accelerators 65
2.3.1 Brief History of the Development of Accelerator-Produced Radionuclides 66
2.3.2 Components and Classification of Accelerators 66
2.3.3 Characteristics of Radionuclides Produced by Accelerators 69
2.3.4 Types of Nuclear Reactions for Radionuclide Production by Accelerators 69
2.3.5 Production of Radionuclides by Accelerators 70
2.3.6 Application of Radionuclides Produced by Accelerators 74
2.3.7 Production of Radionuclides ^{123}I by Accelerators 74
2.4 Radionuclide Generators 76
2.4.1 Fundamentals 77
2.4.2 Types of Radionuclide Generators 78
2.4.3 Requirements for the Preparation of Radionuclide Generators 79
2.4.4 Requirements for Medical Radionuclide Generators 80
2.4.5 Preparation of Major Radionuclide Generators 80
Bibliography 89

3 Nuclear Analytical Techniques and Methods 91
3.1 Overview of Nuclear Analytical Techniques and Methods 92
3.1.1 Classification of Nuclear Analytical Techniques 92
3.1.2 Principles of Nuclear Analytical Techniques 93
3.1.3 Characteristics of Nuclear Analytical Techniques 93
3.2 X-Ray Fluorescence Analysis 94
3.2.1 Principle and Characteristics of X-Ray Fluorescence Analysis 95
3.2.2 Basic Structure of the X-Ray Fluorescence Spectrometer 98
3.2.3 Qualitative and Quantitative Analytical Methods 99
3.3 Neutron Activation Analysis 101
3.3.1 Principle and Characteristics of Activation Analysis 102
3.3.2 Classification of Activation Analysis 105
3.3.3 History of Neutron Activation Analysis Techniques 106
3.3.4 Neutron Activation Source 107
3.3.5 Process of Neutron Activation Analysis 108
3.3.6 Application of Neutron Activation Analysis 109
3.4 Isotopic Tracer Technique 110
3.4.1 Principles and Characteristics of Isotopic Tracing 110
3.4.2 Application of Isotope Tracer Techniques in Life Science 112

3.5 Neutron Diffraction 117
3.5.1 Principle and Characteristics of Neutron Diffraction 117
3.5.2 Neutron Diffraction Device 118
3.5.3 Applications of Neutron Diffraction 119
3.6 Neutron Radiography 123
3.6.1 Principles and Characteristics of Neutron Radiography 123
3.6.2 Classification of Neutron Radiography 125
3.6.3 Neutron Photographic Device 125
3.6.4 Factors Affecting Image Quality of Neutron Radiography 126
3.6.5 Applications of Neutron Radiography 127
Bibliography 129

4 Nuclear Instrumentation 131
4.1 Overview of Nuclear Instrumentation 132
4.1.1 Characteristics and Application of Nuclear Instrumentation 132
4.1.2 Historical Development of Nuclear Instrumentation 134
4.1.3 Technical Advantages and Economic Benefits of Nuclear Instrumentation 136
4.2 Classification and Principle 139
4.3 Core Components—Radioactive Source and Detector 142
4.3.1 Radioactive Sources 142
4.3.2 Detectors 154
4.4 Application of Nuclear Instrumentation 159
4.4.1 Intensity Nuclear Instrumentation 159
4.4.2 Digital Image Processing Instrumentation 170
4.4.3 Energy Spectrum Nuclear Analytical Instrumentation 177
4.5 Trend of Development 179
Bibliography 181

5 Radiation Processing 183
5.1 Basic Knowledge of Radiation Processing 184
5.1.1 Definition of Radiation Processing 184
5.1.2 Irradiation Facility 185
5.1.3 Advantages of Radiation Processing Technology 189
5.2 Radiation Crosslinking 189
5.2.1 Mechanisms of Polymer Radiation Crosslinking 190
5.2.2 Radiation Crosslinking of Thermoplastic Polymers 202
5.2.3 Typical Radiation Crosslinking Formula of Thermoplastic Polymers 218
5.2.4 Main Applications of Thermoplastic Polymer Radiation Crosslinking Products 226
5.2.5 Comparison Between Radiation Crosslinking Technology and Chemical Crosslinking Technology 230
5.2.6 Summary 232

5.3 Radiation Polymerization 233
5.3.1 Liquid Phase Polymerization and Homogeneous Polymerization 233
5.3.2 Solid Phase Polymerization 235
5.3.3 Emulsion Polymerization 236
5.4 Radiation Grafting and New Material Preparation 238
5.4.1 Basic Principle of Radiation Grafting 238
5.4.2 Principle of the Preparation of New Materials by Radiation 240
5.4.3 Main Methods of Preparing Materials by Radiation 242
5.4.4 Applications of Functional Materials Prepared by the Radiation Method 244
5.4.5 Prospects of Nanomaterials Prepared by the Radiation Method 246
5.5 Radiation Degradation 247
5.6 Radiation Curing and Its Applications 251
5.6.1 Basic Principle of Radiation Curing 251
5.6.2 Main Components of Radiation Curing Formulas and Curing Processes 254
5.6.3 Application of Radiation Curing 259
Bibliography 261

6 Application of Nuclear Technology in Medicine 263
6.1 Medical Radionuclides 264
6.1.1 Radionuclides for Diagnosis 264
6.1.2 Therapeutic Radionuclides 266
6.2 Diagnostic Radiopharmaceuticals 266
6.2.1 Cardiovascular Imaging Agents 268
6.2.2 Brain Imaging Agent 273
6.2.3 Tumor Imaging Agent 277
6.2.4 Other Organ Imaging Agents 281
6.3 Therapeutic Radiopharmaceuticals 284
6.3.1 Small Molecule Radiotherapeutic Drugs 285
6.3.2 Targeted Therapy Radiopharmaceuticals 288
6.3.3 Colloidal and Microsphere Formulation-Based Radiotherapeutic 290
6.4 Nuclear Medical Imaging Techniques and the Equipment 290
6.4.1 SPECT 291
6.4.2 PET 292
6.5 Neutron Capture Therapy 293
6.6 Radiotherapy 296
6.6.1 Mechanism of Action 298
6.6.2 Teletherapy 299
6.6.3 Brachytherapy 301

6.7 Application Prospect of Nuclear Technology in Medicine 303
Bibliography 306

7 Application of Nuclear Technology in the Environment 309
7.1 Application of Irradiation Technology in the Environment 310
7.1.1 Reactors in the Environment 311
7.1.2 Accelerators in the Environment 315
7.2 Application of Nuclear Analytical Technique in the Environment 324
7.2.1 Application of Neutron Activation Analysis in the Environment 326
7.2.2 Application of Isotopic Tracer Technology in the Environment 331
7.3 Application Prospect of Nuclear Technology in Environmental Science 336
Bibliography 337

8 Applications of Nuclear Technology in Agriculture 339
8.1 Radiation Breeding 340
8.1.1 History of Radiation Breeding 340
8.1.2 Basic Principles of Radiation Breeding 341
8.1.3 Radiation Breeding Method 351
8.1.4 Application and Prospect of Radiation Breeding 361
8.1.5 Compound Mutation 364
8.2 Radiation Preservation 365
8.2.1 Introduction to Radiation Preservation 365
8.2.2 Research and Application Status of Irradiation Worldwide 369
8.2.3 Prospect 370
8.3 Radiation Disinfestation 371
8.3.1 Introduction to Radiation Disinfestation Method 371
8.3.2 Characteristics of Sterile Insect Technique 377
8.3.3 Lethal Dose 378
8.4 Prospects of Nuclear Technology Applications in Agriculture 379
8.4.1 Water Content Measurement in Large Areas by Cosmic-Ray Neutron Sensor 379
8.4.2 Treatment of Radioactively Contaminated Soil 381
8.4.3 Soil Erosion Assessment and Ocean Acidification Monitoring 381
8.4.4 Other Prospects on Nuclear Agronomy 381
Bibliography 382

9 Peaceful Use of Nuclear Energy 385
9.1 Principles of Nuclear Energy and Characteristics of Nuclear Power Generation 386
9.1.1 Nuclear Fission Energy 387

9.1.2 Nuclear Fusion Energy 388
9.1.3 Characteristics of Nuclear Power Generation 389
9.1.4 Application Field of Nuclear Energy 390
9.2 Nuclear Fission Power Generation 390
9.2.1 Working Principle of Nuclear Power Plants 391
9.2.2 Composition of Nuclear Reactor 391
9.2.3 Structural Form and Classification of Nuclear Fission Reactor 392
9.2.4 History and Current Situation of Nuclear Power Generation 394
9.3 Research Progress of Fusion Power Generation and Thermal Fusion Reactor 398
9.3.1 Advantages of Nuclear Fusion Energy 399
9.3.2 Basic Conditions for Realizing Nuclear Fusion 400
9.3.3 Plasma Confinement 401
9.3.4 History of Controllable Nuclear Fusion 403
9.3.5 Overview of the ITER Project 405
9.4 Other Forms of Nuclear Energy Utilization 406
9.4.1 Space Nuclear Energy 407
9.4.2 Radionuclide Decay Energy Power Generation—Radioisotope Battery 408
9.4.3 Radioluminescence 414
9.4.4 Nuclear Heating 415
9.4.5 Hydrogen Production by Nuclear Energy 415
9.4.6 Desalination of Seawater by Nuclear Energy 416
9.4.7 Other Applications of Nuclear Energy 417
9.5 Sustainable Development of Nuclear Energy 417
9.5.1 Challenges for Nuclear Energy Development 418
9.5.2 Current Spent Fuel Disposal Method 419
9.5.3 Establish an Advanced Nuclear Fuel Cycle System to Ensure the Sustainable Development of Nuclear Energy 421
9.5.4 Solutions to Uranium Resource Shortage 427
Bibliography 428

Appendix A: International System of Units (SI) 431

Appendix B: Legal Unit of Measurement 433

Appendix C: Fundamental Physical Constant 435

Appendix D: Periodic Table of the Elements 437

Chapter 1
Introduction



1.1 History of Nuclear Technology

The development and utilization of nuclear energy and nuclear radiation began in the late 1930s, which deepened the understanding of nuclear radiation and its interactions with materials. Applications of such knowledge to modern scientific and technological research, to explore new fields, interpret new phenomena, and confirm new substances, gradually generated an emergent branch of science and technology with rich connotations and cross-fertilization with multiple disciplines, namely nuclear science and technology or nuclear technology for short. The build-up of nuclear technology is a milestone in the history of human civilization in the twentieth century and one of the significant symbols of social modernization.

Nuclear technology, an important component of modern science and technology, is one of the most significant cutting-edge technologies in contemporary times, widely used in many fields, such as national defense, scientific research, industry, agriculture, medicine, communication, transportation, environmental protection, archaeology, resource development, space exploration, etc. Nuclear technology is a relatively independent and complete research and application system, behaving the characteristics of knowledge-intensity, cross-penetrating, irreplaceability, high efficiency, and wide adaptability. Nuclear technology has been embraced in the arena of the global high-tech competition as the driving force for the innovative development of new technologies, materials, and methods, and global economic growth.

Nuclear technology is generally composed of nuclear weapons technology, nuclear power technology, and isotope and radiation technology (also known as non-power nuclear technology). The scope of this book is controlled within radiation technology, including radionuclide preparation, nuclear analytical techniques, nuclear instrumentation, radiation processing, and the application of nuclear technology in medicine, agriculture, environment, etc., and peaceful usage of nuclear energy.

Following the first discovery of the radioactivity of uranium salts, French scientists Pierre and Marie Curie discovered polonium (Po) and radium (Ra) in 1898 and refined

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6_1

0.1 g of radium salts and a few milligrams of polonium in 1902. The discovery of radium caused revolutionary changes in science and philosophy, which opened the door to explore the mysteries of the atomic world. The following events laid scientific foundations for the birth of nuclear technology and contributed to the rapid development of its applications.

- In 1898, E. Rutherford deflected uranium radiations with a strong magnet and found that at least two types of radiation in opposite directions were present: one is readily absorbed and termed α-radiation, the other one is penetrative and termed β-radiation. In 1900, Paul Villard observed that besides α- and β-radiation, there was a third type of radiation emitted by radium which was unaffected by magnetic fields and termed γ-radiation.
- In 1930, German physicists E. Bothe and H. Becker found mysterious radiation emitted from beryllium, lithium, and boron nuclei bombarded with α-particles, which were of strong penetration ability, and discharged a counter. In 1932, British physicist J. Chadwick argued that this "radiation" consisted of particles of mass nearly equal to that of a proton and with no net charge, termed neutron. After that, the neutron became an important tool for scientists in nuclear science, promoting the rapid development of nuclear science and technology.
- Around 1930, British physicists J. D. Cockcroft and E. T. Walton built the first particle accelerator.
- In 1931, American physicist R. J. Van de Graaft built an electrostatic accelerator, and American physicists E. O. Lawrence and M. S. Livingston designed and built the first cyclotron for accelerating ions. With the development of microwave technology, the traveling wave electron linear accelerator and the standing wave proton accelerator were built in 1947.
- In 1934, Joliot Curie and his wife discovered the artificial radioactivity by bombarding aluminum foil with α-radiation from polonium for the first time, and chemically extracted ^{30}P from the radioactive foil. In the consequent experiments, they found that uranium fission produced multiple neutrons and released large amounts of energy, predicting the feasibility of a nuclear chain reaction.
- In 1938, H. A. Bethe and F. V. Wetabckor independently discovered the fusion reaction, termed "thermonuclear reaction", respectively.
- In 1939, Austrian physicist L. Meitner and her nephew O. Frisch, et al., discovered the phenomenon of nuclear fission of uranium and measured fission energy of around 200 meV.
- In January 1942, Italian-American physicist E. Feimi designed and built the first uranium fission reactor, CP-1 (Chicago Pile 1) in a small courtyard under the west bleachers of a long-abandoned football stadium at the University of Chicago.
- On December 2, 1942, the first natural uranium-graphite reactor successfully started up, achieving the self-sustaining fission chain reaction for the first time.
- At 5:30 a.m. on July 16, 1945, the United States exploded the first atomic bomb in the world for the atomic bombing tests.
- On December 20, 1951, the United States used the surplus heat from its first plutonium-producing breeder reactor to generate electricity at 100 kW.

- On November 1, 1952, the United States exploded the world's first hydrogen bomb on the Coral Island (Marshall Islands) in the Pacific Ocean.
- On January 21, 1954, Nautilus, the first nuclear-powered submarine built in the United States, was launched.
- On June 27, 1954, the Soviet Union built up the world's first nuclear power reactor for electricity with nuclear fuel as electrical power of 5000 kW.
- In 1957, Raychem first produced heat shrinkable materials with accelerator irradiation, creating the history of the radiation chemical industry.
- In 1957, Firestone in the United States made the first use of accelerator irradiation curing technology to produce automotive tires.
- In 1961, Allis-Chalmers and William Myers put the first commercial Anger camera into service at Ohio University.
- On July 21, 1969, the U.S. spacecraft Apollo 11 landed on the moon, heat supplied with two ^{238}Pu (plutonium-238) isotope heaters.
- In 1969, British engineer G. N. Hounsfield successfully designed a computed tomography (CT) instrument, it was introduced in 1972 and promoted the development of nuclear medicine. With the help of CT, doctors improved the detection rate and diagnostic accuracy of lesions.
- In 1970, Ford in the United States used the electron accelerator in curing paint on auto parts for the first time.
- In 1974, the first positron emission computed tomography (PET) scanner was developed, and it was used in clinics in the late 1990s.
- In 1976, John Keyes developed the first multipurpose single-photon emission computed tomography (SPECT) scanner.
- In 1981, J. P. Mach carried out the first single antibody radiopharmaceutical for tumor imaging.
- In 1991, Cytogen first launched a single antibody radiopharmaceutical with FDA clearance for tumor imaging.
- In 2012, the Higgs boson was discovered with the Large Hadron Collider (LHC), which won the 2015 Nobel Prize in Physics.
- In 2015, the Laser Interferometer Gravitational-wave Observatory (LIGO) directly detected gravitational waves for the first time, winning the 2017 Nobel Prize in Physics. □

1.2 Definition, Basic Concepts, and Terminology

1.2.1 Nuclear Technology

Nuclear technology is a comprehensive modern science and technology, based on nuclear physics, radiation physics, radiochemistry, radiation chemistry, and the interaction between nuclear radiation and matter, with accelerators, reactors, nuclear weapons devices, nuclear radiation detectors, and nuclear electronics as supporting technologies. Nuclear technology utilizes the physical, chemical, and biological

effects resulting from the interaction of ionizing radiation from radiation sources (including radiation devices and radioisotope sources) and other forms of radiation with matter, to observe natural phenomena, reveal natural laws, solve scientific problems, and apply them in practice.

Nuclear technology covers a wide range of disciplines and applications. In terms of the predominantly adopted technology, it is divided into radiation technology, isotope technology, and supporting technology. Radiation technology encompasses radiation processing, ion beam processing, nuclear analysis technology, nuclear imaging technology, and radiation detection instrumentation. Isotope technology encompasses isotope preparation technology, isotope products, radiopharmaceuticals, radiological chronology, radioisotope power, and isotope tracing technology. Supporting technology encompasses accelerator technology, reactor technology, nuclear radiation detection, nuclear electronics, radioactive source technology, radiation dosimetry, and radiation protection. In terms of application, nuclear technology can be divided into nuclear technology in the industry, nuclear technology in life sciences, nuclear technology in agriculture, nuclear technology in environmental science, nuclear technology in materials science, nuclear technology in energy/electricity, and nuclear instrumentation.

Summarily, during the development of nearly a hundred years, nuclear technology has infiltrated into other basic disciplines, which spawned generating some newly interdisciplinary or marginal disciplines such as nuclear astronomy, nuclear archaeology, nuclear geology, etc.

1.2.2 Elements, Isotopes, and Nuclides

Element: A collective term for a class of atoms with the same number of protons. For example, the element hydrogen (H) is the collective name for the atoms having one proton in the nuclei, including ^{1}H (protium with no neutron, H), ^{2}H (deuterium with one neutron, D), and ^{3}H (tritium with two neutrons, T).

Radioactive element: An element in which all isotopes are radioactive, such as the elements uranium (U), and plutonium (Pu).

Natural radioactive element: A natural element in which all isotopes are radioactive, such as the element uranium (U).

Isotope: A class of nuclides with the same atomic number but different mass numbers. It is a mutual term for the atoms with the same proton number and different neutron numbers. For example, ^{1}H, ^{2}H, and ^{3}H are isotopes of each other.

Isotopic composition: The atomic percentage of each isotope in an element. For example, the isotopic composition of the element lithium (Li) is 7.59% of ^{6}Li and 92.41% of ^{7}Li.

Stable isotope: The non-radioactive isotopes of an element. For example, ^{1}H (protium, H) is the stable isotope of the element hydrogen (H).

Radioisotope: A radioactive isotope of an element or an unstable isotope is an element that undergoes decay or spontaneous fission accompanied by radiation. For example, ^{3}H (tritium, T) is a radioisotope of the element hydrogen (H).

Isotopic abundance: The atomic ratio of a particular isotope to the total atoms in the isotopic mixture of an element. For example, the isotopic abundance of ^{1}H is 99.985%, and that of ^{2}H is 0.015%.

Natural abundance: The measure of the average amount of a given isotope naturally occurring on Earth. For example, ^{1}H abundance of 99.985% refers to its natural abundance.

Enrichment factor: The ratio of the abundance of a particular isotope in an isotope mixture to its natural abundance. For example, for the uranium fuel with 20% ^{235}U used in the nuclear power industry, the enrichment factor of ^{235}U is about 28 (0.72% natural abundance of ^{235}U).

Nuclide: A class of atoms characterized by the specific mass number, atomic number, and nuclear energy state, whose average lifetime is long enough to be observed. It is a collective term for all known isotopes, including stable nuclides (279) and unstable nuclides (about 2700), such as the ^{1}H-nuclide, ^{2}H-nuclide, and ^{3}H-nuclide in the element hydrogen.

Radionuclide: Another term for radioisotope, radioactive nuclide, or unstable nuclide that spontaneously emits alpha, beta, and other radiations. For example, the ^{3}H-nuclide is a radionuclide of the element hydrogen.

Radioactivity: The nuclear property of some nuclides, which spontaneously emit particles or γ-radiation, capture orbital electrons, and emit X-rays, or spontaneously fission. For example, ^{3}H-nuclide spontaneously emits β-rays with energy of 18.5866 keV, i.e., the ^{3}H-nuclide is radioactive.

Natural radioactivity: The radioactivity of a natural nuclide.

Artificial radioactivity: The radioactivity of an artificial radionuclide, also termed induced radioactivity.

Primordial radionuclide: The initial radionuclide with long half-lives that were present at the birth of the Earth and have not yet decayed completely, such as ^{40}K, ^{235}U, ^{238}U, and ^{232}Th.

Cosmogenic radionuclide: The radionuclide produced by the interaction between cosmic radiation and the atomic nuclei in the atmosphere.

Artificial radionuclide: The radionuclide produced by artificial means.

Long-lived radionuclide: The Radiological Protection Ordinance defines a radionuclide with a half-life of more than 100 days as a long-lived radionuclide.

Short-lived radionuclide: The radiation protection Ordinance defines a radionuclide with a half-life of up to100 days as a short-lived radionuclide.

Isomeric state: A metastable excited state of a nucleus with a long enough average lifetime to be observed.

Nuclear Isomer: A nuclide that has the same number of neutrons and protons but in different energy states and rates of radioactive decay.

Isomeric transition: The transition of a nucleus from a metastable isomeric state to a lower energy state (usually the ground state) while emitting γ-radiation.

1.2.3 Basic Quantities and Concepts

Activity/Radioactivity: Also termed as decay rate, defined as the average decaying number of a given number of radionuclides per second, quantifying the number of radionuclides with a unit of Becquerel or Bq. 1 Bq means a radioactive nucleus decays once per second. Another common unit for radioactivity is Curie (Ci), and $1\ \text{Ci} = 3.7 \times 10^{10}\ \text{Bq}$.

Absorbed dose: The total amount of ionizing radiation energy absorbed by a unit mass of material, with the SI unit of J kg^{-1} or Gy. 1 Gy represents one Joule of ionizing radiation energy absorbed per kilogram of material, $1\ \text{Gy} = 1\ \text{J kg}^{-1}$.

Absorbed dose rate: The absorbed dose per unit time with a unit of Gy s^{-1} or Gy h^{-1}, etc.

Equivalent dose/Dose equivalent: Used to assess how much biological damage is expected from the absorbed dose of a certain type of radiation and is defined as the absorbed radiation dose in an organ or tissue corrected by a radiation weighting factor. Dose equivalent = (Absorbed dose) $\times$ (weighting factor). The SI unit of equivalent dose is J kg^{-1}, or Sievert (Sv), the name it was given to replace the conventional unit of rem (roentgen equivalent in man, $1\ \text{Sv} = 100\ \text{rem}$).

Nuclear transition: The process by which a nuclear system changes from one quantum energy state to another. Examples include the transition from one nuclide to another through α or β decay or changing the nuclear energy level of a system through the absorption (or emission) of photons, orbital electrons, or electron pairs.

Nuclear magnetic resonance (NMR): The resonance phenomenon resulting from the radiofrequency radiation absorbed by a substance in a magnetic field. For the magnetic moments of atomic nuclei spinning into a magnetic field, only those in some definite directions are allowed, with the energetic differences between them related to the magnetic field. Resonant absorption occurs when the energy of the RF quanta happens to equal such energetic differences, resulting in energy level transition and the orientation deflection of the magnetic moments.

Nuclear energy: The energy released during a nuclear reaction (especially fission and fusion) or nuclear transition.

Nuclear fusion: A nuclear reaction with two light nuclei combining into a heavier nucleus.

Plasma: An electrically neutral gas mixture of particles, electrons, and electrically neutral particles. High-temperature hydrogen plasma can be used as a fuel for controlled fusion experiments.

Radioactive decay: A spontaneous nuclear transformation phenomenon in which a nucleus emits particles or γ-radiation, emits X-rays after capturing orbital electrons or undergoes spontaneous nuclear fission.

Decay constant (disintegration constant): The rate of decay.

Decay energy (Disintegration energy): The energy released by radioactive decay.

Decay scheme: A graphical representation of the decay of a radionuclide detailing nuclear data such as energy level, radiation type, and half-life.

Half-life: The time required for half the activity in a single radioactive decay process.

Radioactive equilibrium: A state in which each radionuclide decays exponentially over time with the same half-life of its precursor in the chain, in other words, each radioactive nuclide decays at the same rate of being produced. The radioactive equilibrium is possibly achieved only when the half-life of the precursor nuclide is longer than those of the daughter nuclides in its later generations in the decay chain. If the half-live of the precursor nuclide is long enough that its change during observation is negligible, the radioactivity of all nuclides in the decaying system is nearly equal to each other. Such a radioactive equilibrium is called the long-term equilibrium. Otherwise, it is called a temporary equilibrium.

Specific activity: The activity per quantity of atoms of a particular radionuclide.

Thermal neutron: A neutron in thermal equilibrium with its surroundings.

Cold neutron: A Neutron with the kinetic energy of the order of milli-electron volts or less.

Epithermal neutron (epithermal neutron): The neutron with kinetic energies above that of thermal perturbation. This term often refers only to neutrons with energies just above the energy range of thermal energy (i.e., comparable to chemical bonding energy).

Ultracold neutron (UCN): A neutron with single-digit velocities in m/s. their kinetic energy is of the order of 10^{-7} eV or ~ 1 mK.

Slow neutron: A neutron with kinetic energy below a specific value, selected depending on application scenarios. For example, this value is typically 1 eV in reactor physics, the effective cadmium cut-off energy (about 0.6 eV) in dosimetry, and 1 keV in neutron nuclear reaction studies.

Fast neutron: A neutron with kinetic energy greater than a specified value, selected depending on application scenarios. The value is typically the boundary of entering the indistinguishable resonance energy region (above 10 keV) in neutron nuclear reaction studies and is usually 0.1 meV in reactor physics.

Resonance neutron: A neutron with kinetic energy in the energy range where the neutron's nuclear reaction cross-section appears to resonate. This energy range is highly variable, usually between 1 eV and 1 keV.

Photoelectric effect (absorption): The phenomenon of atoms absorbing photons and emitting orbital electrons. The absorption of photons and emission of electrons from the surface of certain media is also called the photoelectric effect.

Compton effect: The effect whereby X- or γ-radiations are scattered on a material with an increase in wavelength by matter. Scattering occurs when a photon interacts with free electrons or electrons that can be seen as free electrons. Part of the energy and momentum of the incident photon is transferred to the electron and the rest is carried away by the scattered photon.

Cerenkov radiation: The electromagnetic radiation emitted when a charged particle passes through a dielectric medium at a speed greater than the velocity of ling in that medium.

Neutron diffraction: The diffraction of neutrons incident on a crystal when their wavelength is comparable to the lattice space of the crystal. Neutron diffraction is a crystallographic method used to determine the atomic and/or magnetic structure of materials.

Doppler effect: Changes in the wavelength/frequency of radiation produced by the relative motion between the source and observer.

Spallation: A high-energy nuclear reaction in which a nucleus bombarded by an incident particle with sufficient energy (typically greater than ~ 50 meV) splits into numerous lighter nuclei.

Threshold energy: The minimum value of the kinetic energy of an incident particle (laboratory system) required to trigger a specific nuclear reaction.

Cross-section: The measurement of the likelihood of a given particle interacting with a specific species of incident particle, expressed with the unit of the barn (b, $1\text{b} = 10^{-28}\ \text{m}^2$) in terms of area. It is the quotient of the probability of a specific reaction of each target particle divided by the injection of that incident particle, its value depends on the energy of the bombarding particle and the kind of reaction.

Nuclear fission: The splitting of a heavy atomic nucleus into two (in a few cases, three or more) fragments of the same order of mass, usually concomitant with neutron emission and γ-radiation, and in a few cases, lightly charged particles.

Fission energy: The energy released in the atomic nucleus fission.

Fission fragment: The nuclide with certain kinetic energy produced by the fission of a nucleus.

Fission yield: The fraction of given fission products produced per fission. Fission products with mass numbers around 90 and 140 have high fission yields.

Nuclear chemistry: The branch of chemistry that deals with nuclei and nuclear reactions, using chemical methods or methods with a combination of chemistry and physics. Sometimes, nuclear chemistry refers to the subdiscipline that is concerned with the chemical aspects of nuclear science.

Radiochemistry: The branch of chemistry studying the chemical and physical properties of radioactive elements, utilizing both radioactive and chemical characteristics of elements and compounds to address technical needs in many fields.

Nuclear recoil: The movement of the remaining nucleus conferred by nuclear collisions, nuclear transitions, or radiation action.

Radioactive standard: A radioactive source whose properties and activities are known in a defined period, which can be used as a comparative standard or reference.

Radioactive purity: The ratio, expressed as a percentage, of the radioactivity of the desired radionuclide to the total radioactivity of the source.

Radiochemical purity (RCP): The proportion of the total radioactivity in the sample which is present as the desired radiolabelled species.

Cooling: To weaken the radioactive activity of a substance by radioactive decay.

Decontamination: The process of removing or reducing radioactive contamination by physical, chemical, or biological means from a person, object, or place, which can be divided into initial decontamination, deep decontamination, in-service decontamination, accidental decontamination, and decommissioning decontamination.

Decontamination factor: The ratio of activity before and after decontamination of a radioactively contaminated object. It is used to describe the decontamination efficiency of a decontamination operation, either for a specific radionuclide or for the total radioactive contaminant.

Carrier: Another substance that carries a trace amount of a specific substance in an appropriate quantity and participates in chemical or physical processes.

Ion exchange membrane: A polymer membrane bearing ionic groups with selective permeability to the specific ions in solution.

Isotope effect: The variation of certain physical and chemical characteristics of an element by the mass of the isotopes involved.

Isotopic exchange: The chemical exchange in which two atoms belonging to different isotopes of the same element exchange valency states or locations in the same or different molecules. The isotopic exchange involves the substitution of one

isotope of an element by another in the molecules of a given substance without changing their elemental composition.

Isotopic exchange: The chemical reactions in which the reactants and products are chemically identical but have different isotopic compositions. [József Kónya and Noémi M. Nagy. Nuclear and Radiochemistry, 2nd Ed., 2018, Elsevier].

Isotopic equilibrium: An equilibrium state of the distribution of the isotopes achieved in isotope exchange.

Accelerator: A device to elevate the kinetic energy of a charged particle by more than 0.1 meV.

Electron beam (EB): Stream of electrons (e.g. betatron) generated by heat (thermionic emission), the bombardment of charged atoms or particles (secondary electron emission), or strong electric fields (field emission). The high-energy electron beam provided by an accelerator is one of the most important sources of particles and energy for radiation processing and research. It has the advantages of particle beam stability and processing feasibility with reliable and adjustable parameters, while with high initial construction costs, high maintenance costs, and requires specialized knowledge of the operator.

Radiation source: All substances or objects that can cause radiation exposure by electing ionizing radiation or releasing radioactive material. A radioactive source is only one type of radiation source referred to as a source of radiation exposure caused by radioactive materials.

Sealed source: A solid radioactive material sealed in a case or cemented tightly in a cover.

(Orbital) electron capture: The radioactive transformation of a nucleus into another by capturing an orbital electron.

Internal conversion: A nuclear transition competing with γ-radiation to convert the excitation energy of the nucleus directly into that of the shell electrons in that it de-excites the nucleus.

Auger effect: The de-excitation of an atom in an excited state, by releasing orbital electrons instead of X-radiation due to the filling of the inner-shell holes with the outer-shell electrons.

Mossbauer effect: Recoil-free emission and recoil-free resonant absorption of γ-radiation.

1.2.4 Radiation and Rays

The phenomenon of a substance emitting rays is called radiation, including ionizing radiation and non-ionizing radiation. Radiation that causes the ionization of matter

is called ionizing radiation. There are many types of ionizing radiation, including electromagnetic radiation such as X-ray and γ-ray, charged particle radiation such as α-ray, β-ray, electron beam, proton ray, deuteron ray, heavy ion beam, meson beam, etc., and uncharged particle radiation, namely neutrons. Ionizing radiation is predominantly produced by nuclear reactors, accelerators, and radioactive sources. Non-ionizing radiation is the radiation that cannot cause the ionization of matter because of its low energy, such as infrared rays, microwaves, etc.

1.2.5 Nuclear Decay and Nuclear Reaction

Nuclear decay, also known as radioactive decay, is a random process by which an unstable nuclide, resulting from the excess or insufficiency of protons or neutrons in the atomic nucleus, spontaneously transforms to another one, concomitant with emitting radiation or particle. Generally, the nucleus before decay is called the parent, while those formed after decay are the daughter. If the daughter nucleus is still radioactive and decays, the daughters of the parent are in turn the 1st generation, the 2nd generation …, and the nth generation daughter nucleus.

The important low of radioactive decay is that the number of radioactive nuclides decreases exponentially with time. When the initial number of the radioactive nuclei is N_0, the number of nuclei that do not undergo radioactive decomposing during time t is:

$$N = N_0 e^{-\lambda t}$$

where λ (with the unit of s^{-1}) is the decay constant, meaning the decay probability of a nucleus per unit of time. The value of the decay constant is related to the radionuclide, thus, it is independent of physical and chemical conditions (pressure, temperature, chemical environment, etc.).

Nuclear decay is commonly composed of alpha decay, beta decay, and gamma decay. Additionally, there are other forms of decay, such as spontaneous fission, slow-emitting protons, slow-emitting neutrons, etc.

Alpha decay (or α-decay) represents the disintegration of a parent nucleus to a daughter through the emission of the nucleus of a helium atom (alpha particle). In practice, α-decay has only been observed in nuclides that are considerably heavier than a nickel. The lightest known alpha emitters are the lightest isotopes (mass numbers 106–110) of tellurium (element 52). Alpha particles are commonly emitted by all the heavy radioactive nuclei in nature such as uranium, thorium, or radium, as well as the transuranic elements like neptunium, plutonium, or americium.

Beta-decay (or β-decay) represents the disintegration of a parent nucleus to a daughter through the emission of beta particles. If a nucleus emits a beta particle, it loses an electron (or positron). In this case, the mass number of daughter nuclei remains the same, but the daughter nucleus will form different elements. Beta-decay consists of three forms, namely negative beta decay (β^--decay), positive beta decay

(β^+-decay), and inverse beta decay (orbital electron capture). In β^--decay, a neutron-rich nucleus emits a high-energy electron and an antineutrino, and the nuclear charge increases by one unit to compensate for the negative electric charge. In β^+-decay, a proton-rich nucleus emits a positron (antiparticle of electron with the same mass as electrons but positive electric charge) and a neutrino, and the nuclear charge reduces by one unit. In the orbital electron capture process, a proton-rich nucleus captures an outer electron accompanied by emitting a neutrino, and the nuclear charge reduces by one unit. The negative or positive electron released in beta decay is not inherent but generated by the inter-conversion between proton and neutron within the nucleus. The natural radionuclides mainly occur β^--decay.

Gamma decay (or γ-decay) represents the disintegration (gamma radioactivity) of a parent nucleus (in a high energy state and excited state) to a daughter (in a lower energy state) through the emission of gamma rays (high energy photons). In this case, the daughter nucleus remains the same mass number and nuclear charge number but in a different energy state. Gamma decay typically accompanies other forms of decay, such as α- or β-decay, because radionuclides in excited states are generated in the decay of a parent radionuclide in practice.

A nuclear reaction is a process whereby a nucleus interacts with another nucleus or subatomic particle to produce one or more new particles or gamma rays. Consequently, a nuclear reaction must cause a transformation of at least one nuclide to another. The interaction between two nuclei or subatomic particles without any nucleus changes is called a nuclear scattering, rather than a nuclear reaction. Perhaps the fusion reactions in stars and the Sun are the most notable nuclear reactions. A fusion reaction (or thermonuclear reaction) is a nuclear reaction whereby two or more light nuclei (protium, deuterium, tritium, lithium, etc.) collide at very high energy (supplied by the thermal movement under the condition of a high-temperature and high-density state) and fuse into a new nucleus. Fission reaction is the most notable man-controllable nuclear chain reaction in nuclear reactors. A nuclear chain reaction is a self-propagating sequence of nuclear reactions in which one of the reaction products can cause the same kind of reaction. For example, a nuclear fission chain reaction is a self-propagating sequence of fission reactions in which neutrons released in fission produce additional fission in at least one other nucleus.

1.2.6 Interaction of Alpha Radiation with Matter

An alpha particle emitted by nuclear decay is essentially a helium nucleus with two positive charges, with the energy of typically 4–9 meV. The interaction of alpha particles with matter principally consists of ionization, excitation, scattering, and nuclear reactions.

Ionization and excitation. When passing through matter, alpha particles transfer energy to the atomic shell electrons of their surrounding atoms through Coulomb interactions between the positive charge and the negative charge of the electrons in

the atomic shell orbitals. When the electron gains enough energy to overcome the binding of the nucleus, it can break away from the atom and become a free electron, forming ion pairs with positive ions. This phenomenon is known as ionization. If the kinetic energy of free electrons is high enough, they can also cause the ionization of other atoms. We call the former primary ionization and the latter secondary ionization. About 35 eV of energy is required to produce one ion pair in air. An alpha particle of 5 meV can produce about 1.5×10^5 ion pairs in air. An alpha particle passing through matter produces many ion pairs in its track, and the distribution of ion pairs is uneven. The number of ion pairs yielded per unit travel distance of an alpha particle is the specific ionization or ionization density.

If the energy absorbed in Coulomb interactions is inadequate to override the ionization energy, shell electrons cannot become free electrons. In this case, the atom is in an excited state as the absorbed energy raises shell electrons to higher energy levels. This phenomenon is called excitation. The excited atom then returns to the ground state by emitting X-rays bearing specific energy. Additionally, the excited atom can return to the ground state in another way. The excitation energy can be transferred to an orbital electron, which makes the electron gain enough energy to escape and becomes a free electron (i.e., an oscillator). This phenomenon is termed the oscillator effect.

Scattering. The direction of an alpha particle that moves in the matter can be changed by the interactions between the Coulomb force, the electrons outside the nucleus, and the nuclear force from the interaction with the nucleus. Such a phenomenon is termed scatting, including elastic scattering and inelastic scattering. Elastic scattering occurs with no change in the total kinetic energy including the incident alpha particle and the scattered nucleus. Inelastic scattering occurs with the energetic change of the system. Elastic scattering is the principle for the incident alpha particle. For the scattering of alpha particles perpendicularly incident to a scatterer, the small-angle scattering is predominant, and only a little chance of the large-angle scattering occurring. The scattering effect reduces the number of alpha particles traveling along the original direction. However, the loss of alpha particles resulting from scattering is much less than those resulting from ionization and excitation.

Nuclear reactions. Commonly, alpha particles have a rare chance to trigger nuclear reactions. However, when α-particles interact with elements like Be, B, F, Li, Na, and O, the (α, n) reaction occurs and neutrons are released, which is the principal way to prepare isotopic neutron sources.

1.2.7 Interactions of β-Rays with Matter

Beta particles are high-speed electrons (both positive and negative) electing from the nucleus in β-decay. Beta particles (usually with energies less than 4 meV) interact with matter via excitation, ionization, scattering, and secondary radiation.

Excitation and Ionization. As alpha particles do, beta particles can also ionize the atoms/molecules of a substance, and the energy consumption (about 32.5 eV in the air) for a beta particle to produce an ionic pair is almost independent of its velocity. However, the specific ionization value of a beta particle is much less than that of an alpha particle with the same energy. Besides, compared to an alpha particle with the same velocity, a beta particle is also of much lower specific ionization value. For instance, a 5 meV α-particle produces about 3000 ionic pairs of positive and negative charges per micron in water, while a 1 meV β-particle only produces 5 ionic pairs per micron. What we provided here is the average specific ionization value because the β-particle is of a continuous energy spectrum. For monoenergetic fast electrons, the magnitude of the specific ionization value in the air relates to the electronic velocity. The higher the electronic velocity, the smaller the specific ionization value.

Scattering. Because beta particles are much less massive than alpha particles, they are more likely to be scattered. The scattering of beta particles is much more complex than that of alpha particles. Beta particles can be scattered not only by the nucleus but also by orbital electrons. Scattering always occurs multiple times before a beta particle ends its range. The multiple occurrences of large-angle and small-angle scattering will result in backscattering (scattering angles greater than 90°).

Secondary radiation. Scattering in the Coulomb field of orbital electrons and the nuclear force field of a nucleus change the moving direction and speed of beta particles, concomitant with the emission of electromagnetic waves. This process is called bremsstrahlung. Bremsstrahlung has a continuous energy spectrum. Bremsstrahlung occurs with a high probability when beta particles interact with heavy elements.

Besides bremsstrahlung, characteristic X-rays can also be emitted by the interaction between atoms in the matter and fast electrons. Excitation of the target atoms occurs in collisions with Fast-moving electrons. A collision with fast-moving electrons emits an inner-shell electron from the atom, an outer-shell electron then falls into the inner shell to fill the vacancy. In the process, a single photon is emitted by the atom with energy equal to the difference between the inner-shell and outer-shell vacancy states. This energy difference usually corresponds to photon wavelengths in the X-ray region of the spectrum. Additionally, a collision excites the valence electrons of an atom to higher energetic states. When returning to the ground state, they emit visible light and ultraviolet light. These secondary radiations are collectively called fluorescence.

1.2.8 Interaction of Gamma Rays with Matter

Gamma rays are high-energy electromagnetic waves emitted during the nucleus transformations. The wavelength range of gamma rays is 10^{-8}–10^{-11} cm, shorter than that of ultraviolet radiation. Interactions of gamma rays with the matter have a dozen forms, depending on the energy of the incident γ-rays. The neutral γ-rays interact with matter differently from charged particles. As discussed before, charged

particles collide with atoms multiple times in their journey, transferring their energy to the environment in a gradual process. However, γ photons transfer most or all of their energy to atoms in a single interaction with the nuclei or extranuclear electrons. The energy of γ-rays emitted from isotopic radioactive sources is generally in the range of a few keV to 2 meV.

For γ-rays produced in radioactive decay or the inner-shell electronic transition, their interactions with matter are principally classified into three types, termed as the photoelectric effect, the Compton-Wuyouxun effect, and the electron pair effect. Other effects, such as Rayleigh scattering, photonuclear reactions, etc., are generally secondary because their reaction cross-sections are much smaller. The electrons newly yield in the interaction of γ-rays with the matter generally have higher energy and can undergo secondary ionization.

Photoelectric effect. A γ-photon undergoes an interaction with an electron that is bound in an atom. In this interaction, the incident photon completely transfers its energy (E_γ) to a bound electron, and the energetic electron (photoelectron) breaks free and emits from its bond shells. This is termed the photoelectric effect. The kinetic energy of the photoelectron is determined by the following equation.

$$E_e = E_\gamma - E_i \tag{1.1}$$

where E_i is the escape work of electrons or named the binding energy of electrons in atomic energy (shell), wherein i represents the electron subshell, i = K, L, …. E_γ is the energy of the incident photon.

In the photoelectric effect, the direction of photoelectron emission is not isotropic concerning the incident direction of γ-photon, depending on the energy of the incident γ-photon (E_γ). When the incident γ-photon is of relatively small energy (20 keV), the photoelectron emission direction is almost vertical to the incident direction γ-photon. With the increase of incident energy, the direction of photoelectron emission gradually tends to be the same as the incident photon. Like ordinary electrons interacting with matter, photoelectrons are also stopped by gradually losing energy through excitation and ionization. The atom also returns to the ground state and emits characteristic X-rays after emitting photoelectrons.

Compton-Wu Youxun Effect. For γ-rays with higher energy, the binding energy of shell electrons can be ignored and regarded as free electrons. The inelastic collision between the incident γ-photons and free electrons deflect the incident gamma photon through an angle (θ) concerning its original direction and decreases its energy (decrease in photon's frequency). This is the Compton-Wu Youxun Effect. In this effect, the electron gains energy $E_\beta = E_\gamma - E_\gamma'$, where E_γ is the energy of the incident proton, and E_γ' is the scattered photon. Besides absorber, the probability of the Compton-Wu Yusen effect depends on the energy of the incident γ-rays E_γ, the higher the E_γ, the lower the occurrence.

Electron–positron pair effect. A gamma-ray with energy greater than twice the electron rest mass (1.022 meV) is annihilated in the nuclear electric field of a nearby

atomic nucleus, resulting in the creation of an electron–positron pair. In this process, the gamma-ray converts part of the energy into the rest mass of the electron–positron pair and the others into the kinetic energy of the electron–positron pair. Besides absorber, the probability of producing the electron–positron pair also depends on the energy of the incident γ-particle ($E_\gamma \geq 1.022$ meV), the higher the E_γ, the larger the kinetic energy of the electron–positron pair. The electron is stopped by gradually losing energy through excitation and ionization in interaction with matter, whereas the positron combines with an electron and converts to γ-ray after losing its kinetic energy. This process is called annihilation.

For the three interactions of γ-rays with the matter mentioned above, the Compton-Wu effect and the photoelectric effect are always present simultaneously, and the electron–positron pair effect is also present when $E_\gamma \geq 1.022$ meV.

1.2.9 Interaction of Neutrons with Matter

Neutron, present in all atomic nuclei except hydrogen, is an important component of an atomic nucleus. The mass of neutrons is approximately equal to that of protons. Neutrons are divided into fast neutrons, medium-energy neutrons, and thermal neutrons according to their kinetic energy. Neutrons of kinetic energy greater than 100 keV are commonly named fast neutrons. Neutrons in thermal equilibrium with the surrounding medium are commonly named thermal neutrons or slow neutrons, the most probable energy of thermal neutrons at 20 °C for Maxwellian distribution is 0.025 eV. Neutrons with energy between those for fast and thermal neutrons are named medium-energy neutrons or superthermal neutrons.

Like γ-rays, uncharged neutrons interact with matter in completely different ways from charged particles. Neither the orbital electrons nor the electric field caused by a positively charged nucleus affects a neutron's flight, it only interacts with a nucleus when it's in the interaction range of the nucleus (10^{-15} m), or it incident into the nucleus. Four interactions occur between neutrons and matter, including scattering, capture, nuclear reaction, and nuclear fission, of which scattering can be divided into elastic and inelastic scattering. Besides the nature of the nuclear matter, the probability of each interaction aforementioned depends principally on the energy of the incident neutron. For example, neutron capture is prevailing for slow neutrons, elastic scattering is prevailing for medium-energy neutrons and fast neutrons, and inelastic scattering is predominant for the fast neutrons with energy greater than 10 meV.

In addition to elastic scattering, the above interactions between neutrons and matter will lead to secondary radiation. From the viewpoint of radiation protection, secondary radiation caused by neutrons is of considerable importance. What we usually encounter in practice are fast neutrons. For these neutrons, the energy lost in the elastic scattering is greater when they collide with light matters than that with heavy matters. When collides with a hydrogen nucleus, a fast neutron can transfer almost half of its energy to the recoil proton. Therefore, the substances bearing many

hydrogen atoms in the structure are good neutron shielding materials. For example, water and paraffin are the most commonly used neutron shielding materials, which are cheap, easily available, and effective.

The probability of the reactions is commonly described as their microscopic cross-sections. The microscopic cross-section represents the effective target area of all the nuclei contained in the volume of the material (such as fuel pellet). The units are given in cm^{-1}. It is the probability of neutron-nucleus interaction per centimeter of neutron travel. All the reactions including elastic scattering, inelastic scattering, radiation capture, nuclear reaction, and nuclear fission have a chance to occur independently. The total microscopic cross-section σ_t expresses the probability of any interaction taking place.

Scattering. Scattering includes elastic and inelastic scattering. Elastic scattering occurs when a target nucleus deflects the incident neutron by an angle and simultaneously recoils. The neutron-neutron interaction system does not lose energy and momentum after elastic scattering. It is to say, elastic scattering cannot excite the target nucleus, and therefore no γ-rays are emitted. The incident neutron distributes its kinetic energy to the recoil nucleus and the scattered neutron. The lighter the target nucleus, the more energy it gains, in other words, the incident neutron loses more energy. The fast neutron loses its kinetic energy through multiple times elastic scattering and becomes a thermal neutron. However, if the incident neutron consumes part of the energy to excite the target nucleus and emits γ-rays when the nucleus returns to the ground state, inelastic scattering occurs. Inelastic scattering is essential only for the scattering of fast neutrons with heavy nuclei.

Radiation capture. Radiation capture is a nuclear reaction in which the incident neutron is completely absorbed, resulting in a compound nucleus. The compound nucleus then decays to its ground state by gamma emission with an energy of a few keV. This capture reaction is also called the (n, γ) reaction. Sometimes, some isotopes have a great chance to capture the neutrons of specific energy in the superthermal region. This phenomenon is called resonance capture or resonance absorption.

(n, α), (n, p), (n, d) reactions. (n, α), (n, p), and (n, d) reactions are the nucleus reactions caused by the collision with neutrons, named after the emitting, charged helium nuclei (α), protons (p), and deuterons (d), respectively. Nuclear reactions emitting charged particles are less common than radiation capture. Charged particles must overcome the Coulombic attraction to escape from the nucleus. Consequently, the reactions with the emission of charged particles are likely to occur in the collision of light nuclei with fast neutrons. But there are exceptions, for instance, the 7Li(n, α) reaction is easy to happen through collision with thermal neutrons.

Nuclear fission. Nuclear fission is a nuclear reaction in which a heavy nucleus interacts with a neutron split into two or more fission fragments (lighter nuclei) and emits one or more neutrons, with the release of a large amount of energy concomitantly. Nuclear fission occurs when ^{233}U, ^{235}U, and ^{239}Pu interact with thermal neutrons and heavy nuclei interact with fast neutrons.

1.2.10 Radioanalytical Technology

Labeling and labeled compound: Labeling is to replace one or more atoms or chemical groups in a compound with easily recognizable atoms or groups. The product is called a labeled compound, and the readily recognizable atoms or groups in a labeled compound are tracer atoms or groups. Labeling with radionuclides as tracers are called radioactive labeling, which produces radioactively labeled substances such as $Na^{18}F$, $^{14}CH_3COOOH$, etc.

Stable nuclide labeled compound: Labeled compound produced by changing the stable isotopic abundance of an element to an observable degree such as $NH_2{}^{13}CH_2COOH$, $^{15}NH_3$, etc.

Non-isotopically labeled compound: Labeled compound obtained by replacing given atoms in its molecule with non-isotopic tracer atoms. For example, selenium-labeled cysteine is produced by replacing the sulfur atom in a cysteine molecule with ^{75}Se.

Multi-labeled compound: The labeled compound introduced two or more tracers to their molecule such as $^{14}CH_3CH(^{15}NH_2)COOH$,$^{14}CH_3CH(NH_2)\ ^{13}COOH$, etc.

Specific labeling (S): Label a compound at given positions with the given number of tracer atoms. A specifically labeled compound can be named by providing the name, number, and labeling positions of the tracer atoms before or after the compound name. For example, when alanine is labeled with ^{14}C on methyl (i.e. $^{14}CH_3CH(NH_2)COOH$), it is named S-3-^{14}C-alanine; if ^{14}C is labeled on both methyl and carboxyl (i.e. $^{14}CH_3CH(NH_2)^{14}COOH$), it is named S-1,3-^{14}C-alanine. The symbol S can be omitted when the specific labeling positions are clearly marked out.

Uniform labeling (U): Uniform labeling is to produce a uniform labeled compound in which the ^{14}C-tracer atoms are of uniform distribution in their labeling molecule. In other words, ^{14}C-tracers in a uniform labeled compound are statistically homogeneous for all carbon atoms in the molecule. For example, by labeling a glucose molecule with $^{14}CO_2$ through photosynthesis in plants, the uniform labeled glucose in which ^{14}C-atoms are of uniform distribution in statistics over the six carbons of the glucose molecule can be obtained, which is called U-^{14}C-glucose. In radiopharmaceutical advertising, the symbol UL commonly represents Uniform Labeling.

Nominal location labeling (N or n): Also known as quasi location labeling, refers to that in the labeled compound tracer atoms predicted from the labeling method should be at a specific position, but the identification labeling ratio of tracers at the given position is certainly no more than 95%, depicted with “N” or “n” after the tracer’s name. For example, 5-T(n)-uracil indicates that the tritium atom is mainly labeled at the fifth position of the molecule, but more than 5% of the tritium atoms distribute at other positions.

General labeling (G): Refers to that tritium atoms can probably label all hydrogen atoms at any position in a molecule, the degree of labeling varies with the locations of hydrogen atoms. For example, in a tritium-labeled cholesterol molecule prepared by gas exposure, the hydrogen atoms located in the rings, the angular methyl groups, and the side chains of the molecule are more or less labeled by tritium atoms, but the degrees of labeling at different positions are not the same, which can be named G-T-cholesterol.

(Radioactive) Tracing: Refers to a unique technology that adds a radioactive element or compound in the system of interest to indicate the behavior of its internal substances in a specific chemical or biological process by monitoring the changes of radioactive tracers in situ with radioactive detectors.

Isotope dilution analysis (IDA): A highly accurate and precise analytical technique for measuring element concentrations in a wide array of samples in the natural sciences. In IDA, the initial isotopic composition of the sample is altered by the addition of known amounts of one or more isotopic labeled species, the so-called spike. The quantification is only based on the measurement of isotopic ratios of the sample, spike, and sample-spike mixture.

Radiometric analysis: A quantitative analysis technique that determines the mass of a substance by measuring the radioactivity of the component of the substance.

Neutron activation analysis (NAA): An analytical technique for the qualitative and quantitative determination of elements based on the measurement of radiation released by the decay of radioactive nuclei formed by neutron irradiation of the material. The most suitable source of neutrons for such an application is usually a research reactor. The samples that can be analyzed with this method stem from many different fields including medicine, nutrition, biology, chemistry, forensics, the environment, and mining.

Ion beam analysis: An important family of modern analytical techniques involving the use of MeV ion beams for compositional and structural characterization of materials, which combines the advantages of non-destructive and standardless analysis of the surface and near-surface regions (0–2 μm) of solids. IBA is most advantageously applied to analyze problems where information on elemental composition and depth or thickness are needed.

Neutron radiography: A photographic technique that uses a collimated beam of neutrons to generate an image of an object placed in the beam. The image can provide computer-readable data that generates on photographic film or newer electronic devices.

Radiocrystallography: A technique that uses the diffraction of X-rays, electrons, neutrons, etc. by a solid system to perform crystal structure (especially the parameters of the crystal) and the identification of the crystalline material.

Radioactive dating: A technique of dating objects such as rocks and minerals by determining the components of radionuclides (uranium, carbon-14, potassium-40, etc.) or their decay products.

1.2.11 Radiation Processing Technology

Radiation crosslinking: Radiation crosslinking is based on the effect of high-energy beta and gamma rays. When a polymer material absorbs radiation energy, the microscopic molecular linear long chains are broken, and free radicals are formed. The reaction of free radicals with other chains or radicals and the rearrangement of the polymer chains generate T-shaped structures. Consequently, the two-dimensional polymer chains crosslink each other into a three-dimensional "network", improving the mechanical properties, electrical properties, stress cracking resistance, and service life of polymer material. Radiation crosslinking is one of the mainstream techniques for polymer material modification.

Radiation grafting: The substrate material absorbs radiation energy and produces free radicals, which react with unsaturated monomer molecules to graft the monomers onto the substrate. Organic Polymers, inorganics, woods, paper, and other materials that can produce free radicals are the possible substrates and receive specific properties or functions after radiation grafting. Radiation grafting can be conducted in liquid, solid, and gas phases by co-irradiation or pre-irradiation grafting. For example, radiation grafting with monomers like acrylics or acrylates can significantly elevate the appearance, mechanical strength, coloring performance, processing, washing resistance, and wrinkle resistance of silk, while maintaining its natural advantages.

Radiation polymerization: A polymerization reaction initiated by exposure to radiation rather than a chemical initiator. A significant advantage of radiation polymerization is that no chemical initiator residues and fragments are presented in the materials produced with radiation polymerization, which is of significance for biological and pharmaceutical products. The presence of chemical initiator residues may cause allergy in human cells causing inflammation or leading to blood clotting and blockage of capillaries. Another advantage is that radiation polymerization is normally performed under conditions without high temperature and pressure (also called cold polymerization), which avoids complex chemical process equipment and reduces investment.

Radiation decomposition: The decomposition of larger molecules into small molecules caused by incident radiation. This term here refers to the decomposition of polymer molecules. Due to the main chain fracture triggered by free radicals produced by incident radiation, polymer molecules are decomposed into smaller molecules. Radiation decomposition is used not only to obtain products with special properties but also to protect the environment. From the production aspect, Teflon powder is made of polytetrafluoroethylene by radiation decomposition with inks, coatings,

and wear-resistant oils added to achieve excellent lubricating performance. As for environmental protection, natural polymers such as cellulose and shells of marine organisms are made into glucose, chitin, and other widely used products through radiation degradation, which can control pollution and create certain economic benefits as well.

Radiation sterilization: Refers to the use of high-energy radiation to destroy the protein molecular structure and genetic material of bacteria or viruses to kill the bacteria. Radiation sterilization is mainly used for the safe, rapid, and effective disinfection of medical devices and materials that cannot be disinfected by high temperature and high pressure. Additionally, killing mold and spoilage bacteria to prolong the fresh-keeping period of food is also a typical use of radiation sterilization.

1.2.12 Basic Knowledge of Radiation Protection

Since radionuclides and/or ionizing radiation are involved in all areas of nuclear technology research and application, knowledge of radiation protection is important for practitioners in nuclear technology and related industries. Radiation protection is an essential branch of atomic energy science and technology, arising from and developing in the development and utilization of ionizing radiation, radioactive substances, and nuclear energy. Radiation protection is a comprehensively fringe discipline that studies the protection of human beings from or less from exposure to the hazards of ionizing radiation. It involves the disciplines of atomic nuclear physics, radiochemistry, radiation dosimetry, nuclear electronics, radiological medicine, radiobiology, radioecology, etc. The essential task of radiation protection is to protect the environment and safeguard the health and safety of practitioners and the public, and their future generations. Specifically, radiation protection aims to prevent non-random biological effects caused by ionizing radiation and to limit the incidence of random biological effects to an acceptable level. The basic principle of radiation protection is to take appropriate measures to reduce the radiation dose under the maximum permissible dose level (also called the safe dose) for the radiation operators and others working around to ensure personal safety.

In practice, the protection principle for external radiation is that under the premise of source strength controlling, radiation protection measures mainly adopt shielding protection, time protection, and distance protection. For internal radiation, the protection principles are enclosed isolation, purification and ventilation, sealing and containment, and waste disposal. For different radiation sources, different materials can be selected to achieve effective shielding protection. High-density metals like lead (Pb), ordinary concrete, and heavy concrete are generally the shielding materials for γ-rays. Substances with a lower atomic number such as Plexiglas and aluminum (Al) are usually the shielding materials for β-rays, which can reduce the transformation portion of β-rays in the shielding materials to tough radiation. For

fast neutron shielding, substances with a low atomic number such as boron (B), especially those with more hydrogen atoms such as water and paraffin can be selected. With the development of protection science and technology, and people's awareness of safety and environmental protection, nuclear technology is becoming more and more widely accepted by the public as a relatively safe and environmentally friendly high-tech industry, while gradually penetrating all sectors of the national economy and transforming traditional technology.

1.3 Applications and Developments of Nuclear Technology

Starting in the mid-1940s, nuclear technology and its applications developed rapidly. The crossover and integration of nuclear technology with other disciplines have contributed to the emergence of many frontier disciplines. Many modern scientific and technological achievements are inseparable from the contribution of nuclear technology. Studies of the interaction of radiations and energy particles with matter, together with the physical, chemical, and biological changes resulting from these interactions constitute the main contents of radiation physics, radiation chemistry, and radiation biology. With the application and rapid development of nuclear technology in medicine, medical physics and nuclear medicine have emerged, involving radionuclide preparation, radionuclide labeled compounds, radiation dose, etc.

The penetration of nuclear technology into various regions of the national economy has contributed to many new industries such as radiation processing, non-destructive testing, nuclear medicine diagnostic equipment, radiotherapy equipment, radiopharmaceutical production, etc. In addition to military use, nuclear technology has also been used in various civil fields such as energy security, industrial testing and processing, agriculture, forestry, fishery, medicine and life science, environmental protection and governance, food preservation, and disinfection of goods. The applications of nuclear technology exhibit its essential capabilities: firstly, information acquisition, such as isotope tracing, neutron activation analysis, neutron photography, process monitoring, non-destructive detection, fire warning and alarm, resource detection, human organ imaging, radioactive immunoassay, etc.; secondly, material modification and processing, such as radiation processing, neutron doping, electrostatic elimination, radiation breeding, ion injection, and others; thirdly, decay energy utilization, such as isotope batteries, light sources, and heat sources.

1.3.1 Nuclear Technology in Energy

Nuclear energy is first applied in national defense. The atomic bomb, hydrogen bomb, as well as various reactors and accelerators that provide the supporting technology and materials for nuclear weapon research and manufacture, represent the technological cutting-edge of the application of nuclear technology. The atomic bomb utilizes

the wink release of the huge nuclear energy in the fission of ^{235}U or ^{239}Pu, while the hydrogen bomb uses the fission energy produced by the atomic bomb explosion to trigger the fusion of deuterium and tritium to release huge energies. The power of a hydrogen bomb is generally hundreds of times that of an atomic bomb. The military applications of nuclear technology in national defense are out of the scope of this book.

Nuclear technology is also of increasing significance in addressing the energy crisis. Nuclear power is about 20% of globally total electric power, while in France this figure reaches more than 70%. China, India, and other developing countries are stepping up the construction of nuclear energy to provide adequate energy for the growing industrial production. Especially in China, nuclear power plays a significant role in alleviating the outstanding conflicts in energy production, transmission, and usage caused by unbalanced economic development, unreasonable power industry structure, and imperfect layout of energy production enterprises. Nowadays, civil nuclear mainly uses ^{235}U fission energy to generate power. However, the production and development of fission power are facing insurmountable difficulties such as limited global uranium resources (the inferred resources in the < USD 260/kgU cost category in 2019 is 3346400 tU), growing demand and consumption, nearly no spent fuel for reprocessing, and long-term radiation pollution to the environment. Fusion power, which utilizes the nuclear fusion energy of deuterium and tritium, shall be the final way to solve the energy crisis in the future. The huge ^{2}H reserves in the oceans are an inexhaustible supply of civil fusion power, estimated to last 10^{9} years.

1.3.2 Nuclear Technology in the Industry

Nuclear technology is commonly used in detection and analysis, radiation processing, and isotope tracing in industrial processes. Various nuclear instrumentations, nuclear microprobes, and large container detection systems are widely used in industries, which obtain non-electrical parameters and other information in industrial processes using the rays emitted by radionuclides as a source of information. For example, various isotope monitoring instruments such as level meters, density meters, thickness meters, nuclear scales, neutron moisture meters, X-fluorescence analyzers, γ-ray flaw detectors, container detectors, and smoke and fire alarms, have been used for monitoring, nondestructive testing, component analysis, and fire detection of the production processes. ^{60}Co (cobalt-60) container CT detection system, neutron imaging detection system, high-energy electron beam sterilization system, and nuclear technology-based explosives detection device are the latest achievements in the application of nuclear technology.

Radiation processing is a material processing technology using ionizing radiation. It is one of the significant application fields of nuclear technology, including radiation-chemical processes, radiation sterilization, and radiation preservation. Radiation processing has made remarkable achievements on industrial scales in cross-linked cables, heat-shrinkable materials, rubber vulcanization, foam plastics,

positive temperature coefficient of resistance (PTC) devices, surface curing, green coatings, neutron transmutation doped monocrystalline silicon, medical and health care products, radiation sterilization, food irradiation, and wastewater and waste gas treatment.

Radiation-chemical processes are novel technological processes in which ionizing radiation is used to change the chemical or physical properties of the system. Material irradiation modification is a typical radiation-chemical process that aims to produce materials with special performances and high additional value, whose products are widely used in communication and electronics, electric transportation, petrochemical industry, aerospace, and many other fields. More than 80 countries around the world have carried out research and application of radiation-chemical processes at present. More than 1000 electron accelerators with a total power of about 45 MW, and approximately 250 irradiators bearing ^{60}Co radioactive sources with the intensity of 9.25×10^{18} Bq (9.25 EBq) have been built up for radiation processing.

High-energy radiation is used in radiation sterilization to kill bacteria and viruses. Compared with traditional sterilization by heating and chemical treatment, radiation sterilization has the advantages of low energy consumption, ambient temperature sterilization, thorough sterilization, easy and quick operation, no chemical residue, and no secondary pollution. It has replaced traditional high-temperature steam-sterilization and chemical sterilization and becoming the prevailing sterilization for medical supplies. Radiation sterilization can be applied to sterilizing thousands of species of medical supplies, including metal products and plastic products, as well as Chinese and Western medicines and cosmetics.

Food irradiation is a technology that improves the safety and extends the shelf life of foods by reducing or eliminating microorganisms and insects. Food irradiation kills bacteria without damaging the food or its health benefits. It is a safe and effective food processing technology. The benefits of food irradiation include prevention of foodborne illness, anticorrosive, control of insects, delay of sprouting and ripening, and sterilization. In November 1980, the Food and Agriculture Organization of the United Nations (FAO), the International Atomic Energy Agency (IAEA), and the World Health Organization (WHO) announced in Geneva that food irradiation underwent an overall average dose of 10 kGy wouldn't result in toxicological hazards and issues related to special nutritional or microbiological safety. Food irradiation is used in many countries to reduce food storage consumption, prevent the spread of foodborne diseases, quarantine the import and export of convenience food, and improve the quality of human life. To meet the needs of radiation processing, isotope irradiation devices and high-power irradiation accelerators with their complete sets of equipment, as well as the large-scale industrial online detectors, safety detection equipment for dangerous goods, and radiation therapy equipment that take γ-isotope and accelerator as ray sources have formed an industrial scale.

Ion implantation is a process in which an energetic ion beam is injected into the surface of solid material, resulting in changing surface composition, and thereby changing the properties of the material surface. Ion implantation is an integral part of integrated circuit manufacturing. This technology pioneered in the first half of the twentieth century has become the dominant method of semiconductor doping.

Nowadays, there are more than 3000 ion implanters for integrated circuits worldwide. The radiation modification of silicon rectifier parts (SCR) by a 12 meV electron accelerator has been widely applied. The technology of injecting metal ions into the material surface by metal vapor vacuum arc (MEVVA) to enhance the mechanical strength and friction resistance of the material surface has also been widely used in tool manufacturing, the automotive industry, and the aerospace industry. The N-type high resistance silicon prepared in the nuclear reactor by the neutron transmutation doping (NTD) technology is suitable to produce high-quality high-resistance materials. Ion beam etching (IBE) is a thin-film technology that utilizes an ion source to carry out material removal processes on a substrate. IBE is a type of ion beam sputtering that helps ensure excellent adhesion and precise formation of 3D structures, whether used for pre-clean or patterned etching. IBE offers excellent process control, precision for multilayer stacks, thorough substrate preparation, and high uptime. As an industrial technique, ion implantation exhibits high controllability and accuracy, implanting any element into the target materials without introducing other impurity elements. Ion implantation also has important applications in the field of material synthesis, including nanoparticles (NPs), positive–negative (PN) junctions, and quantum dots.

1.3.3 Nuclear Technology in Agriculture

Nuclear technologies provide competitive and unique solutions to help fight hunger, reduce malnutrition, improve environmental sustainability, and ensure food safety and authenticity. The application of nuclear technology in agriculture embraces the following four main areas: controlling pests/insects, improving animal health, increasing crop production, and improving food processing.

The nuclear-derived sterile insect technique (SIT) is the most proven and common method where nuclear technology has been utilized to control or eliminate insects. SIT can sterilize mass-raised male pests through radiation including γ-rays and X-rays, and release them back into pest-infested areas and mate with wild females without reproducing. This technique reduces reproduction and suppresses or eradicates established insect pests. It can also prevent the proliferation of invasive species—and is much safer for the environment and human health than applying conventional insecticides. This technique provides sustainable, cost-effective, and environmentally-friendly insect control. Over the past 50 years, the Sterile Insect Technique (SIT) has been successfully used to tackle pests that destroy fruit and kill livestock around the world.

Nuclear technology also plays a significant role in ensuring livestock health in various aspects, such as the research and manufacture of the radiation-attenuated vaccines for helminth parasites and protozoan parasites and the radiation-attenuated microbial pathogens, the diagnosis of infectious diseases, and the diagnosis and characterization of parasitic infections and microbial infections by the radiolabeled probes and radioimmunoassay. Radioisotopes are used to trace the paths of food

within an animal's digestive system. This process provides insight into where and how quickly the food is broken down into body tissues or milk, allowing for the determination of the nutritional value of food, and therefore ensuring that commercial feeds can meet the needs of each animal.

In terms of increasing crop yield, the role of nuclear technologies can be seen in a couple of areas. Nuclear technology used in crop breeding can develop improved varieties that better adapt to climate change and help vulnerable countries to ensure their food and nutritional security. Seeds can be irradiated with gamma rays, X-rays, ion, or electron beams to initiate genetic changes. This method increases diversity and allows for a wider selection of genetics for breeding techniques. The resulting crop varieties can have higher yield and better quality, drought, heat, or flooding tolerance, better pests and disease resistance, or shorter growth cycles. More importantly, nuclear technology can reduce the usage of fertilizer. Labeling different quantities and types of fertilizers with radioisotopes allows farmers to directly know the nutrient situation of the land because the labeled fertilizers are tracked as they are absorbed into specific areas of the crops.

The preservation of already harvested or produced food is the final focus area that nuclear technology has influenced in the broad field of agriculture. This technique is called food irradiation, beginning in the early 1920s. Food irradiation aims to discontinue the reproductive cycle of bacteria that often causes the spoiling of food. When exposing the food to controlled amounts of ionizing radiation, the DNA bonds of the targeted bacteria can be broken, which allows for longer shelf life and a less likelihood of food-borne diseases developing.

1.3.4 Nuclear Technology in Medicine

Medicine and life sciences are the most active fields in the applications of nuclear technology, including medical diagnostics, therapy, and life science research.

Nuclear medicine diagnostics involves the use of radiation sources (mostly X-rays) and radionuclides, in which radionuclide diagnosis is the most widely used. Radionuclide diagnosis is based on the principle of radioactive tracing, including in vivo imaging and in vitro diagnosis. In vivo imaging is to introduce radiopharmaceuticals into the body, imaging and measuring the global or regional function of an organ with special instruments. Nowadays, in vivo imaging has developed from the sole use of single-photon emission computed tomography (SPECT) or positron emission computed tomography (PET) diagnosis to the fusion imaging technology combining SPECT or PET with magnetic resonance imaging (MRI) or computed tomography (CT). In vitro diagnosis is to micro-analyze the biologically active substances in the patient's body fluids from outside the body, adopting radioimmunoassay (RIA) methods.

Nuclear medicine therapy utilizes ionizing radiation to kill diseased tissue cells, including external radiation therapy and intra-corporeal radiotherapy (also called radioactive source therapy). External radiation therapy is currently one of the three

efficient cancer treatments, which can be divided into external long-range irradiation, intra-cavitary post-mounted brachytherapy, interstitial short-range irradiation, and internal interventional irradiation. Gamma rays and high-energy electrons are the most commonly used radiation sources for external radiotherapy. Intra-corporeal radiotherapy is injecting or placing a radiopharmaceutical or radioactive source into the body for treatment. It has been the focus of clinical medicine for many years. Radio-immune targeted therapy, receptor-mediated targeted therapy, radionuclide gene therapy, and radionuclide particle inter-tissue targeted implantation therapy are all indispensable treatments for malignant diseases like tumors. Intra-corporeal radiotherapy can be superior to external irradiation therapy and chemotherapy in some aspects.

Molecular nuclear medicine drives today's nuclear medicine to a new era, it plays an irreplaceable role in researching receptors, genes, antigens, antibodies, enzymes, neurotransmitters, and various bioactive substances. Besides, cardiac nuclear medicine and neurotransmitter nuclear medicine has received more attention from the medical community. In competition with other imaging technologies and therapeutic methods, nuclear medicine imaging is developing from organ perfusion imaging to molecular nuclear medicine functional imaging (e.g. ^{99m}Tc and ^{123}I receptor-ligand imaging), and the integration of various imaging technologies (such as MRI-PET, MRI-SPECT, CT-PET, and CT-SPECT) acquires three-dimensional (or even four-dimensional) imaging with spatial resolution and good temporal resolution. Nowadays, nuclear medicine therapy is evolving from embolization and internal intervention to molecular-specific targeted therapy (e.g. ^{188}Re receptor-ligand therapy).

Nuclear medical devices and equipment have been continuously refined and updated in developed countries and popularized in developing countries. At present, there are about 2000 ^{60}Co (cobalt-60) devices and 6000 accelerators worldwide for the treatment of cancerous tissues deep inside the human body. The continuous popularization and upgrading of advanced diagnostic instruments (such as PET, SPECT, CT, and MRI) and radiotherapy devices (such as the radioactive sources of ^{60}Co, ^{192}Ir, and ^{137}Cs and accelerators), as well as the continuous development of new radioactive diagnostic and therapeutic drugs, offers the strong impetus to the development of nuclear medicine.

The development of specific radioactive receptor drugs for diagnostic and therapeutic imaging has become one of the most dynamic fields today which marks the level of research and application of radiopharmaceuticals in vivo. PET imaging drugs are the main direction of the development of nuclear medicine imaging for a long period of the future. The focus of the research is to take ^{18}F (fluorine-18) as the main object, including ^{11}C (carbon-11),^{13}N (nitrogen-13), ^{15}O (oxygen-15), etc. to explore the new methods and technologies for the automated and rapid synthesis of drugs. Diagnostic and therapeutic radiopharmaceuticals focusing on ^{99}mTc (technetium-99 m) and $^{186、188}$Re (rhenium-186, 188) are still hot research directions in radiopharmaceutical chemistry and the new light will emerge in the research

of internal conversion electron (or oxyelectron) nuclides and their radiopharmaceuticals, and new radiopharmaceuticals such as nano-radiopharmaceuticals (radionanopharmaceutics). New radiopharmaceuticals such as radio-nanopharmaceutics, magnetically guided drugs, and new therapeutic methods such as boron neutron capture therapy (BNCT), proton therapy, and heavy ion therapy will appear in clinical applications in the near future.

1.3.5 Nuclear Technology in Environmental Protection

Nuclear technology is commonly used to treat the waste, such as purifying coal-fired flue gas with accelerator electron irradiation and treating wastewater and hard-to-degrade organic waste with gamma rays and electron rays. Compare with traditional methods like landfilling, sea casting, and incineration, nuclear technology has significant advantages in the treatment of wastewater and other radioactive biological wastes, the most prominent of which is that it does not cause secondary pollution of the environment. For example, SO_2 and NO_x are the main atmospheric pollutants of coal-fired flue gas emitted from the coal-fired power plants. By irradiating coal-fired flue gas with the electron beam, SO_2 and NO_x react with the oxidation components like H_2O and O_2 and produce H_2SO_4 and HNO_3. H_2SO_4 and HNO_3 react with NH_3 to produce ammonium sulfate and ammonium nitrate by-products, which can be used directly as fertilizer. Such treatment is the only technology that can remove both sulfur and nitrogen pollutants at the same time, it exhibits many advantages including high efficiency, no secondary pollution, no wastewater treatment, and recyclable by-products. More than 20 devices with variable scales of flue gas desulfurization and denitrification are in operation in Japan, the United States, Germany, Russia, Poland, and other countries. Radiation technology in the treatment of atmosphere, wastewater, and sludge are to use the strong penetrating or ionizing effect of gamma rays and electron rays to cause a series of physical, chemical, and biological reactions, destroying the nucleases or proteins of microorganisms to achieve disinfection and sterilization. When using radiation technology to treat industrial organic wastewater, active substances (such as OH group) produced by irradiation can oxidize and decompose organic pollutants in water to reduce pollution levels. The sludge treated with radiation technology still maintains its original nutrients and can be used directly on farmland as fertilizer or made into compost. Radiation technology is of low treatment cost, short cycle time, and good effect on the treatment of municipal wastewater and sludge. Nowadays, more than 40 radiation treatment wastewater plants in the United States are in use, and almost all the indicators of the effluent are better than those of conventional treatment plants.

In the twenty-first century, nuclear technology has new development opportunities in environmental science and environmental monitoring and protection. Nuclear analytical techniques have become an important part of the quality assurance system for environmental monitoring and analysis. Using the unique characteristics of

nuclear analytical techniques such as ultra-sensitivity, high accuracy, and adaptability to harsh conditions, real-time and long-distance environmental monitoring systems can be built, which helps to analyze and assess the chemical species of environmental pollutants for environmental effects assessment, and to identify new pollutants for pollution tracing analysis. Moreover, plasma technology has unique technical advantages for waste treatment, such as the decomposition of harmful substances, high-temperature incineration of municipal waste, and the treatment of various wastewater and waste gas. In the chemical industry, acetylene is known as the "mother of organic synthesis industry". The development of hydrogen plasma technology creates the opportunity for the research of coal into acetylene. Coal and hydrogen ions interact at about 3700 K to produce acetylene. But the petroleum-ethylene processing has gradually replaced traditional coal-acetylene processing, which reduces pollution and achieves the comprehensive use of resources.

In addition, nuclear technology is a powerful tool for scientific research, including in the basic sciences, life sciences, and other disciplines. Using a wide range of analytical and experimental research tools provided by isotopes and ionizing radiation, man's vision extends from macro to micro, dynamically observing natural phenomena from molecular, atomic, and nucleus levels.

Based on the ultrasensitive detection of radionuclides which is incomparable to conventional chemical analysis, isotopic tracing technology plays an irreplaceable role in improving the level of technology in scientific research. Isotope tracing technology is currently the only way to explore the structural and pathological changes of in vivo body on the levels from cell to molecule, which is widely adopted in the research on genes, nucleic acids, proteins, and so on to observe the process of circulatory metabolism and disease occurrence, development, prognosis, and evolution, and explore the pathogenesis of diseases and realize a correct diagnosis. Dynamic tracing technology in agriculture uses trace radionuclides with short half-lives, which is applied for the investigation of the effectiveness and mechanism of fertilizers, the decomposition of harmful substances and residue detection, biological nitrogen fixation, for animal husbandry and veterinary research, and water conservation including the inspection and leakage determination in dams and reservoirs.

The application of nuclear technology significantly contributes to national economic construction during the decades of its development. Its ratio of input to output is as high as 1:5–1:10. Reportingly, the isotopic irradiation technology in developed countries contributes about 2–5% of the total income of the national economy.

In 1991, the contribution of non-power applications of radionuclides and radioactive materials to the U.S. economy reached $257 billion, 3.5 times that of nuclear power ($73 billion), accounting for 3.9% of U.S. GDP and creating about 3.7 million jobs. In 1995, the contribution of U.S. isotopic irradiation technology to the U.S. economy grew to $331 billion, 3.67 times that of nuclear power ($90.2 billion), accounting for 4.7% of U.S. GDP, and creating 3.95 million jobs. In 2000, the Japan Isotope Association announced that the economic scale of Japan's isotope irradiation technology was $71.4 billion, 1.18 times that of nuclear power ($60.6 billion) and 1.7% of Japan's GDP. According to the Chinese Society of Isotope and Radiation

Industry, the output value of nuclear technology applications in China was about CNY300 billion in 2018, with an average annual growth rate of about 15%, which far exceeded the growth rate of China's GDP. Therefore, being a sunrise industry, nuclear technology will be more widely used in line with the rapid growth of the world economy and the rapid development of science and technology.

Exercise

1. What is the definition of nuclear technology?
2. What are the main disciplines involved in nuclear technology?
3. Briefly describe the main application fields of nuclear technology and the main directions in various fields.
4. How to understand that "isotope and radiation technology" is the "light industry in the nuclear industry"?

Bibliography

Collins, E. D., & Ottinger, C. L. (2003). Isotopes, separation and application. In R. A. Meyers (Ed.), *Encyclopedia of physical science and technology* (3rd ed.). Elsevier.

Gooch, J. W. (2011). Radical polymerization. In J. W. Gooch (Ed.), *Encyclopedic dictionary of polymers*. Springer.

IAEA. (2020). *Uranium 2020: Resources, production and demand* (NEA-7551). Retrieved from: https://www.oecd-nea.org/jcms/pl_52718/uranium-2020-resources-production-and-demand?details=true

Issa, Z. F., Miller, J. M., & Zipes, D. P. (2019). Complications of catheter ablation of cardiac arrhythmias. In Z. F. Issa, J. M. Miller, & D. P. Zipes (Eds.), *Clinical arrhythmology and electrophysiology* (3rd ed., pp. 1042–1067). Elsevier.

Knudsen, D. J., Burchill, J. K., Cameron, T. G., Enno, G. A., Howarth, A., & Yau, A. W. (2015). The CASSIOPE/e-POP suprathermal electron imager (SEI). *Space Science Reviews, 189*(1–4).

Kónya, J., & Nagy, N. M. (2018a). Interaction of radiation with matter. In *Nuclear and radiochemistry* (2nd ed., pp. 85–131).

Kónya, J., & Nagy, N. M. (2018b). *Nuclear and radiochemistry* (2nd ed.). Elsevier.

Li, W., Zhan, X., Song, X., Si, S., Chen, R., Liu, J., Xiao, X., et al. (2019). A review of recent applications of ion beam techniques on nanomaterial surface modification: design of nanostructures and energy harvesting. *Small, 15*(31), 1901820. https://doi.org/10.1002/smll.201901820

Parker, S. P. (2003). *McGraw-Hill dictionary of scientific and technical terms* (6th ed.). McGraw-Hill.

Stracke, A., Scherer, E. E., & Reynolds, B. C. (2014). Application of isotope dilution in geochemistry. In H. D. Holland & K. K. Turekian (Eds.), *Treatise on geochemistry*. Elsevier.

Viljoen, G. J., & Luckins, A. G. (2012). The role of nuclear technologies in the diagnosis and control of livestock diseases—a review. *Trop Anim Health Prod, 44*, 1341–1366.

Waltar, A. (2003). *The medical, agricultural, and industrial applications of nuclear technology*. Paper presented at the Global 2003: Atoms for Prosperity: Updating Eisenhowers Gloal Vision for Nuclear Energy, New Orleans, LA.

Williams, W. S. C. (1991). *Nuclear & particle physics* (illustrated ed.). Clarendon Press.

Zucchiatti, A., & Redondo-Cubero, A. (2014). Ion beam analysis: New trends and challenges. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 331*, 48–54.

Chapter 2
Preparation of Radionuclides



Radionuclides include natural radionuclides and artificial radionuclides. Artificial radionuclides are widely used because they have easily controlled radiation intensity and can be made into radioactive sources of various required shapes, with usually short half-lives (easy disposal of radioactive waste). Artificial radionuclides are mainly produced by reactors and accelerators, and generators made from radionuclides produced by the above two methods can be used to obtain short-lived radionuclides. Reactors can produce various radionuclides in large quantities with relatively low production costs. Producing radionuclides by accelerators has a much smaller production capacity compared with that by reactors, but the radionuclides produced are mostly carrier-free with high specific activity and more varieties. In the process of producing radionuclides, a large amount of radioactive waste is usually generated. Optimizing the production process to reduce the generation of radioactive waste and controlling and properly disposing of radioactive waste to avoid greater harm to the environment are important technical problems to be solved in radionuclide production. Therefore, advanced radionuclide production technologies, perfect radionuclide production processes, and efficient three-waste treatment technologies are currently the focus of attention in the fields of radionuclide research, production, and application. This chapter will focus on the preparation of artificial radionuclides.

2.1 Sources of Radionuclides

Radionuclides are obtained in two ways: one is extracted from naturally occurring ores, usually referred to as natural radionuclides; the other one is prepared by artificially intervening nuclear reactions, usually referred to as man-made radionuclides, also known as artificial radionuclides. Artificial radionuclides are mainly obtained through nuclear reactor production, accelerator production, and nuclide generator production.

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6_2

2.1.1 Natural Radionuclides

Natural radionuclides are divided into primordial radionuclides and cosmogenic radionuclides. The primordial radionuclide is the radionuclide that was originally present in nature, while the cosmogenic radionuclide is the radionuclide produced by the interactions between cosmic rays and the matter in the atmosphere and the earth's surface.

The primordial radionuclides are mainly three decay series using ^{232}Th, ^{235}U, and ^{238}U as initial nuclides, i.e., thorium series (4n series, starting from ^{232}Th), uranium or uranium-radium series (4n + 1 series, starting from ^{238}U), and actinium series (4n + 3 series, starting from ^{235}U). The three natural decay series are shown in Figs. 2.1, 2.2, and 2.3. The final decay products of these series are the stable nuclides^{208}Pb, ^{206}Pb, and^{207}Pb, respectively. In these decay series, the isotopes of protactinium (Pa), actinium (Ac), radium (Ra), francium (Fr), radon (Rn), astatine (At), and polonium (Po) were produced. The half-lives of the longest-lived radionuclides of these elements vary widely, resulting in a great difference in the amount of these nuclides in nature. For example, both protactinium and radium have relatively long-lived isotopes (^{231}Pa, $T_{1/2} = 3.25 \times 10^7$a, ^{226}Ra, $T_{1/2} = 1622$a), while the lives of the longest-lived radionuclides of the isotopes of francium and astatine such as ^{223}Fr ($T_{1/2} = 22$ min) and ^{219}At ($T_{1/2} = 0.9$ min) are only a few tens of minutes with a very low stock in nature. As intermediate products of the three decay systems, they can be separated from uranium ore or thorium ore, so they are not classified as artificial radionuclides. The initial nuclide ^{237}Np (neptunium) of the fourth decay system, the neptunium system (as shown in Fig. 2.4), is synthetic, and the half-lives of all the nuclides in the neptunium system (starting with ^{237}Np and ending with ^{209}Bi) are much shorter than the age of the Earth. Thus, they cannot be found in nature but can be obtained artificially.

In addition, there are at least 22 naturally occurring single or non-series primitive radionuclides in nature. Most of these nuclides are characterized by their long half-lives and small isotopic abundances, and therefore their environmental radiation doses are small. Among these nuclides, ^{40}K is the most important, which is the only radioactive nuclide of the three natural isotopes (i.e., ^{39}K, ^{40}K, and ^{41}K) of potassium, with a half-life of 1.28×10^9a.

Besides the above-mentioned primary radionuclides, other radionuclides such as ^{3}H, ^{7}Be, ^{14}C, and ^{22}Na also exist in nature. The production of these nuclides may be due to the gradual settlement of the products of the interaction between cosmic rays and N, O, and Li in the atmosphere (see Table 2.1) to the earth's surface; or the nuclear reactions triggered by the capture of cosmic rays, neutrons produced by the spontaneous fission of uranium (each gram of ^{238}U emits 60 neutrons per hour), and neutrons produced by the (α, n) reaction between α particles and light nucleus (e.g., Be, B), etc., such as the trace ^{239}Pu present in uranium ores.

Among these natural radionuclides, ^{235}U, ^{238}U, and ^{232}Th are some important ones. ^{235}U and ^{239}Pu (produced by neutron capture of ^{238}U) are susceptible to fission under the action of thermal neutrons and release enormous energy (A ^{235}U atom

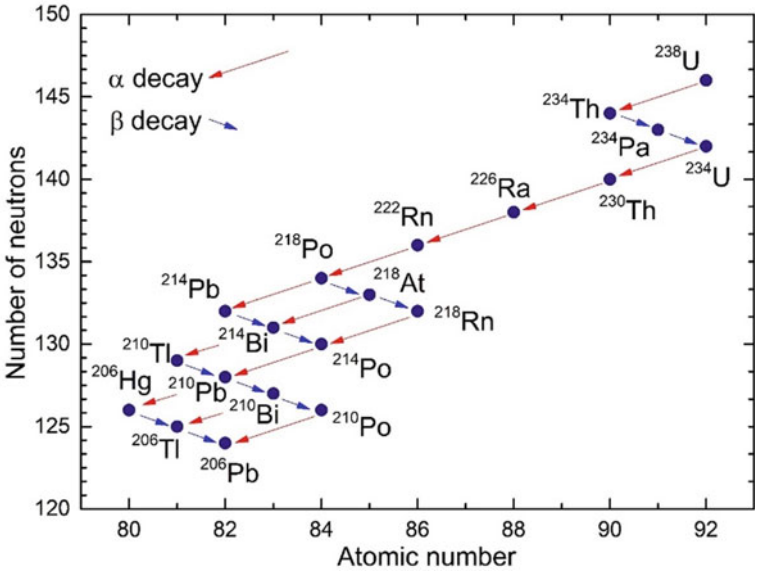


Fig. 2.1 Uranium series

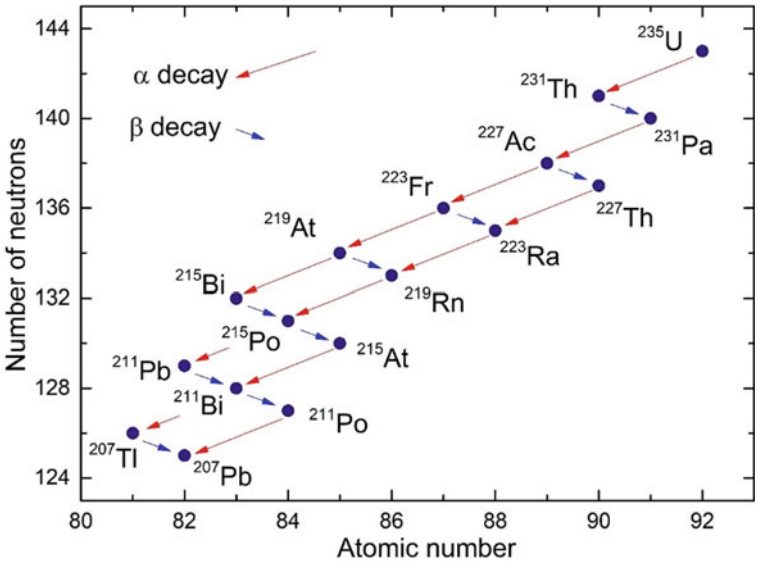


Fig. 2.2 Uranium-actinium series

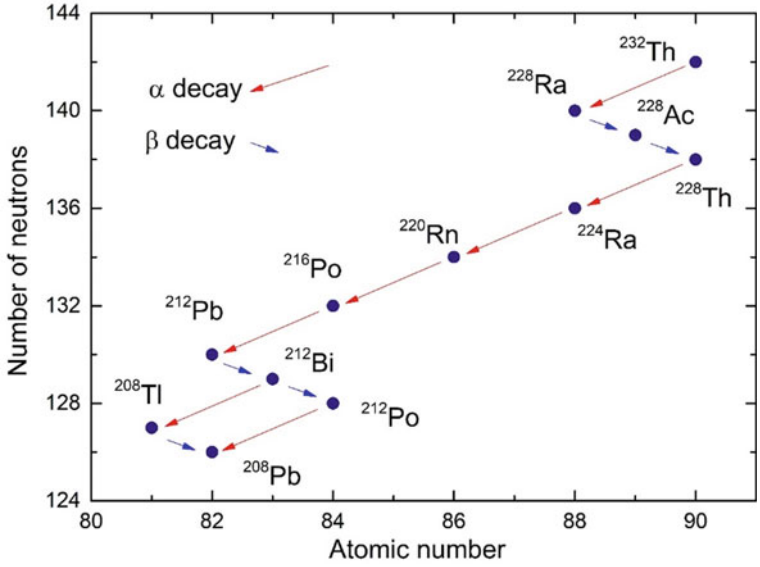


Fig. 2.3 Thorium series

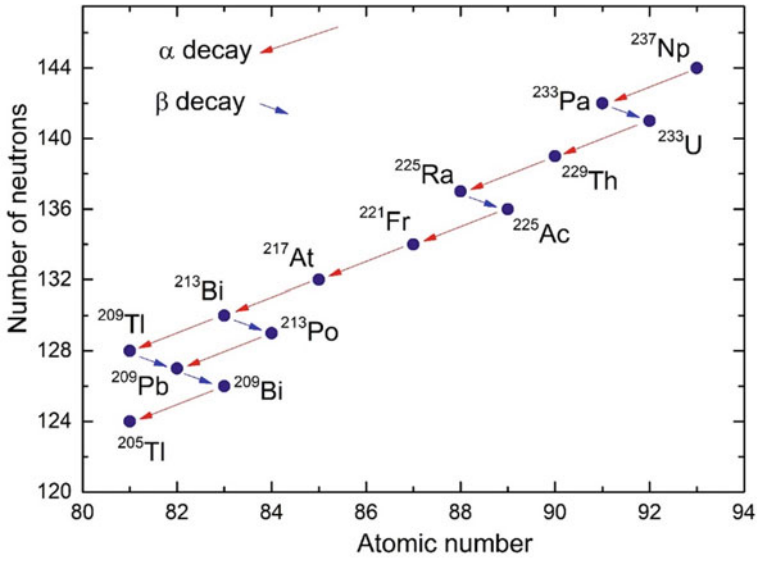


Fig. 2.4 Neptunium series

Table 2.1 Example of cosmogenic radionuclides

Nuclides	Half-lives	Origins	Natural activity
^{14}C	5730a	Activation by cosmic rays. $^{14}N(n, p)^{14}C$	~ 15 Bq g^{-1}
^{3}H	12.3a	Interact of cosmic rays with N and O; Spallation by cosmic rays. ^{6}Li (n, p) ^{3}H	~ 1.2 × 10^{-3} Bq kg^{-1}
^{7}Be	53.28d	Interact of cosmic rays with N and O	~ 0.01 Bq kg^{-1}

fission can produce about 200 meV of energy and 2–3 neutrons) and have been widely used in radionuclide production, nuclear energy utilization, etc. Since ^{232}Th can produce ^{233}U after fast neutron bombardment, it will become one of the potential alternative nuclear fuels when ^{235}U resources are scarce. Other nuclides are also widely used in scientific research, such as measuring the amount of ^{14}C in ancient relics to infer the age of the relic. This method has been widely used by archaeologists, paleoanthropologists, and geologists since its inception.

2.1.2 Artificial Radionuclides

Most of the natural radionuclides are heavy elements and are of relatively small variety and quantity. The production of some important natural radionuclides such as ^{235}U and ^{238}U is the basis of the atomic energy industry and its metallurgical technology has been well established (refer to relevant books). This chapter focuses on the production of artificial radionuclides.

Radionuclides widely used in industry, agriculture, medicine, and other fields are mainly derived from artificial radionuclides. Since the French scientists, the Curies (in 1934) obtained the first artificial radionuclide by bombarding aluminum with α particles to produce a nuclear reaction, a large number of artificial radionuclides have been prepared by reactors, accelerators, etc. Among the more than 2000 types of radionuclides discovered so far, more than 1600 of them are artificial radionuclides.

Artificial radionuclides are mainly prepared by nuclear reactions triggered by bombarding natural stable isotopes or fissile materials such as ^{235}U with neutrons and charged particles such as protons and deuterons. There are many ways to classify nuclear reactions, two of which are commonly used, namely by the type of the incident particles and by the energy of the incident particles.

According to the type of incident particles, nuclear reactions can be classified into four categories: neutron nuclear reactions, charged particle nuclear reactions, photonuclear reactions, and heavy particle nuclear reactions.

According to the energy of incident particles, three categories can be divided: low-energy nuclear reactions (E < 50 meV); medium-energy nuclear reactions (50 meV < E < 1000 meV); and high-energy nuclear reactions (E > 1000 meV).

Since fission reactors and particle accelerators can provide neutrons and charged particles with various energies required for nuclear reactions, they have become important facilities to produce artificial radionuclides.

Reactors can provide neutrons of different energy spectra and a large irradiation space, so the production of radionuclides by reactor irradiation has the advantages of simultaneous irradiation of multiple samples, a large volume of irradiated samples, easy target materials preparation, simple irradiation operation, low cost, etc. In addition, a large number of radionuclides can also be extracted from the fission products of nuclear fuel during reactor operation. It has been confirmed that there are about 400 fission products of ^{235}U induced by slow neutrons. Fission products with an atomic number distribution in the range of 30–65 and mass numbers around 95 and 139 have larger yields, which can be produced in large quantities. Producing radionuclides by nuclear reactors has become a major source of radionuclides.

Bombarding various targets with accelerated charged particles can cause different nuclear reactions and produce radionuclides (e.g. ^{18}F and ^{201}Tl) that cannot be provided by a variety of reactors. Accelerators can produce a large variety of radionuclides, accounting for more than 60% of the total number of radionuclides known to date. They mostly decay by orbital electron capture or β^+ decay, emitting simple low-energy γ-rays, X-rays, or β^+ rays. After the target is irradiated by an accelerator, carrier-free radionuclides can be obtained by dissolving, separating, and purifying. But the production capacity of producing radionuclides with this method is much lower than that of a reactor. Due to the increasing demand for accelerator-produced radionuclides, which have special applications in industry, agriculture, and especially biomedicine, it has now become an indispensable method of radionuclide production.

In addition, some radionuclides produced by reactors and accelerators are made into radionuclide generators that can provide short-lived radionuclides such as ^{99m}Tc, ^{68}Ga, etc. away from reactors and accelerators. The so-called radionuclide generator is a device that continuously separates short half-life daughter nuclides from a longer half-life parent nuclide. Since radionuclides accumulate with the decay of the parent nuclide, they can be easily separated from the parent nuclide and collected at regular intervals. This process of producing radionuclides is also more vividly known as "milking", and thus the radionuclide generator is also called a "cow".

2.2 Production of Radionuclides in Reactors

The production of radionuclides in nuclear reactors mainly utilizes the nuclear reaction between neutrons and the target nucleus. Nuclear reactors have become an important mode of radionuclide production because of their ability to continuously provide neutrons of medium to low energy (0.025 eV–15 meV). Nuclear reactors can generally provide neutron fluence rate in the range of 10^{12} cm^{-2} s^{-1}–10^{14} cm^{-2} s^{-1}, but this figure of some high-power reactors can reach 5×10^{15} cm^{-2} s^{-1}.

There are two main methods to prepare radionuclides in nuclear reactors.

(1) Irradiate the target material with the neutron stream produced by the reactor, to produce radionuclides either directly or by simple processes, i.e., the (n, γ) method.
(2) Separate radionuclides from fission products (e.g. ^{235}U) generated from irradiated fissile materials, i.e., the (n, f) method.

The former is characterized by large production capacity, large variety, a small amount of radioactive waste, and low production cost, while the latter can extract fission products such as ^{95}Zr, ^{137}Cs, and ^{144}Ce for national defense and industrial use. Carrier-free medical radionuclides such as ^{99}Mo and ^{131}I can also be mass-produced.

Since the production of radionuclides in nuclear reactors is based on the nuclear reaction between neutrons and target atoms, it is necessary to first understand neutron nuclear reactions and their characteristics.

2.2.1 Neutron Nuclear Reactions and Their Characteristics

Neutrons are not charged. Since there is no Coulomb barrier, when interacting with the nucleus, neutrons of different energies can all initiate nuclear reactions. Slow and intermediate neutrons with very low energy mainly initiate (n, γ) reactions, and slow neutrons can also initiate (n, p) reactions, (n, α) reactions, (n, f) reactions, etc. For fast neutrons, the main reactors are elastic scattering (n, n) reactions and inelastic scattering (n, n′) reactions, followed by (n, α) reactions, (n, p) reactions, and (n, γ) reactions. High-energy neutrons can cause (n, n) reactions, (n, n′) reactions, (n, p) reactions, (n, α) reactions, (n, 2n) reactions, (n, 3n) reactions, etc. The nuclides produced by neutron nuclear reactions are usually neutron-rich radionuclides, mostly decaying in the β^- form.

There are many types of nuclear reactions using reactors to produce radionuclides, and the main nuclear reactions are (n, γ), (n, p), (n, α), (n, f), and multiple neutron capture.

1. **(n, γ) reaction**

The (n, γ) reaction is the most important and commonly used nuclear reaction to produce radionuclides. A variety of radionuclides can be produced using the (n, γ) reaction. There are several ways to produce radionuclides from the (n, γ) reaction.

(1) The required radionuclide can be produced directly by the (n, γ) reaction such as ^{59}Co(n, γ) ^{60}Co, ^{191}Ir(n, γ) ^{192}Ir, ^{31}P(n, γ) ^{32}P, ^{152}Sm(n, γ) ^{153}Sm, ^{165}Ho(n, γ) ^{166}Ho, etc. Since the radionuclides directly produced by the (n, γ) reaction are all isotopes of the target element, the target nuclides cannot be separated from their target elements by chemical methods. Therefore, the prepared radionuclides generally have carriers. At the same time, due to the possible existence of multiple isotopes of target elements, all these isotopes may undergo (n, γ) reactions and become radioactive impurities when irradiated in the reactor.

(2) Through the (n, γ) reaction, the required radionuclides can be generated through nuclear decay. For example,

$$^{98}\text{Mo} \xrightarrow{(n,\gamma)} {}^{99}\text{Mo} \xrightarrow{\beta^- 65.94\,\text{h}} {}^{99\text{m}}\text{Tc}$$

$$^{130}\text{Te} \xrightarrow{(n,\gamma)} {}^{131}\text{Te} \xrightarrow{\beta^- 15\,\text{min}} {}^{131}\text{I}$$

$$^{176}\text{Yb} \xrightarrow{(n,\gamma)} {}^{177}\text{Yb} \xrightarrow{\beta^- 1.9\text{h}} {}^{177}\text{Lu}$$

$$^{226}\text{Ra} \xrightarrow{(n,\gamma)} {}^{227}\text{Ra} \xrightarrow{\beta^- 42.2\,\text{min}} {}^{227}\text{Ac}$$

Since the target element is not the same as the target nuclide, the target element can be physically or chemically separated from the target nuclide to obtain a carrier-free target nuclide with high specific activity, radiochemical purity, and radionuclide purity. This method has been used in production processes such as reactor irradiation-^{99}Mo/$^{99\text{m}}$Tc generators, ^{131}I dry production, etc.

(3) The required radionuclide can be produced directly through two or more (n, γ) reactions, or by nuclear decay. For example, irradiating the enriched ^{186}W on a high flux reactor generates ^{188}W via two times neutron captures, ^{188}W then generates ^{188}Re through β^- decays. The ^{188}W/^{188}Re generator can be prepared by this nuclear reaction method.

$$^{186}_{74}\text{W} \xrightarrow{(\text{n},\gamma)} {}^{187}_{74}\text{W} \xrightarrow{(\text{n},\gamma)} {}^{188}_{74}\text{W} \xrightarrow[69\text{d}]{\beta^-} {}^{188}_{75}\text{Re}$$

$$^{187}_{74}\text{W} \xrightarrow[23.7\text{h}]{\beta^-} {}^{187}_{75}\text{Re}$$

(4) Radionuclides can be produced by thermal-atomic effects in the (n, γ) reaction. This method can obtain radionuclides with higher specific activity such as ^{51}Cr, ^{65}Zn, etc.

2. (n, f) reaction

^{235}U and other fissionable nuclides capture neutrons and generate (n, f) reactions to produce hundreds of fission nuclides (products). Thus, the composition of fission products is quite complex. Take ^{235}U as an example, the fission products produced by its nuclear reaction with thermal neutrons include more than 160 nuclides of 36 elements (A = 72–161). Through chemical separation, radionuclides such as ^{90}Sr, ^{95}Zr, ^{99}Mo, ^{131}I, ^{137}Cs, ^{144}Ce, etc., which have important applications in the national defense industry and national economy, can be extracted from these fission products.

3. **(n, p) reaction**

(n, p) reactions require high neutron energies and are generally induced by fast neutrons. Since the potential barrier in the nucleus increases with the increase of atomic number, the (n, p) reaction is suitable for preparing radionuclides with a low atomic number such as ^{14}C, ^{32}P, ^{58}Co, etc. Besides, as the nuclides prepared by the (n, p) reaction have different atomic numbers from the target elements, radionuclides with no carrier and high specific activity are generally obtained by chemical separation. However, due to the high threshold of this type of nuclear reaction and the small reaction cross-section of the target nuclide, it is difficult to realize large-scale production by the (n, p) reaction.

4. **(n, α) reaction**

As with the (n, γ) reaction plus β^- decay and the (n, p) reaction, carrier-free radionuclides can also be produced by the (n, α) reaction. For example, this nuclear reaction is adopted for the production of tritium from enriched ^6Li uses, namely $^6Li(n, \alpha)\ ^3H$.

2.2.2 Production of Radionuclides by Reactor Irradiation

The yield and product quality of radionuclides produced by reactor irradiation are not only affected by irradiation conditions but also related to the selection of nuclear reaction, the preparation of the target material, the extraction process, etc. In addition, attention must be paid to the safety of the target during irradiation in the reactor.

1. **Conditions required in reactors by radionuclide production**

(1) High neutron fluence rate

Since most radionuclides are prepared by (n, γ) reactions, a high proportion of thermal neutrons is required. In the reactor, the fission of nuclear fuel ^{235}U mostly produces fast neutrons, which need to be slowed down to thermal neutrons by materials such as water, heavy water (D_2O) graphite, etc., and the neutron fluence rate in the irradiated channel can be improved by wrapping cadmium (Cd) and beryllium (Be) reflecting layers. In general, a neutron fluence rate is required to be more than 5×10^{13} cm^{-2} s^{-1} for mass production of radionuclides. For some nuclides with small nuclear reaction cross-sections, especially those that can be obtained only after multiple neutron capture, the requirement for the neutron fluence rate is higher. For instance, the neutron fluence rate required for producing ^{192}Ir and ^{188}W with high specific activity (obtained after two times neutron captures of ^{186}W) is preferably to be more than 1×10^{15} cm^{-2} s^{-1}.

(2) Sufficient irradiation space

Under the same irradiation conditions, the yield of radionuclides is proportional to the number of target materials put into the reactor for irradiation. Therefore, it is necessary to irradiate as many target materials as possible while ensuring irradiation safety. A typical reactor usually has dozens of irradiation channels. The sizes of different channels and the neutron energy spectrum in them are different. Therefore, different channels can be used to mass-produce a variety of radionuclides at the same time.

(3) Operation mode

How the reactor is operated has a large impact on the yield of radionuclides. The duration of continuous operation time and shutdown time of the reactor (or frequency of shutdown) are also important factors affecting the mass production of radionuclides. For the production of long half-life radionuclides, the yield is greatly affected by the irradiation time and reactor power (or neutron fluence rate), while the frequency of shutdown has little effect. For the production of short half-life radionuclides, the yield is greatly affected not only by the irradiation time and reactor power (or neutron fluence rate) but also by the frequency of shutdown. Therefore, different reactor operation modes must be determined according to the nuclear properties of the produced radionuclides (e.g., half-life, nuclear reaction target cross-section of target nuclide, etc.).

(4) Reactor safety assurance

The channels used for sample irradiation in the reactor are mainly divided into dry channels and wet channels according to the cooling method. The dry channel uses air to cool the target, while the wet channel uses deionized water. For isotope targets with large calorific value during irradiation, water is generally used as a coolant to ensure the safety of the target and reactor operation. For some special targets such as ^{235}U targets with large loading, a circulating water cooling system needs to be established on the reactor to provide forced cooling conditions for the targets if necessary.

2. **Preparation of the target**

(1) Selection and treatment of target materials

The following points should be noted in the selection of the target material.

① Suitable chemical form. When selecting the suitable chemical form of the target, it should be required that the chemical purity and content of the target element should be as higher as possible, the target can be easily treated and transformed into the required chemical form after irradiation, and the stability of the target (chemical stability, thermal stability, and irradiation stability) during in-reactor irradiation should be good.

The content of target elements in target materials with different chemical forms affects the yield of target nuclides. The chemical form with high target element content should be selected as far as possible, such as directly using the target material as the target. When selecting the chemical form of the target, the difficulty of post-irradiation treatment and conversion of the target to the required chemical form must be considered. If it is difficult to dissolve or convert the metal wire or oxide of some targets into the required chemical form after irradiation, its salt compounds or other chemical forms can be selected as an alternative. In addition, when selecting the chemical form of the target, the safety of target irradiation should also be considered. For example, the target element of some chemical forms is unstable under irradiation and high temperature, which will decompose and release gas. This may swell or even rupture the target, block the target, or escape radioactive gas in the reactor, affecting the safety of the target and the reactor. In order to reduce the introduction of radioactive impurities, high-purity and high-abundance target materials should be selected.

② The abundance of target nuclide. On the premise of considering the cost and meeting the needs, high abundance nuclides should be used as the target as far as possible. For some nuclear reactions with small cross-sections, requiring two times neutron captures to produce, or requiring a high specific activity of target nuclides, it is difficult to meet the above requirements by using natural or low-abundance nuclides as the target. Given this situation, the enriched high-abundance nuclide can be used. For example, for the production of radionuclide ^{113}Sn, the natural abundance of the target nuclide ^{112}Sn is 0.96% and the thermal neutron cross-section is 0.71b. If the element Sn with natural abundance is used as the target material, the specific activity of ^{113}Sn obtained by (n, γ) reaction is low. To obtain ^{113}Sn with high specific activity, only ^{112}Sn with high enrichment can be irradiated.

Before the target material is loaded into the irradiation target barrel, it generally needs to be pretreated to ensure the purity of the final product and irradiation safety. Pretreatment includes water and gas removal (crystallization water, combined water, volatile gas) via heating, chemical purification, cleaning and oil removal, etc. Sometimes, in order to increase the loading of the target, the powder material needs to be pressed and sintered.

(2) Structural design and preparation of the target

The structural design of the target includes the design of the target barrel structure, the structure of the target core (the shape of the target), and its distribution in the target barrel. The target material shall be designed according to the parameters of the irradiation channel provided by the reactor (channel size, neutron type, and neutron fluence rate distribution), loading and calorific value of the target, the cooling mode of the irradiation pipeline of the target, and the grasping tools for the target passes in and out of the reactor, so as to ensure the safety of the target and the reactor during irradiation. At the same time, the structural design of the target should also consider

the convenience of the target passes in and out of the reactor and the convenience of the target anatomical operation.

The material used to prepare the target barrel is required to have sufficiently high mechanical strength, good machinability, no introduction of radioactive impurities, small neutron capture cross-section, or no generation of long-lived nuclides to avoid excessive radiation dose. At present, high-purity aluminum is mostly used as the outer shell material. For some high-pressure gas targets such as ^{124}Xe, or targets that may produce (release) gas during irradiation such as ^{235}U, stainless steel can be used as the inner cylinder material to increase the anti-deformation ability of the target. The target barrel should be cleaned after fabrication to remove oil and other contaminants introduced during the production processes.

For some targets that need to be irradiated in the reactor for a long time, it is often necessary to carry out anti-corrosion treatment on the outer surface such as oxidation passivation treatment on the surface of aluminum targets.

For targets that are irradiated for a long time or generate large amounts of heat, improving the internal thermal conductivity of the target needs to be considered to ensure the safety of the target and the reactor during irradiation. In special cases, forced convection can also be used to accelerate heat dissipation.

When preparing the irradiation targets, the loading capacity of the target, the internal and external packaging forms, etc. should also be considered. The loading capacity of the target is determined by its heat capacity under certain irradiation conditions and the cooling conditions provided by the reactor. The target is usually directly encapsulated in a high-purity aluminum cylinder of irradiation. If the target material can react chemically with aluminum, the target should be sealed in a quartz ampoule bottle and then encapsulated in an aluminum cylinder.

(3) Welding and sealing of the target

In order to ensure that the target material does not leak radioactive substances during reactor irradiation, welding is generally used to seal the target inside the barrel. The common methods used to weld are argon arc welding, laser welding, cold welding, etc. Argon arc welding is the most widely used welding method in the preparation of isotope production targets.

(4) Quality control of the target

The target needs to be tested for tightness and surface contamination and can be irradiated in the reactor only after the quality is qualified. The common detection methods of target tightness include helium mass spectrum leak detection, boiling leak detection, and so on. Boiling leak detection is the early method, which has been replaced by helium mass spectrum leak detection. During the preparation of some targets, the surface will be stained with easily activated substances such as target materials. Therefore, before irradiation in the reactor, the target surface must be cleaned, and the surface contamination must be measured. Only after passing the inspection can the target be put into the reactor for irradiation.

For some targets (such as highly enriched uranium targets), non-destructive testing of welding quality and distribution uniformity of target elements in the target is also required. Currently, the available method includes industrial computed tomography, neutron imaging technology, γ spectrometer measurement, etc. For targets requiring long-distance transportation, further tests such as compressive and drop strength tests are required.

3. **Irradiation of the target**

When producing radionuclides by reactor irradiation, it is essential to select the appropriate irradiation conditions and ensure the safety of the irradiation process. The following points should be noted for the irradiation of targets.

(1) Select appropriate nuclear reaction and neutron spectrum

A given radionuclide may be obtained by a variety of nuclear reactions. The type of nuclear reaction and its corresponding cross-section is related to the neutron energy. Therefore, the selection of an appropriate neutron spectrum has a great impact on the quality of the target nuclide and the cost-effectiveness of the production. The selection of nuclear reaction type and neutron spectrum should ensure that the reaction products have high specific activity, high radioactive purity, and high yield. At the same time, it also needs easy chemical separation, as well as simple and economic production processes.

The atomic number of radionuclides suitable for the production of radionuclides in reactors is generally required to be more than 20. For the production of radionuclides with atomic numbers between 20 and 35, fast neutrons with high energy can be selected. When the atomic number is greater than 36, (n, γ) reaction is usually chosen.

(2) Highest possible neutron fluence rate

The yield of radionuclides produced by the reactor is proportional to the neutron fluence rate. Therefore, the neutron fluence rate should be selected as high as possible to increase the yield of target nuclides, especially for nuclides with small nuclear reaction cross-sections or that can be obtained only after multiple neutron capture such as ^{113}Sn, ^{188}W, etc.

(3) Suitable irradiation period

For the same target nuclide, the nuclear reaction and its cross-section caused by neutrons with different energy are also different. Because the energy of the fission neutrons in the reactor after moderation is not single, and the energy of the slow neutrons decreases with the increase of the depth of the target, it is difficult to accurately determine the value of the nuclear reaction cross-section. In addition, the nuclear reaction products of the target can recapture neutrons to continue the nuclear reaction, and generate new substances through decay. Based on the above reasons,

the theoretical yield of a given nuclear reaction will deviate from the actual situation, but estimating the yield in advance based on the average neutron energy is helpful to select more reasonable irradiation conditions.

Assuming that stable nuclide S is bombarded by incident particles to generate radionuclide A, nuclide A only decreases in decay and generates stable nuclide B. The following equation can represent this process.

$$S \xrightarrow{(n,\gamma)\sigma_s} A \xrightarrow{T_{1/2}} B \text{ (stable)}$$

$$^{23}\text{Na} \xrightarrow{(n,\gamma)\,0.53b} {}^{24}\text{Na} \xrightarrow{T_{1/2}=14.96\,\text{h}} {}^{24}\text{Mg (stable)}$$

During the irradiation, the yield of nuclide A is proportional to the fluence rate of incident particle Φ ($cm^{-2}\ s^{-1}$), the cross-section of thermal neutron capture σ_s (b, $1b = 10^{-24}\ cm^2$), and the number of target nuclei N_s, i.e., the productivity of nuclide A is $\Phi\sigma_s N_s$, and it decreases with the decay rate of $\lambda_A N_A$ at the same time. Thus, the net growth rate of nuclide A is

$$\frac{dN_A}{dt} = \Phi\sigma_s N_s - \lambda_A N_A \tag{2.1}$$

where N_A is the number of atoms of nuclide A after irradiation time t.

If the incident particle flux and thermal neutron capture cross-section are constants, the number of atoms N_s of the target nucleus is almost unchanged during irradiation in most cases. When using the initial condition $t = 0$, $N_A = 0$. The solution of the above differential equation is

$$N_A(t) = \frac{\Phi\sigma_s N_s}{\lambda_A}\left(1 - e^{-\lambda_A t}\right) \tag{2.2}$$

The radioactivity of nuclide A is

$$A_A(t) = \lambda_A N_A = \Phi\sigma_s N_s\left(1 - e^{-\lambda_A t}\right) \tag{2.3}$$

The above two equations are the yield equations. Obviously, the activity of nuclide A increases gradually with the increase of irradiation time t. When the irradiation time $t \geq T_{1/2}$, $e^{-\lambda_A t} \to 0$, then A_A reaches the maximum value. Therefore, $\left(1 - e^{-\lambda_A t}\right)$ is called the saturation factor. After stopping irradiation for a time t', the activity of nuclide A is

$$A_A\left(t'\right) = A_A(t)e^{-\lambda_A t'} = \Phi\sigma_s N_s\left(1 - e^{-\lambda_A t}\right)e^{-\lambda_A t'} \tag{2.4}$$

The above is only the yield calculation of the simplest nuclear reaction.

The yield of target radionuclides can be calculated by Eqs. (2.2), (2.3), and (2.4). It should be noted that the yield is related to many factors such as the neutron energy spectrum of the reactor, the yield of reactor irradiation and the energy of incident

neutrons, the neutron fluence rate, the nuclear reaction cross-section, the number of target atoms, the irradiation time, and the half-life of radionuclides. At the same time, situations such as the changes in neutron fluence rate and energy spectrum during irradiation, the self-shielding effect of the target material, and the continuous consumption of target atoms (especially under the conditions of large target nuclear reaction cross-section and long irradiation time) will also affect the yield. Therefore, it is unrealistic to accurately calculate the yield of the radionuclides. When designing the target and selecting irradiation process conditions, the yield of radionuclides is usually obtained by consulting manuals or software calculations. Based on the calculated or consulted yield, the required quantity of raw target materials can be deduced for target preparation.

The optimum irradiation time can be determined from the above yield equation or can be obtained by conversion after consulting the radionuclide production manual. In the actual production process, the cost-effectiveness of reactor operation, the convenience of operation, and the control of radioactive purity content also need to be considered.

4. **Treatment of irradiated targets**

The treatment of irradiated targets includes physical treatment, chemical treatment, and their further processing. The irradiated target generally needs further chemical treatment (separation and purification of target nuclides) before they can be made into radionuclide products to meet the needs of users. The chemical treatment methods adopted include solvent extraction, precipitation, ion exchange, distillation (or dry distillation), electrochemical separation, hot atomic recoil separation, and so on.

Take the production of gel-^{99}Mo/^{99m}Tc generator by irradiated MoO_3 and the preparation of ^{131}I by irradiated TeO_2 as examples. To prepare the gel-^{99}Mo/^{99m}Tc generator, dissolve the irradiated MoO_3 with ammonia, then add $ZrOCl_2$ solution to produce the zirconium molybdate gel, filter, granulate, dry the gel, and load the gel into the column. As for the preparation of ^{131}I by irradiated TeO_2, the distillation method can be used. That is, to dissolve the irradiated TeO_2 by NaOH and acidify it with H_2SO_4, add H_2O_2 for heating and distillation, or directly heat the target material in a retort furnace to distill ^{131}I and prepare the Na^{131}I oral liquid.

Some samples can be used without chemical treatment after irradiation (i.e., only need simple physical processing) such as ^{60}Co, ^{192}Ir, etc. Make these samples into the final shape before irradiation. After irradiation, the sample can be physically welded and sealed to become a radioactive source.

The radiochemical treatment involving radioactive operations requires a series of facilities that can process radioactive substances, and radioactive waste treatment and monitoring systems, including hot cells, workboxes, glove boxes, target transport and cutting devices, chemical separation and purification devices, dose measurement and radiation monitoring equipment, product sub-packaging device, product quality measuring equipment, etc., as well as facilities related to radioactive waste such as temporary storage, treatment, sorting, and so on.

5. Quality of radionuclide products

The quality of radionuclide products is guaranteed by physical, chemical, and biological inspections. The quality indicators of radionuclide products include radioactivity, radioactive purity, radiochemical purity, chemical purity, carrier content, sterility and heat source free detections of medical preparations, etc.

6. Production of some radionuclides with important application values

Table 2.2 lists some important radionuclides produced by reactor irradiation. This section will briefly introduce ^{131}I produced by the dry distillation process and ^{125}I produced by the intermittent circulation circuit process.

(1) Production of ^{131}I with dry distillation

① Characteristics and production method of ^{131}I

Due to its excellent nuclear properties, ^{131}I has become one of the important nuclides in nuclear medicine for the diagnosis and treatment of a variety of diseases. It is widely used in the diagnosis and treatment of thyroid cancer, hyperthyroidism, hypothyroidism, and kidney diseases.

There are two main ways to produce ^{131}I. One is the (n, f) method, i.e. ^{235}U(n, f)^{131}I, in which the fission product ^{131}I is separated from the irradiated ^{235}U target. Since the fission product of ^{235}U contains a variety of isotopes of ^{131}I, it needs to be placed for 1–2 weeks to allow the short-lived nuclides to sufficiently decay to reduce the radioactivity before extracting ^{131}I. This method is mostly used via the evaporation of the acidic solution to collect the volatilized ^{131}I. It has a low extraction rate (the efficiency is only about 60%) and will produce a large amount of radioactive waste. The other is the (n, γ) method, in which a single Te or various compounds of Te are used as raw materials. After irradiation in the reactor, the Te undergoes ^{130}Te(n, γ)^{131}Te and β^- decay to produce ^{131}I, which is then separated from the target material. Currently, the main methods for separating ^{131}I from irradiated Te are wet distillation, electrolytic distillation, and dry distillation. Wet distillation is rarely used now because it uses highly concentrated sulfuric acid and hydrogen peroxide, with complex operation processes, high risks, long operation cycle (> 24 h), and a large amount of strong radioactive waste liquid. At present, the main method of separating ^{131}I worldwide is dry distillation. The main advantages of producing ^{131}I by dry distillation include short separation time, high product recovery, high product-spec activity, low impurities, and no liquid waste. Due to the high specific activity of the product, it is conducive to preparing various labeled compounds and radioactive products with excellent performance, which are used in scientific research, clinical diagnosis, and treatment.

② Dry distillation production systems

The ^{131}I dry distillation production system mainly includes three parts—heating and distillation, alkali liquid absorption, and waste gas treatment. Other accessories include vacuum pump, vacuum gauge, air flow meters, etc. A typical ^{131}I dry distillation production system is shown in Fig. 2.5.

Table 2.2 Some important radionuclides produced by reactors

Nuclide	Half-life	Nuclear reaction	Target material	Production method
^{3}H	12.33a	^{6}Li (n, α) ^{3}H	Li/Mg Li/Al	After irradiation, the target is heated to 500–600 °C in a vacuum tube and ^{3}H can be separated
^{14}C	5730a	^{14}N (n, p) ^{14}C	Be_3N_2 $Ba(NO_3)_2$	The irradiated target is dissolved with 65% sulfuric acid and H_2O_2 is added. The generated $^{14}CO_2$, ^{14}CO, and $^{14}CH_4$ are brought out with N_2 gas flow. After flowing through the heated CuO (750°C), the generated $^{14}CO_2$ is absorbed with NaOH and then precipitated into $Ba^{14}CO_3$
^{32}P	14.282d	^{32}S (n, p) ^{32}P	Distilled purified S	After irradiation, the target is distilled under reduced pressure at 180°C to remove sulfur, 0.1 mol L^{-1} HCl and H_2O_2 were added, and $H_3{}^{32}PO_4$ can be obtained after heating and purification for 2 h
^{60}Co	5.271a	^{59}Co (n, γ) ^{60}Co	Co wire with purity > 98%	Neutron-Irradiated cobalt can be directly made into radioactive sources of various forms and activities

(continued)

Table 2.2 (continued)

Nuclide	Half-life	Nuclear reaction	Target material	Production method
^{99}Mo/^{99m}Tc	^{99}Mo: 2.7477d ^{99m}Tc: 6.006 h	^{98}Mo(n, γ)^{99}Mo $\xrightarrow{\beta^-,\gamma}$ ^{99m}Tc → ^{99}Tc	MoO_3 powder	The irradiated target is dissolved in 10 mol L^{-1} ammonia solution, the excess ammonia is removed with 0.05 mol L^{-1} HCl, and the pH of the solution is adjusted to 3–4 and loaded onto the alumina column, Mo is adsorbed and ^{99m}Tc is finally eluted with physiological saline
^{113}Sn/^{113m}In	^{112}Sn: 115.09d ^{113m}In: 1.658 h	^{112}Sn (n, γ) ^{113} Sn Ec → ^{113m}In IT → ^{113m}In	^{112}Sn enrichment target	The target irradiated with high neutron flux for one year is heated and dissolved with 6 mol L^{-1} HCl and evaporated to dryness, oxidized to Sn^{4+} with Br_2 water, and then adsorbed on a zirconia adsorption column, eluting ^{113m}In with 0.05 mol L^{-1} HCl
^{125}I	59.407d	^{124}Xe (n, γ)^{125}Xe β$^-$ → ^{125}I	^{124}Xe gas	After irradiation, ^{124}Xe gas is taken out from the reactor, cooled and decayed for a week, and then ^{125}I can be absorbed with NaOH
^{131}I	8.040d	^{130}Te (n, γ) ^{131}Te β$^-$ → ^{131}I	TeO_2	The irradiated TeO_2 is placed in the muffle furnace and distilled at 750–800 °C, and the evaporated ^{131}I is absorbed with NaOH solution

a. **Heating distillation unit**: Consists of a tubular heating electric furnace (with temperature controller), purification heating furnace, quartz boat, and quartz heating tube.

   Tubular heating electric furnace: Used to control the large diameter temperature of the quartz heating tube, with the maximum operating temperature of 1200 °C, and the accuracy is controlled at ± 2 °C.

   Purification heating furnace: Used to control the small diameter temperature of the quartz heating tube, with the maximum operating temperature of 500°C, and the accuracy is controlled at ± 2 °C.

   Quartz boat: Used to hold irradiated TeO_2 samples, with the maximum loading capacity of 300 g per boat.

b. **Alkali liquor absorption unit**: Consists of two-stage alkali absorption columns. The volume of the first absorption column is 50 mL and that of the second stage is 250 mL.

c. **Waste gas treatment unit**: Consists of three-stage strong alkali scrubbers. The volume of each stage of the scrubber is 1000 mL, with a concentration of 5.0 mol L^{-1} (NaOH). In addition, the operating workbox or hot chamber shall be equipped with an iodine filter.

③ Dry distillation production process

Load the irradiated TeO_2 into a quartz boat and place the boat in the dry distillation furnace, connecting the system. Heat the system to 700–900 °C, the distilled ^{131}I

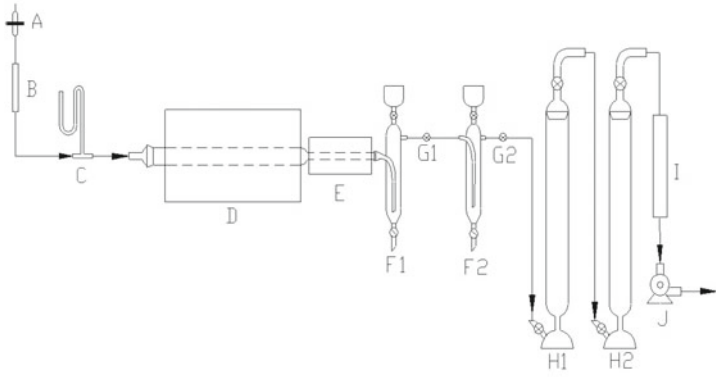


Fig. 2.5 Schematic diagram of the ^{131}I dry process production system. A—filter, B—flowmeter, C—manometer, D—evaporation furnace, E—purification furnace, F—absorption column, G—valve, H—activated carbon column, I—activated carbon measuring column, J—vacuum pump

can be carried by the carrier gas to the purification furnace (200–400 °C), where the distilled TeO_2 comes out with the carrier gas is cooled and deposited to separate TeO_2 from ^{131}I. The radioactive gas containing ^{131}I after TeO_2 removal is absorbed in the alkali solution. The unabsorbed ^{131}I is further removed from the tail gas mainly through the alkali solution (5.0 mol L^{-1} NaOH) to reduce the emission of ^{131}I, and the escaped ^{131}I is further absorbed by activated carbon.

④ Product quality control

Quality requirements: colorless transparent liquid, pH = 7–9, no obvious impurity nuclide that can be detected by γ spectrometer, radiochemical purity > 95%.

(2) Production of ^{125}I with intermittent circulation circuit

① Characteristics and production method of ^{125}I

^{125}I is a commonly used radionuclide in medicine. It is a radioactive isotope of iodine that decays by orbital electron capture, with a half-life of 59.407 d, and mainly releases 27 keV X-rays. It can effectively kill tumor cells, is easy to shield, and has less radiation to the people around the patient. Prostate cancer and breast cancer can be treated with ^{125}I seed, which can change the traditional treatment methods and reduce the risk of patients with an effective rate of over 95%.

The main nuclear reaction to produce ^{125}I is $^{124}Xe(n, \gamma)^{125}Xe \rightarrow {}^{125}I$. Currently, there are two methods of production.

One method is to package ^{124}Xe in a stainless-steel cylinder to make an inner target, then place the target in a high-purity aluminum cylinder for irradiation after welding and leak detection. Place the irradiated target for a period to cool so that ^{125}Xe can fully decay to ^{125}I, and then absorb ^{125}I with NaOH. The unactivated ^{124}Xe can be recycled after recovery. This method was established by the Russian Institute of Physical and Power Engineering (IPPE). Using this method to obtain ^{125}I, the ^{124}Xe gas target needs to be prepared, and the production capacity is low. In addition, the content of ^{126}I in the products must be strictly controlled, otherwise, it won't be able to be used for the preparation of ^{125}I medical seed.

Another method to produce ^{125}I is the intermittent circulation circuit method. This method does not require the preparation of the ^{124}Xe gas target, and it is relatively simple. The purity of ^{125}I obtained with this method is higher, and the production capacity is higher than that of the former method.

② Intermittent circulation circuit production system

The main process to produce ^{125}I by the intermittent circulation circuit method is shown in Fig. 2.6. Inject a high purity of ^{124}Xe gas into the irradiation bottle in the

reactor through the circulation circuit. After irradiation for a certain period (usually 1.5–2 $T_{1/2}$ of ^{125}Xe), cool the decay bottle outside the reactor. Since cooling will lead to negative pressure in the decay bottle, the irradiated ^{124}Xe gas can be sucked into the decay bottle through the circulation circuit. Place the bottle for 3–5 d and wait for most of ^{124}Xe to decay and generate ^{125}I. The unused ^{124}Xe is then led back to the circulation circuit for repeated use. The ^{125}I generated by decay is dissolved in NaOH solution is sub-packaged into products after measurements of nuclear purity, activity, etc. In order to better use the irradiation conditions of the reactor, multiple bottles can be connected to the circulation circuit for recycling.

③ Production examples

China Institute of Atomic Energy (CIAE) has produced ^{125}I using its self-developed intermittent circulation circuit method. After 6 days of continuous irradiation of enriched ^{124}Xe, 4.81×10^{11} Bq (13 Ci) of ^{125}I can be obtained. The concentration of ^{125}I obtained reached 1.85×10^{10} Bq-mL^{-1}(500 Ci-L^{-1}), radiochemical purity > 98%, the relative content of impurity ^{126}I is less than 10^{-8}, and ^{137}Cs was not detected.

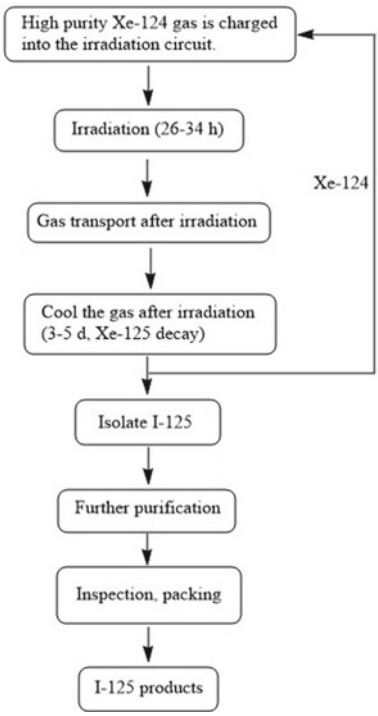


Fig. 2.6 ^{125}I intermittent circulation circuit production process

2.2.3 Extraction of Radionuclides from Fission Products

The second method of producing radionuclides in the reactor is to extract fission elements and transuranium elements produced by ^{235}U and other fissile materials after irradiation. Fission products include radionuclides with a wide range of atomic numbers, and a variety of fission radionuclides with high specific activity can be obtained by separation.

1. **Fission nuclear reactions**

Nuclear fission is a nuclear reaction or a decay process in which the heavy nucleus splits into smaller parts (lighter nuclei). The fission process often produces free neutrons and photons (in the form of γ-rays) and releases a large amount of energy.

In most cases, the heavy nucleus splits into two fission fragments. Some may also split into three or four fission fragments, but the probability of occurrence is very small. Figure 2.7 shows a diagram of binary nuclei fission.

The following equation represents the slow neutron bombardment of ^{235}U

$$^{235}U + n \rightarrow {}^{236}U \rightarrow X + Y$$

X and Y represent the two fission fragments produced by fission, which are often of unequal mass and distributed in a wide range. If the fission fragments contain too many neutrons, it is unstable and will immediately emit two to three neutrons (and γ-rays). The prompt neutrons produced with fission are generally emitted within 10^{-14} s, accounting for more than 99% of fission neutrons. Fission neutrons are absorbed by nearby uranium nuclei and fission occurs again, producing second-generation neutrons. The neutrons are absorbed again, and fission occurs again, producing third-generation neutrons. If there is no loss of neutrons or less loss, such a chain reaction will continue, and the fission reaction will gradually increase.

Fission reactors utilize fissionable heavy elements such as ^{235}U, ^{233}U, and ^{239}Pu. Under the impact of neutrons, the composition of heavy nuclear fission products is complex. Take ^{235}U as an example,

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow \begin{cases} \rightarrow {}^{114}_{56}Ba + {}^{89}_{36}Kr + 3{}^{1}_{0}n \\ \rightarrow {}^{140}_{54}Xe + {}^{94}_{38}Sr + 2{}^{1}_{0}n \\ \rightarrow {}^{133}_{51}Sb + {}^{99}_{41}Nb + 4{}^{1}_{0}n \end{cases}$$

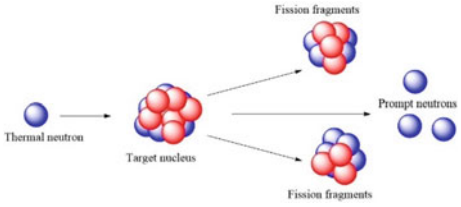


Fig. 2.7 Schematic diagram of neutron-induced nuclear fission

2. **Composition and mass distribution of fission products**

When the fission of heavy nuclei is initiated by neutrons, the composition of fission products is extremely complex. At present, more than 400 nuclides have been found, including stable nuclides and short-lived nuclides with a half-life of less than one second. The mass numbers of these nuclides are widely distributed (from 66 to 172) and include all elements from zinc to lutetium in the periodic table of the elements. Fission products with mass numbers less than 66 or greater than 172 may also exist, but due to their extremely low yields, isolation and identification can be difficult. Therefore, with the improvement of separation technology and measurement means, it is possible to find new fission products with a shorter half-life and lower yield.

The composition of fission products changes with time. When a target of fissionable material is irradiated in the reactor for T time and cooled for t time, the radioactivity A_i of the fission nuclide i can be expressed by the following equation.

$$A_i = NI\sigma Y_i\left(1 - e^{-\lambda_i T}\right)e^{-\lambda_i t} \tag{2.5}$$

where N is the number of nuclei of fissionable material, I is the neutron energy, σ is the fission cross-section, Y_i is the fission yield of nuclide i, and λ_i is the decay constant of nuclide i.

It can be observed from Eq. (2.5) that the radioactivity of fission products is related to the fission yield Y_i and changes with T and t when N, I, and σ remain constant. The longer the irradiation time and cooling time, the greater the relative content of long-lived nuclides. Conversely, the relative content of short-lived nuclides increases. Using this feature, long-lived and short-lived nuclides can be produced separately.

Fission yield is defined as the probability of a nuclide or a mass chain of fission products produced in the heavy nuclear fission process. It is usually expressed by the number of atoms of fission products per 100 nuclear fissions (%). Since most heavy nuclei are binary fission (the probability of ternary fission and quaternary fission is very small), the total decay yield of all mass chains is 200%. If the fission yield is expressed in logarithmic form, its relationship with the mass number shows a "double hump" curve (as shown in Fig. 2.8).

3. **Separation of fission products**

The fission products include all elements from zinc to lutetium in the periodic table of elements (more than 400 nuclides). Due to the continuous decay of unstable nuclides, the composition of the fission product system is also changing. In addition, as the fission yields of fission products differ by several orders of magnitude, the separated object of fission products is extremely complex with strong radioactivity.

(1) Separation method of fission products

The methods of separating fission products usually include ion exchange, solvent extraction, extraction chromatography, and precipitation. In the past two decades, some new separation technologies such as supercritical fluid extraction technology

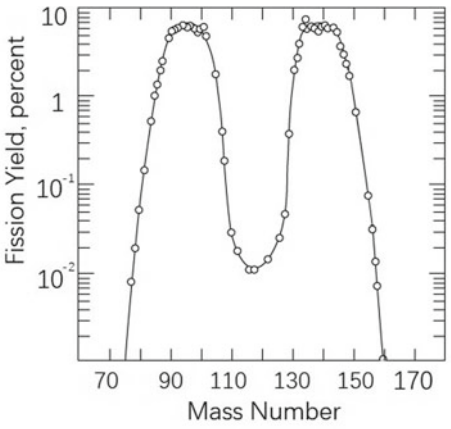


Fig. 2.8 Mass-yield diagram for neutron-induced ^{235}U fission

and ionic liquid extraction technology have also gradually shown good application prospects in nuclear waste treatment.

Due to the complexity of the fission product system, it is sometimes difficult to meet some separation requirements by using a single separation method. Therefore, a variety of technologies are often combined to make full use of the properties of the separated nuclides to obtain better separation results. This section will briefly introduce the principles, advantages, and disadvantages of the above methods. A systematic understanding can be found in the pertinent literature.

① Ion exchange

The ion exchange method uses a selective ion exchanger to adsorb the fissile nuclides to be separated, then selectively elute them with various eluents (inorganic acid, carboxylic acid, and various chelating agents) to achieve the purpose of separation.

When used for separation, the ion exchange method has the advantages of good selectivity, high recovery rate, easy automation, easy radioactive shielding, etc., which is the most widely used method in the separation of fission products. The ion exchange method is effective for separating homologous elements with very similar chemical properties such as rare earth, actinide elements, alkali metals, alkaline earth metals, etc. However, ion exchange also has its shortcomings, such as slow separation speed, time-consuming, difficult treatment of waste ion exchange resin, and so on.

When using the ion exchange method to separate fission products, appropriate ion exchange resin and eluent can be selected according to the separation system and the properties of the elements to be separated.

Ion exchangers are divided into inorganic ion exchangers and organic ion exchange resins. Organic ion-exchange resins are mainly used for the separation of fission products. According to the properties of their functional groups, organic ion exchange resins can be divided into cation exchange resin, anion exchange resin, and special

ion exchange resins. When the ion exchange method is used for separation, it can be selected and combined according to the specific separation object and system.

② Solvent extraction

Solvent extraction is to separate the target nuclide from the solution by using selective extractant and realize the separation by washing and stripping.

The solvent extraction method is simple, rapid, highly selective, easy to operate continuously and control remotely. But for some elements with similar properties, the effect of separation is relatively poor. This method is generally used for crude separation of fission products. For example, divide the fission solution cooled for more than three months into three or four groups: Ru–Sr–Rb–Ba–Cs, rare earth elements (except Ce), Ce, and Zr–Nb. Commonly used extractants include tri-butyl phosphate, di (2-ethy-lhexyl) phosphate, etc.

③ Extraction chromatography

Extraction chromatography is a chromatographic separation method in which an organic extractant is fixed on inert support as the stationary phase and an aqueous solution as the mobile phase. It combines the selectivity of solvent extraction with the efficiency of ion exchange chromatography to become an effective separation technology. Extraction chromatography is divided into paper chromatography, thin-layer chromatography, column chromatography, etc.

The extractants that can be used as the stationary phase of extraction chromatography include liquid anion exchanger (e.g. long carbon chain aliphatic amines—primary amine, secondary amine, ternary amine, quaternary amine, etc.), liquid cation exchanger, neutral complex extractant (e.g. tri-butyl phosphate, trioctylphosphine oxide, etc.), neutral ketone extractant (e.g. methyl isobutyl ketone, etc.) and chelating extractant (e.g. thennvltrifluoraafc, N-Benzoyl-N-phenyl hydroxylamine, etc.). There are 20–30 kinds of supports for column chromatography, including inorganic substances containing silicon (e.g. silica gel, silanized silica gel, diatomaceous earth) and various polymer substances such as polyethylene.

Extraction chromatography is similar to solvent extraction in terms of extraction mechanism, but it is equivalent to a multi-stage extraction process, so its separation effect is better than the solvent extraction method. For some elements with similar properties such as the separation of actinides and lanthanides with positive trivalent in solution, the advantages of this method can be better shown. In terms of experimental technology, extraction chromatography is similar to the ion exchange method. Thus, it has some advantages of the ion exchange method with higher selectivity. In addition, since this method requires less amount of organic extractant, it is more economical and can save a lot of extractants.

However, due to the limited amount of organic extraction on the extraction chromatographic column, the extraction capacity of the column is small and the processing speed is low.

④ Precipitation separation

Precipitation separation usually needs to add stable isotopes of the fission products to be separated or other carrier elements. When separating multiple elements, multi-step precipitation is required, and the connection between each step needs to be treated accordingly. Therefore, this method has complicated operation, lengthy procedure, low recovery, and low decontamination rate. In addition, the separation process of fission nuclides often involves strong radioactive operation, which is inconvenient for precipitation separation. In general, precipitation is not simply used as a means of separation, but only in the individual steps of the separation procedure, especially the final step.

⑤ Other methods

Two novel methods have been developed in recent years—supercritical fluid extraction and the method using ionic liquid as an extraction medium.

The supercritical extraction technology uses a supercritical state of CO_2 instead of kerosene and other organic solvents in the PUREX process for nuclide separation. The supercritical CO_2 fluid can directly leach the spent fuel because TBP and HNO_3 are dissolved in it, which reduces the target dissolution and other processes in conventional treatment. The extracted fluid can realize the separation of CO_2 and extracted matter by depressurization. This technology has the characteristics of a simple process, high extraction rate, and significant reduction of the amount of secondary waste. In the past 30 years, significant progress has been made in the treatment of spent fuel by supercritical fluid extraction technology. In 2004, a two-year pilot project on supercritical extraction technology for the treatment of spent fuel was launched in Japan, and a pilot plant was established to verify the feasibility of this technology. The results showed that the input of this technology was only 2/3 of that of the PUREX process, and the amount of radioactive waste was only 5% of that of the PUREX process. This technology is very promising for the treatment of spent fuel after solving the reliability of the equipment. However, the decontamination ability of this technology is not strong, thus, it can be used as the initial separation of U, Pu, transuranic elements, and fission products in spent fuel.

The ionic liquid is a class of full-salt substances in a liquid state at conventional ambient temperature, consisting of organic cations and anions with large structures. It has the advantages of a wide liquid temperature range (up to hundreds of degrees Celsius), high stability, and low vapor pressure (almost non-volatile). The ionic liquid can dissolve many organic and inorganic materials, and their main physical and chemical properties can be controlled by adjusting the structures of anions and cations. Because of the above unique characteristics, the ionic liquid can replace the conventional flammable, explosive and volatile organic solvent, and become a "green" solvent. The synthesis and applied research of new ionic liquids have become a new hot topic. In order to realize the application of ionic liquids in the nuclear fuel cycle, a lot of basic research has been carried out from various angles, but it has not been applied to the engineering treatment of nuclear waste.

(2) Separation of long-lived fission products and transuranic elements

It can be seen from Eq. (2.5) that only when the nuclear fuel is irradiated in the reactor for a long time can a large number of long-lived fission products and transuranic elements be produced. At the same time, since the radioactivity of the spent fuel is mainly contributed by medium and short-lived nuclides and long-lived fission products (such as ^{90}Sr and ^{137}Cs), it is necessary to cool the nuclear fuel for a long time after long-term radiation to decay the medium and short-lived nuclides, so as to significantly reduce the dose of radioactivity operating.

Currently, long-lived fission nuclides and transuranic elements are mainly extracted from the spent fuel discharged from production reactors. The main purpose of spent fuel post-processing is to recover ^{235}U and extract ^{239}Pu. After ^{235}U and ^{239}Pu are extracted and recovered, all other fission products and transuranic elements are transferred to the liquid waste. The waste contains several nuclides with high fission yields and long half-lives such as fission elements ^{90}Sr, ^{137}Cs, ^{147}Pm, and ^{99}Tc, and the transuranic elements ^{237}Np, ^{241}Am, and ^{242}Cm, which have important applications in the national economy and national defense industry.

There are some monographs on the separation and analysis of nuclides in fission products, such as *Radiochemical Studies: The Fission Products* in the Manhattan Project of the United States, and the *NAS-NS-3XXX* series reports prepared by the United States Atomic Energy Commission (e.g. *NAS-NS-3029*). Most of these monographs apply to medium and long-lived nuclides, which are available for reference. This section will not introduce them in detail.

(3) Separation of short and medium-lived fission products

A large number of short- and medium-lived nuclides such as ^{99}Mo, ^{95}Zr, ^{103}Ru, ^{131}I, ^{133}Xe, ^{140}Ba, and ^{147}Nd are produced by short-term radiation of fissile materials like ^{235}U. These short- and medium-lived nuclides have important application values in medicine and many other fields. Among them, fission nuclides such as ^{99}Mo, ^{131}I, etc. are most widely used in clinical diagnosis and treatment with a large demand. Therefore, this section focuses on the extraction process of fission ^{99}Mo and ^{131}I.

① Extraction of fission ^{99}Mo

The thermal-neutron-induced fission yield of ^{99}Mo is 6.06%, so a large amount of ^{99}Mo can be extracted from ^{235}U fission products.

The production of fission ^{99}Mo includes preparation and irradiation of high abundance ^{235}U targets, cutting and dissolution of the targets, extraction and subpackaging of fission ^{99}Mo, etc. At present, the targets used to produce fission ^{99}Mo mainly include uranium-aluminum alloy targets, uranium-magnesium dispersion targets, and molten salt electroplating targets. According to different types of targets, the dissolution method can be divided into alkaline dissolution or acid dissolution. For the uranium-aluminum alloy target, alkaline dissolution is generally used. During

dissolution, except for a few nuclides such as ^{99}Mo, most fission products are separated from uranium in the form of precipitation. For the uranium-magnesium dispersion target, 6–12 mol L^{-1} nitric acid is generally dissolved under heating, ^{235}U, and most of the fission products are dissolved in nitric acid.

Fission ^{99}Mo is generally extracted by Al_2O_3 chromatography, Di-(2-Ethylhexyl) phosphoric acid solvent extraction or extraction chromatography, α-benzoin oxime precipitation separation, etc.

Take the Japanese fission ^{99}Mo production processes as an example, the technology of producing fission ^{99}Mo will be introduced below.

a. Preparation of ^{235}U targets

Press 24 g UO_2 into a disk shape (Φ14.5 mm × 14 mm). After sintering, use the disk as the source core of the ^{235}U target. Put 5 UO_2 target cores into the stainless-steel cladding and weld the cladding to make a ^{235}U target.

b. Irradiation and cooling of ^{235}U targets

Irradiation conditions: neutron fluence rate equals 2×10^{13}–3×10^{13} cm^{-2} s^{-1}, irradiates for 4–7 d.

After 2 d of cooling, a target will produce 2.81×10^{12} Bq ^{99}Mo, 4.1×10^{12} Bq ^{131}I, 2.59×10^{12} Bq ^{133}Xe, and other fission products.

c. Treatment of ^{235}U targets after irradiation

When the ^{235}U target is cut after irradiation, radioactive ^{131}I and rare gases such as ^{133}Xe will be released, and the released radioactive gases will be collected and stored in a vacuum container.

Then the target material is dissolved with 10 mol L^{-1} nitric acid. During the dissolution, radioactive gases such as ^{131}I and ^{133}Xe are released. ^{131}I can be absorbed in an alkaline absorption tower, while ^{133}Xe is captured by the cooling of liquid nitrogen.

After complete dissolution, a carrier of iodine is added to further remove ^{131}I. The solution after ^{131}I removal is extracted with di-(2-Ethylhexyl) phosphoric acid to extract ^{99}Mo, ^{235}U, and a small number of fission products into the organic phase, while most of the fission products remain in the aqueous phase and become radioactive liquid waste. ^{99}Mo can be back-extracted from the organic phase with dilute nitric acid containing H_2O_2 at a concentration of 0.5 mol L^{-1}, while ^{235}U and a small number of fission products remain in the organic phase.

Add $NaNO_2$ to the stripping solution to remove H_2O_2, and reduce the volume of the stripping solution by distillation. Then, add the treated stripping solution to the alumina chromatographic column, where the ^{99}Mo is adsorbed by the alumina. After that, elute the column with 0.1 mol L^{-1} dilute nitric acid and water. The ^{99}Mo can be eluted and extracted with 0.1 mol L^{-1} ammonia.

② Extraction of fission ^{131}I

Fission ^{131}I is one of the by-products of ^{99}Mo production by fission methods. Since the yield of fission ^{131}I is 3.1%, ^{131}I can be extracted from fission products on a large scale. Countries with relatively mature research and production of extracting ^{131}I from fission products mainly include Russia, Belgium, the United States, and so on. Another promising production method for ^{131}I production is to use aqueous nuclear reactors, which are researched and applied in countries around the world with the United States and Russia taking the lead.

In the process of fission isotope production, ^{131}I escapes during target cutting and acidic dissolution of target materials, which can be collected by negative pressure. Regardless of dissolution methods, the ^{131}I left in the solution is generally separated by acidification before distillation or hot gas carrier. Since the separated ^{131}I contains impurities such as ^{103}Ru, further purification is required. The purification methods of ^{131}I include activated carbon—Pt adsorption, hot gas carrier, ion exchange, and distillation, among which distillation is the most commonly used. In order to improve the chemical and radiochemical purity of the ^{131}I product, platinum compounds with high prices are generally used as adsorption materials. From the perspective of reducing production cost, the cheaper activated carbon—5% platinum can also be used as an adsorbent.

The following paragraphs will briefly introduce the process of separation and purification of ^{131}I from an alkaline solution of target dissolving adopted in Belgium and Iran.

The process proposed by the National Institute for Radioelements (IRE) in Belgium is to dissolve the irradiated target material with an alkaline mixture of 3 mol L^{-1} NaOH and 4 mol L^{-1} $NaNO_3$, and to separate and purify ^{99}Mo, ^{133}Xe, and ^{131}I. During the dissolution process, an appropriate oxidant is added to ensure the complete dissolution of molybdenum. Uranium and most fission products exist in the form of hydroxide precipitation, which is conducive to the recovery of waste in the future. ^{133}Xe is released in gaseous form, while the main products ^{99}Mo and ^{131}I are dissolved in the alkali solution in the form of MoO_4^- and I^-.

Unlike dissolving the target with the acidic solution, when using the alkaline dissolution, most of the fission products exist in the solid-state, and only a small amount of other fission elements is dissolved with molybdenum. The dissolved radioactive impurities are less than those in acidic target dissolution, which reduces the amount of waste generated and decreases the difficulty of the process and waste disposal.

After removing uranium and most of the fission elements by filtration, acidify the alkaline solution with concentrated nitric acid, 80–90% of ^{131}I can be separated by distillation, and then use asbestos-platinum to adsorb the separated ^{131}I. The crudely separated ^{131}I is further purified by distillation to obtain ^{131}I products. The ^{131}I adsorbed on the platinum surface can be purified by electrochemical adsorption or directly electrolytic desorption from the alkaline solution.

Following the process of extracting fission ^{99}Mo by Atomic Energy Corporation (AEC), South Africa, Iranian WVan Zyl de VillIers dissolved the irradiated target material with concentrated NaOH solution and studied the production process of ^{131}I.

After alkaline dissolution, control the speed of the solution flowing through the anion exchange resin to make ^{99}Mo and ^{131}I adsorbed on the anion resin as much as possible. After ^{99}Mo is eluted, place the resin adsorbed with ^{131}I for at least 10 d before eluting and purifying ^{131}I. ^{131}I is purified by distillation. Control the distillation speed to volatilize ^{131}I from the eluent, then absorb to form the product with 0.05 mol L^{-1} NaOH solution.

The nuclear purity of the product obtained by this process is greater than 99.9%, with the purity of other radioactive impurities such as ^{133}I and ^{135}I less than 0.01%. The radiochemical purity of the product is > 95% (I^-). Specific activity $\geq 3.7 \times 10^{10}$ Bq cm^{-3}.

The yield of ^{131}I is not mentioned in this process, but considering that ^{131}I has been placed on the resin for at least 10 days after the separation of ^{99}Mo and ^{131}I, and the subsequent distillation and purification efficiency is generally around 85%, the ^{131}I rate of recovery of this process should be below 40%.

4. **Production of radionuclides by solution reactors**

Solution reactor is a type of reactor proposed in the 1940s, which uses nuclear fuel is not the usual form of solid fuel rods, but fissile materials such as ^{235}U homogeneous aqueous solution. Therefore, it is also called an aqueous homogeneous solution reactor. Solution reactor has been applied in power reactor and breeder reactor. In addition, it is also used as a neutron source in research for nuclear analysis, nuclear physics experiments, neutron radiography, nuclear criticality safety, fission product extraction, etc. Solution reactors have been constructed and operated safely for decades, which shows that it has a high safety performance. In the research of uranium solution reactors, ^{235}U solutions such as uranyl nitrate, uranyl sulfate, uranyl fluoride, and uranyl phosphate have been used as nuclear fuel, among which uranyl sulfate and uranyl nitrate systems are mostly used. These two systems are beneficial to the chemical post-processing of uranyl solutions in the solution reactor.

(1) Development of aqueous solution reactors

In 1944, Richard Feynman first proposed a new type of nuclear reactor in which the nuclear material used was not the normally used solid fuel, but a solution of highly abundant uranium salts (such as uranyl nitrate or uranyl sulfate) dissolved in ordinary light water. In the same year, Los Alamos National Laboratory (LANL) in the United States built the first homogeneous solution reactor (LOPO) with a power of 0.01 kW. Since then, researchers have done a lot of research and development on the solution reactor. So far, more than 70 research aqueous solution reactors have been built. For example, in the United States, LANL has HYPO, SUPO, LAPRE-1, and LAPRE-2 solution reactors, ORNL has HRE-1, HRE-2, and HRE-3 homogeneous

solution reactors; and Russia has the ARGUS solution reactor. These reactors are used in medical isotope production, nuclear physics experiments, neutron photography, neutron activation analysis, fission product extraction, and so on.

In the 1990s, the use of medical isotopes such as ^{99}Mo, ^{89}Sr, and ^{131}I increased significantly, and conventional production methods no longer met the demand. Based on the characteristics of short production cycle, large output, simple operation (no processes like target preparation, transportation, cutting, dissolution, etc.), high utilization rate of uranium, and small waste production, people began to explore the production of medical isotopes by using solution reactor. In 1992, CHOPELA and BALL of Babcok&Wicox (B&W) of the United States put forward the concept of a medical isotope production reactor (MIPR). In 1997, they presented the design scheme of producing ^{99}Mo and other MIPRs with weak acidic uranyl nitrate solution as nuclear fuel in an aqueous solution reactor with operating power of 100–300 kW and applied for a patent. A nuclear research institute in China subsequently proposed a process for separating ^{99}Mo from the solution reactor. The United States then proposed a method of extracting ^{89}Sr by continuous gas tube separation. Besides, in cooperation with Russia's Kurchatov Institute, the U.S. Department of Energy has carried out the extraction research of ^{99}Mo, ^{89}Sr, ^{131}I, and other isotopes using Russia's 20 kW ARGUS reactor and applied them to the production of these fissile nuclides. In recent years, many countries have shown great interest in the production of ^{99}Mo, ^{89}Sr, and ^{131}I solution reactors, and have stepped up their research work in this field. But up to now, only the Russian 20 kW ARGUS reactor has been publicly reported.

The Russian 20 kW ARGUS reactor can use ^{235}U with different enrichment as raw material and fuel, such as 20L 93% high enrichment ^{235}U and 100L 20% low enrichment ^{235}U. After extracting fission products (such as ^{99}Mo) and substances threatening the safety of the solution reactor, the uranium solution used in MIPR adjusts the acidity of the uranium solution and then returns to the solution reactor for further use as fuel.

(2) Characteristics of MIPR

Compared to general reactors, MIPR has the following characteristics:

① Large negative temperature coefficient. This endows MIPR with the self-regulation ability of response and good inherent safety.
② Low cost for construction. At present, compared with the construction of a conventional radioisotope production reactor with the same production capacity as ^{99}Mo, the cost of plants and operating systems of MIPR is about 1/3. Combined with the costs of together with the purified hot chamber device, equipment maintenance, waste disposal, and reactor decommissioning, the total cost is less than 1/2 of that of a conventional reactor.
③ Large production capacity. According to the theoretical calculation, a MIPR operating at 200 kW can produce 3.33×10^{15} Bq ^{99}Mo, 7.4×10^{14} Bq ^{131}I, and 1.48×10^{15} Bq ^{89}Sr in one year.

④ Low demand and high utilization of ^{235}U. For a 200 kW MIPR, only 0.12 g ^{235}U operates is consumed if it operates at full power for 1 d. To produce the same amount of ^{99}Mo, the consumption of uranium is only 0.36% of that in the irradiation target of a conventional reactor. Besides, the remaining unburned ^{235}U can be recycled without complicated treatment, which makes the utilization rate of ^{235}U of the MIPR close to 100%.

⑤ Simple radionuclide extraction process and less radioactive waste. Since there is no need for target preparation, transportation, cutting, and dissolution when extracting fission products from MIPR, less radioactive waste will be generated. The amount of radioactive waste is about 1/100 of that of conventional target irradiation methods.

To summarize, the use of aqueous solution reactors to produce medical isotopes has the advantages of low cost, high yield, less uranium consumption, good inherent safety, and less waste generation, which makes it an ideal reactor type for medical isotope production.

(3) Structure and functions of MIPR

The MIPR is mainly composed of core vessel, nuclear fuel solution transfer system, heat exchange system, gas circuit system, and purification system. Up to present, many types of MIPR have been developed in the world, among which the MIPR designed by B & M of the United States and Kurchatov Institute of Russia is the most representative.

The MIPR designed by B & W uses 20% low enriched uranium (with a concentration of 117 g L^{-1}) as fuel. Its main structure includes reactor core, control rod, heat exchanger, cooling tower, control rod brake, gas recombiner, product purification column, and product extraction column. During MIPR operation, radionuclides such as ^{99}Mo, ^{131}I, and ^{89}Sr are generated by the fission of ^{235}U in the fuel solution. After the reactor shutdown, ^{99}Mo and ^{131}I can be extracted by the fuel solution through the product extraction column, while medical radionuclides such as ^{131}I and ^{89}Sr can be extracted from the MIPR gas circuit.

The main structure of the Russian ARGUS reactor includes reactor core, heat exchanger, gas circuit, molybdenum extraction circuit, ^{131}I and ^{89}Sr extraction circuit, water pump, molybdenum extraction column, cooler, hydrogen oxygen recombiner. Its structure and functions are as follows:

a. **Core vessel**: A cylindrical nuclear fuel container and the site where the nuclear reaction occurs. The material is 304 L stainless steel. A control rod conduit and an upper cover are on the top of the core.
b. **Heat exchange system**: Water or other cooling medium flow through the cooling pipes and bring the heat of the core out to prevent safety accidents due to boiling of core fuel.
c. **Gas circuit system**: Mainly used to condense the vapor generated during reactor operation into water. At the same time, H_2 and O_2 produced by irradiation decomposition in the solution reactor are combined into the water by hydrogen oxygen recombiner and returned to the reactor.

d. **^{99}Mo extraction system**: Composed of a water pump, an extraction column, and a cooling chamber. It is mainly used to inject the fuel solution in the core into the cooling chamber and then separate ^{99}Mo through the extraction column after cooling.
e. **^{131}I and ^{89}Sr extraction system**: Used to extract ^{131}I and ^{89}Sr produced in the gas phase during the operation of the solution reactor.

(4) Trends of MIPR development

① Development of multi-core aqueous solution reactor

At present, the United States and Russia have jointly proposed the production of medical radionuclides by multi-core solution reactor. A multi-core aqueous solution reactor is composed of two, four, or eight cores of the low-power solution reactor. Although the operating power of each core is low, the total power of the reactor is doubled. Besides, it has mature technology and low cost, with no effect on the inherent safety of the reactor.

The production of medical isotopes by multi-core aqueous solution reactors can increase the yield of medical radionuclides several times, which has good development prospects.

Taking Russia's 50 kW ARGUS reactor as an example, when operating with multiple cores, the ^{99}Mo yield is expected to be:

$$\begin{aligned} &2 \times 50\,\text{kW cores} \quad 1.85 \times 10^{13}\,\text{Bq/week} \\ &4 \times 50\,\text{kW cores} \quad 3.7 \times 10^{13}\,\text{Bq/week} \\ &8 \times 50\,\text{kW cores} \quad 7.4 \times 10^{13}\,\text{Bq/week} \end{aligned}$$

② Construction of high power aqueous solution reactor

It is reported that the 50 kW ARGUS aqueous solution reactor can produce 3.7×10^{14} Bq (1.0×10^4 Ci) ^{99}Mo and 4.6×10^{12} Bq (125 Ci) ^{89}Sr per year, and a 200-kW aqueous solution reactor can produce 3.7×10^{15} Bq (1.0×10^5 Ci) ^{99}Mo and 1.48×10^{13} Bq (400 Ci) ^{89}Sr per year. It can be seen that increasing the power of the aqueous solution reactor is the most direct and effective way to improve the production capacity of medical radionuclides. Since high-power aqueous solution reactors can greatly improve the production capacity of medical radionuclides, this type of reactor also has a good prospect for development.

Although it is theoretically feasible to build a high-power aqueous solution reactor, there are still many technical problems to be solved in practical engineerings, such as precipitation of UO_2^{2+} ions during high-power operation, improvement of hydrogen–oxygen recombination efficiency to prevent possible combustion and explosion, control of fluctuation of the reactor power, and heat dissipation of the reactor.

(5) Production of medical radionuclide ^{89}Sr by MIPR

① Production principle

During MIPR operation, the fission of ^{235}U will produce gaseous radioisotopes such as Kr and Xe. The radioactive gas produced by this fission quickly (about 2 s) escapes from the solution and enters the gas circuit. The daughter nuclides generated after the decay of these radioactive inert gases include various isotopes of Sr, as well as ^{137}Cs, ^{138}Cs/^{138}Ba, ^{139}Cs,^{140}Ba/^{140}La,^{141}Ce, etc. Among these nuclides, Cs, Ba, and Ce can be separated from Sr isotopes by chemical methods, while ^{89}Sr and ^{90}Sr are difficult to be separated by chemical methods. Therefore, the key to obtaining ^{89}Sr products from the gas circuit of MIPR is the separation of ^{89}Sr and ^{90}Sr. ^{90}Sr is an extremely toxic radionuclide with a half-life of 29 years. If it enters the human body, it will cause long-term radiation damage to human tissues. Thus, the activity ratio of ^{90}Sr to ^{89}Sr in medical ^{89}Sr products should be strictly controlled (less than 10^{-6}).

The yield of ^{89}Kr ($T_{1/2}$ = 197.7 s) in uranium fission is 4.88%, ^{89}Kr decays to ^{89}Rb ($T_{1/2}$ = 15.4 min) and then decays to ^{89}Sr ($T_{1/2}$ = 52.5 d). The yield of ^{90}Kr ($T_{1/2}$ = 33 s) in uranium fission is 5.93%, ^{90}Kr decays to ^{90}Rb ($T_{1/2}$ = 2.91 min) and then decays to ^{90}Sr ($T_{1/2}$ = 29 a). Using the difference of half-life between ^{89} and ^{90}Kr, their decay products ^{89}Sr and ^{90}Sr can be separated. In general, the gas bypass set in the MIPR gas circuit is used to introduce the fission gas generated from the reactor core into the gas bypass, and the extraction of ^{89}Sr is realized through the separation of ^{89}Kr and ^{90}Kr in the gas bypass.

② Production process of ^{89}Sr

Kurchator Research Institute of Russia and Technology Commercialization International (TCI) of the United States jointly designed a process for extracting ^{89}Sr from the bypass of the Argus reactor gas circuit in Russia. The schematic diagram of the processing unit for extracting ^{89}Sr is shown in Fig. 2.9.

This paragraph will briefly describe the process of producing ^{89}Sr by using the gas circuit bypass after Argus operates for 20 min in Fig. 2.9. Open valve 3 and valve 9, and turn on pump 5 to input the gas generated in the core to the ^{90}Sr settlement section (tube 4). ^{90}Kr in the ^{90}Sr settlement section gas decays sufficiently to ^{90}Sr

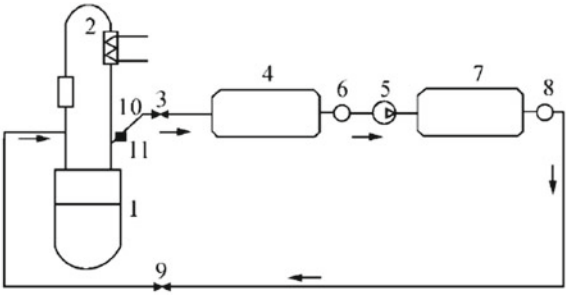


Fig. 2.9 Schematic diagram of the ^{89}Sr extraction process unit. 1—core; 2—heater; 3—valve; 4—90Sr settlement tube, 5—pump; 6—filter; 7—89Sr settlement tube; 8—filter

and settles on the tube wall or is filtered when passing through filter 6. The remaining gas enters the ^{89}Sr extraction section (tube 7) through filter 6, in which most of the ^{89}Kr finally decays into ^{89}Sr and settles on the tube walls, while the unsettled solids are removed through filter 8. In the ^{89}Sr settlement section, it is important to control the flow rate of the gas and the time required for the gas to pass through (the time required for the complete decay of ^{90}Kr to ensure that as much ^{89}Kr decays in the ^{89}Sr extraction section to obtain as much ^{89}Sr as possible), both of which determine the content of ^{90}Sr impurities in the product and the output of ^{89}Sr. The size of the ^{90}Sr settlement tube can be determined by the gas flow rate and the time required for the gas to pass through. For example, if the velocity of airflow is 2 L min^{-1}, the gas passing time is 10 min, when the tube diameter is 10 mm, the tube length is 255 m; when the tube diameter is 20 mm, the length of the tube will reduce to 64 m. After ^{90}Kr in the gas decays for 10 min in the ^{90}Sr settlement section, the activity ratio of ^{90}Sr to ^{89}Sr in the ^{89}Sr products obtained in the ^{89}Sr extraction section can reach 10^{-8}. The design principle of the ^{89}Sr settlement section is the same as that of the ^{89}Sr settlement section, which is also determined according to the time and flow rate required for ^{89}Kr decay. After ^{89}Sr extraction, close valve 3 and valve9, turn off pump 5. The solid settled in the ^{89}Sr extraction section is dissolved by acid, and the impurities such as Cs, Ba, Ce, and La are separated by chemical methods. Finally, ^{89}Sr products meeting the medical standards can be obtained.

2.3 Production of Radionuclides by Accelerators

While nuclear reactors can produce radionuclides in large quantities, the varieties and properties of the nuclides do not fully meet the needs of the application. As a production route of radionuclides, the accelerator makes up for this deficiency to a great extent. The required radionuclides can be prepared by bombarding a target containing selected stable nuclides with high-speed charged particles produced by an accelerator. Most of the radionuclides produced by accelerators are neutron-deficient nuclides, which decay in the form of positrons or low-energy γ-rays, with generally short half-lives and high specific activity. Carrier-free radionuclides can be obtained with this method. Although the accelerator has a relatively low production capacity, as the nuclides it produced have special uses in industry, agriculture, and especially biomedicine (and with an increasing usage), it has become an indispensable means of radionuclide production. Currently, the types of radionuclides produced by accelerators account for more than 60% of the total known radionuclides, typified by the use of cyclotrons to produce ^{18}F for positron emission tomography (PET).

2.3.1 Brief History of the Development of Accelerator-Produced Radionuclides

Since the discovery of artificial radionuclides in 1934, cyclotron has been used for the preparation of radionuclides. In just three years, the number of artificial radionuclides increased from 3 to 197, certain production capacity for a few radionuclides such as ^{131}I, ^{32}P, and ^{14}C that can be used for tracer research was achieved. After 1945, the reactors began to mass-produce and supply cost-effective radionuclides. This once affected the production of accelerator-produced radionuclides due to their low productivity and high price. In the mid-1960s, many special and important uses of neutron-poor radionuclides were discovered. For example, ^{57}Co, ^{22}Na, ^{109}Cd, etc. are used in Musburger spectroscopy, positron annihilation technique, and X-ray fluorescence spectroscopy, ^{67} Ga, ^{201}Tl, ^{123}I, etc. are used in nuclear medicine diagnosis, and ^{11}C, ^{13}N, ^{15}O, etc. are used in the study of life process dynamics. These cannot be replaced by reactor-produced radionuclides. In particular, with the wide application of positron emission computed tomography in clinical nuclear medicine diagnosis, the demand for corresponding radionuclides is increasing, which makes the development and production of accelerator radionuclides begin to revive. From the early 1960s to the present, the number of accelerators used to produce radionuclides in the world has soared from less than five to hundreds, and 80% of the newly added diagnostic radionuclides are produced by accelerators. In recent years, the consumption of neutron-poor radionuclides for medical diagnostics has gradually increased, with accelerator-produced radionuclides gradually replacing some reactor-produced radionuclides.

2.3.2 Components and Classification of Accelerators

The accelerator consists of three main components.

① **Ion source** The particle used to provide the required acceleration, including electrons, positrons, protons, antiprotons, and heavy ions.
② **Vacuum acceleration system** The system has a certain form of accelerating electric field, which accelerates the particles without scattering by air molecules, and the whole system is placed in a vacuum chamber with a very high vacuum level.
③ **Guiding and focusing system** A certain form of the electromagnetic field is used to guide and confine the accelerated particle beam so that it receives acceleration from the electric field along a predetermined trajectory.

The performance of an accelerator is measured by two indicators: the energy that the particles can reach, and the intensity of the particle flow (flux). According

to different working principles, accelerators can be classified as electrostatic accelerators, linear accelerators, cyclotrons, electron induction accelerators, synchrocyclotrons, colliders, etc. In this section, only a few types of commonly used accelerators are briefly described.

1. **Cockcroft-Walton electron accelerator**

This is the first high-voltage device used to accelerate charged particles. It uses the medium and low-frequency voltage through voltage doubling rectification to generate DC high voltage to accelerate ions. Although the energy of the accelerated particles is not high (generally less than 1 meV), the number of high-speed ions obtained with it is large and the beam current is strong. So, it is still used in laboratories to accelerate particles.

2. **Electrostatic accelerator**

The electrostatic accelerator is a direct current high voltage accelerator. It obtains high DC voltages and accelerates charged particles by transferring and accumulating charges to a metal electrode insulated from the ground using mechanical means. An electrostatic accelerator is a low-energy accelerator, it can be used to accelerate electrons and protons. It was first developed by R. J. van de Graaff in 1931 and is also known as the Van de Graaff accelerator.

The energy of the accelerated charged particles is limited by the breakdown voltage of the insulating material used. To increase the operating voltage and beam strength of the electrostatic accelerator, modern electrostatic accelerators are placed in steel cylinders, which are filled with high-voltage gas with good insulating properties to increase the voltage strength of the electrostatic high-voltage generator, and the energy of the accelerated particles can reach 14 meV.

3. **Cyclotron**

The cyclotron is a device that uses a magnetic field to make charged particles move in a cyclotron motion way, which is repeatedly accelerated by a high-frequency electric field. The main structure of the cyclotron is as follows: two semicircular flat metal boxes (D-boxes) are separated and placed opposite each other in the vacuum chamber between the magnetic poles. Apply an alternating voltage to the D-boxes and generate an alternating electric field at the gap. The central particle source generates charged particles and emits them. The particles in the D-shaped box are accelerated by the electric field and are subject to the Lorentz force of the magnetic field between the poles and move in a circular motion in the vertical magnetic field plane. The time of half a circle is $\pi m \cdot qB^{-1}$, where q is the particle charge, m is the mass of the particle, and B is the magnetic induction of the magnetic field. If the frequency of the alternating voltage applied to the D-box is exactly equal to the frequency of the particle in a circular motion in the magnetic field, the particle will catch up with

the polarity change on the D-box after half a circle, and the particle is still in the accelerated state. Since the time for the particle to travel half a circle is independent of the particle's speed, the particle is accelerated once every half-circle and the radius of travel increases. After many accelerations, the particles are led out from the edge of the D-box along the spiral orbit with energies up to several tens of megaelectron volts (MeV). The energy of the cyclotron is limited by relativistic effects that increase with the particle velocity. With the increase of the mass of particles, the period of particle orbit becomes longer, which gradually deviates the particle from the acceleration state of the alternating electric field. A further improvement of this accelerator is the synchrocyclotron.

4. **Linear accelerators**

The linear accelerator is the device that accelerates electrons, protons, and heavy ions using a high-frequency electric field distributed along a linear orbit. Microwaves are fed into a cylindrical metal hollow tube (waveguide) to excite various modes of electromagnetic waves, one of which has a large component of the electric field along the axis direction and can be used to accelerate charged particles. To keep the charged particles running along the axis in an accelerated state, the phase velocity of the electromagnetic wave in the waveguide is required to be reduced to synchronize with the motion of the accelerated particles, which can be achieved by placing diaphragms with circular holes or drift tubes at regular intervals in the waveguide. The mass of the electron is small, only a few mega electronvolts of energy can make the speed of the electron close to the speed of light. A diaphragm device with a circular hole is suitable for accelerating electrons. For protons or ions with a larger mass and lower velocity, devices with drift tubes are often used.

Among the above-mentioned types of accelerators, those that can be used for radionuclide production include electrostatic accelerators, linear accelerators, and cyclotrons, and the cyclotron is the most commonly used. Most cyclotrons are designed with isochronous azimuthal variation fields and come in different types. Compact cyclotrons are compact, easy to use, and accelerate p, d, α, and ^{3}He with energies of 15–52 meV and flow strengths of 50–200 μA, which are suitable to produce ^{67} Ga, ^{111}In, ^{201}Tl, ^{123}I, and other medium-lived and short-lived nuclides. Miniature cyclotron is very small, easy to operate, with low construction costs, proton acceleration energy of 15–20 meV, deuteron 8–10 meV, ^{3}He, α particle energy of 15–30 meV, flow strength up to 30–100 μA, which is suitable for the situ preparation of short-lived nuclides like ^{11}C, ^{13}N, ^{15}O and ^{18}F in the hospital.

A few large accelerators (e.g., the meson plant at LANL in the United States) produce protons with energies of 200–800 meV and flow strengths of 0.2–1 mA. Via the scattered nuclear reactions caused by the stronger beam currents remaining after the production of mesons, longer-lived nuclides or nuclides, such as ^{82}Sr, ^{52}Fe, etc., can be produced whose preparation is difficult in general.

2.3.3 Characteristics of Radionuclides Produced by Accelerators

The radionuclides produced by the accelerator have the following characteristics.

(1) The high Coulomb potential of charged-particle nuclear reactions is suitable for the preparation of radionuclides of light elements such as ^{11}C, ^{13}N, ^{15}O, and ^{18}F. These nuclides are usually not efficiently obtained at the reactor due to the small (n, γ) reaction cross-section, but they can be easily produced by accelerators for clinical diagnostic use.
(2) When the accelerator produces nuclides, the incident particles are charged particles, and the resulting radionuclides are almost all neutron deficient nuclides. They mostly decay by electron capture (EC) or emission of positrons (β^+), emitting low photon energies (50–300 keV), and are more homogeneous, usually not accompanied by the emission of other charged particles, and are particularly suitable for nuclear medicine diagnosis.
(3) Radionuclides produced by accelerators are generally not the same element as the target nucleus, so they can be easily separated chemically, and high specific activity or carrier-free radionuclides can be obtained.

Accelerator production of radionuclides also has some disadvantages, such as much smaller production capacity and higher production costs (for most nuclides) compared to reactor production, difficult target preparation technology, and target cooling technology, and a shorter half-life that limits its use (time, space).

2.3.4 Types of Nuclear Reactions for Radionuclide Production by Accelerators

The main nuclear reactions in which radionuclides are produced by accelerators are alpha-initiated nuclear reactions, deuteron-initiated nuclear reactions, proton-initiated nuclear reactions, ^{3}He-initiated nuclear reactions, etc.

The nuclear reactions initiated by α particles are (α, n), (α, p), (α, 2n), etc. For example, ^{79}Br (α, n) ^{82}Rb. This type of nuclear reaction is widely used for the preparation of transuranic elements, such as ^{253}Es (α, n) ^{256}Md.

Important deuteron reactions used for radionuclide production are the (d, n), (d, 2n), and (d, alpha) reactions. The (d, n) reaction is usually exergonic, so this type of reaction can occur at low deuteron energies. (d, 2n) is an energy-absorbing reaction and can occur only when the deuteron energy is 10–15 meV. The radionuclides produced by this type of reaction are ^{11}C, ^{131}I, ^{18}F, ^{51}Cr, etc. Due to the high Coulomb potential of the (d, α) reaction, it can only be used to prepare light radionuclides such as ^{24}Mg (d, α) ^{22}Na.

Accelerators provide proton beams with strong beam currents and high energies. The proton-initiated (p, n) reaction is the main pathway for accelerators to produce

radionuclides, which can produce a wide range of nuclides such as ^{22}Na, ^{32}Si, ^{51}Cr, ^{52}Mn, ^{57}Fe, ^{67} Ga, ^{69}Ge, ^{82}Sr, ^{88}Y, ^{97m}Tc, ^{111}In, ^{123}I, ^{127}Xe, ^{208}Pb, etc.

The nuclear reactions caused by ^{3}He are (^{3}He, n), (^{3}He, 2n), (^{3}He, p), etc., which can be used to prepare nuclides like ^{18}O (^{3}He, p) ^{18}F, ^{50}Cr (^{3}He, p) ^{52}Fe.

2.3.5 Production of Radionuclides by Accelerators

Producing radionuclides by accelerators involves accelerators, nuclear reactions, preparation of targets, separation, and purification of products, etc. The production method needs to be selected according to the radionuclide produced and the type of accelerator used.

1. **Selection of nuclear reactions**

A radionuclide can be produced by a variety of nuclear reactions. The most suitable nuclear reaction should consider the actual parameters of the accelerator (type of particles and energy provided), reaction yield, radioactive impurities, specific activity, production process, separation time, recovery of enriched targets, etc.

The selection of nuclear reactions is mainly based on the following aspects.

(1) Accelerator parameters

Two conditions are necessary for the production of radionuclides by accelerators: (i) the charged particle beam must have sufficient energy to initiate a nuclear reaction; (ii) the charged particle beam must have sufficient particle flux to obtain a yield with a practical production value. Thus, the selection of nuclear reaction is governed primarily by parameters such as the type of charged particles accelerated by the accelerator and the energy range. For example, in the production of ^{57}Co, high yields and high purity can be obtained via the nuclear reactions and ^{58}Ni (p,2n) ^{57}Cu $\rightarrow$ ^{57}Co, which is the most widely used nuclear reaction in ^{57}Co production today. But these two nuclear reactions require proton energies greater than 15 meV. If the proton energy is below this value, only the ^{56}Fe (d, n)^{57}Co reaction can be used.

(2) Nuclear reaction yield

Since charged particles (p, d, α, etc.) cause energy loss in the target, the nuclear reaction cross-sections are different at different depths of the incident target nucleus. Besides, the range of charged particles in the target varies with the target material. Both factors affect the yield of the target radionuclide. For the nuclear reaction of different atomic number (Z) target nuclei and different incident particles with different energies (p, d, α, etc.), the theoretical calculation of the thick target yield shows that the smaller the rest mass of the incident particles, the higher the energy, and the smaller the atomic number of the target nuclei, the higher the yield. Therefore,

the yield of (p, n) reactions is higher than that of (d, n) reactions and (α, n) reactions under the same energy.

(3) Nuclear purity of the product

When selecting the energy of nuclear reactions and incident particles, while increasing the target nuclide yield as much as possible, the purity of the product should also meet the requirements. In general, when nuclear reactions occur, competitive reactions will also occur, which affect the purity of the target nuclide. For example, when ^{57}Co is prepared by the nuclear reaction of ^{56}Fe (D, n) ^{57}Co, although the yield of ^{57}Co is higher when the deuterium energy is greater than 8 meV, the competitive reaction gradually strengthened ^{56}Fe (D, 2n) ^{56}Co at the same time. Since ^{56}Co impurities will affect the use of ^{57}Co products, it is necessary to limit the deuterium beam energy to 7.5–8 meV.

2. **Preparation of targets for accelerators**

The irradiated targets used on accelerators can be classified as solid targets, liquid targets, and gas targets based on the physical state of the target material.

(1) Solid target

There are two types of irradiations for solid targets, namely internal target, and external target beam irradiation. The internal target method is to irradiate the target in the vacuum chamber of the accelerator. This method is highly productive but complex to operate. The external target method is to lead the particle beam out of the vacuum chamber and irradiate the target outside the vacuum chamber. Due to the problem of the particle beam extraction efficiency, the beam current of the external target is generally smaller than that of the internal target. But this problem does not exist for accelerators that accelerate negative hydrogen ions.

For solid targets for accelerators, in addition to meeting the requirements of irradiation stability, chemical stability, ease of access, ease of handling, etc., the target also needs to withstand the bombardment of charged particles with high energy and strong current during the radiation process, the following special requirements should also be considered:

① Target material

a. Thickness of the target material: Because the target has a high ability to prevent charged particles, after charged particles are shot into the target, with the increase of the thickness of the target, the current intensity and energy of charged particles rapidly weaken, the cross-section of nuclear reaction also decreases. This may even change the type of nuclear reaction. Therefore, it is important to choose the appropriate thickness. If the target thickness is less than the range of bombarding particles in the target, the charged particle beam passes through the target with little change in energy and reaction cross-section. Such a target is usually called

a thin target. Conversely, the target whose thickness is greater than the range of particles in the target and can significantly change the energy and reaction cross-section of the particle beam is called a thick target. To make full use of charged particles, thick targets of 50–100 μm are generally used.

b. High-temperature resistance: To achieve nuclear reaction, the target needs to be bombarded with charged particles with energies of tens or even hundreds of MeV. Therefore, when the target is irradiated, the high-energy particle flow hits the target with a small area, resulting in a large thermal power density (usually greater than 1 kW/cm^2) and a temperature gradient of up to several thousand degrees per millimeter. At such high temperatures, even refractory metals and compounds will melt and volatilize. When the accelerated particles bombard the target surface, it will also cause the sputtering of the target material. The usual approaches to solving the problem of heat dissipation of the target are: (a) reducing the angle between the target surface and the direction of the beam to increase the area of the particle beam bombardment target and reduce the thermal power density of the target surface; (b) adopting the rotating moving target to make the target surface subject to intermittent irradiation; (c) cooling the target with water.

② Other materials for targets

To make the target material withstand the irradiation of the strongly charged particle flow, metals and alloys with good thermal conductivity, good thermal stability, and high melting point should be selected as the target material as far as possible.

Solid targets are prepared by welding, electroplating, sintering, etc. It is important to ensure firmness, good heat conduction, and convenient loading/unloading of the target, without affecting the purity of the product.

Copper with good thermal conductivity is often used as the target holder in the preparation of the accelerator target. The metal target is evenly deposited (coated) on the copper holder by vacuum spraying, electroplating, precision machining, etc. When using alloys or compounds as targets, a row of shallow grooves can be made on the copper holder. Then, by sintering, melting, vacuum spraying, and other methods, the target can be combined with the holder. In addition, by electroplating in a non-aqueous medium-molecular electroplating method, some compounds can also be plated on the copper holder. This making process of the target can make it further purity.

(2) Liquid target and gas target

Systems of liquid target and gas target have dedicated inlet/outlet pipes of target materials. Therefore, unlike solid targets, once these two types of targets are established, there will be no need to prepare a large number of targets anymore. Especially for the liquid target, it can automatically fill the target liquid into the container, and the irradiated liquid can be directly transferred to the hot chamber or working box through the pipe.

3. **Calculation of irradiation yield**

An important feature of charged particle nuclear reactions is that a charged-particle can cause nuclear reactions only by overcoming the Coulomb barrier of the target nucleus (i.e., there is an energy threshold). The height of the Coulomb barrier is related to the atomic number of the target nucleus and the charge of the charged particle. In addition, the reaction cross-section of nuclear reaction caused by charged particles strongly depends on the energy of bombarding particles. After the bombarding particles enter the target, the energy gradually decreases, and therefore the reaction cross-section of the target nucleus changes accordingly at different depths. This functional relationship of the variation of nuclear reaction cross-section with incident particle flux is called the excitation function.

When the excitation function is known, the total radioactivity A of radionuclides expected to be obtained when irradiating the "thick target" can be expressed as follows:

$$A = \frac{1 - e^{-\lambda t}}{3.7 \times 10^4} \cdot \frac{nJ}{Z} \cdot 6.25 \times 10^{12} \int_0^{Em} 10^{24} \sigma(E) S(E) dE \tag{2.6}$$

where

A total radioactivity, 3.7×10^4 Bq.
λ radioactive decay constant, h^{-1}.
t irradiation time, h.
n number density of target nuclei suitable for activation in the target material (number of atoms-cm^{-3}).
J velocity intensity of bombarding particle, μA.
Z number of positive charges of the bombarding particles.
σ(E) reaction cross-section between the bombarding particle and the target nucleus, energy-dependent, bar.
S(E) the distance the bombarding particle passes through the target in the energy interval E, E + dE, cm.
E_m the energy of the bombarding particle on the target surface, MeV.

The definition of a "thick target": the target thickness is slightly greater than the range of the charged particles in the target. If the thickness of the target greatly exceeds the range of the particles, it will not only waste the target material but also increase the workload of chemical separation.

When the irradiation time is much lower (at least 5 times) than the half-life of the target nuclide, the above equation can be approximately expressed as follows.

$$A = 7 \times 10^7 \cdot \frac{Jt}{ZT} \int_0^{Em} \sigma(E) S(E) dE \tag{2.7}$$

4. **Treatment of irradiated targets**

The target after particle beam bombardment can be treated by various physical and chemical methods to obtain carrier-free radionuclides. For solid targets, if the products are easily volatile substances such as ^{123}I and ^{75}Br, they can be separated and extracted by dry distillation technology, and the solid targets can be used repeatedly. If the products are difficult to volatile, the target materials must be dissolved, extracted, chromatographed, co-precipitated, etc. In this case, the processes will be cumbersome to operate and the targets can only be used once. Liquid targets and gas targets are relatively simple to treat. But no matter what kind of target, the separation and purification processes should be efficient with no introduction of the carrier. For very short-lived radionuclides, direct on-line synthesis of labeled compounds is also required.

2.3.6 Application of Radionuclides Produced by Accelerators

Accelerator-produced nuclides have a wide range of applications. In industry and scientific research, ^{57}Co, ^{22}Na, and ^{109}Cd can be used as radioactive sources for the Musburger effect, positron annihilation techniques, and X-ray fluorescence analysis. In agriculture and environmental protection, ^{47}K, ^{74}As, and ^{203}Pb are used as tracer atoms. In medical applications, accelerator-produced nuclides are more widely used. ^{67}Ga citrate is used for tumor diagnosis, showing its location, and also for lymph node, lung, and bone imaging. ^{111}In-labeled diethylenetriamine pentaacetic acid is used for brain imaging. ^{123}I-labeled sodium iodide is used for the diagnosis of thyroid disease, producing only 1% of the radiation dose of ^{131}I to the patient. Fatty acids labeled and O–o-iodohippuric acid labeled with ^{123}I are used for the diagnosis of myocardial and renal diseases respectively. Tl-labeled sodium chloride is used as a tracer atom, and thallium chloride labeled with ^{201}Tl can be used to diagnose myocardial infarction. ^{81m}Kr with a very short half-life can be used to diagnose pulmonary obstruction, emphysema, bronchitis, etc. ^{11}C, ^{13}N, ^{15}O, and ^{18}F-labeled biomolecules can display images of metabolic dynamics in living bodies with exactly the same biochemical behavior as natural substances and can give a relatively accurate position in three-dimensional space on a positron computed tomography.

2.3.7 Production of Radionuclides ^{123}I by Accelerators

Accelerator-produced radionuclides such as ^{11}C, ^{13}N, ^{15}O, ^{18}F, ^{68}Ga, and ^{123}I have been widely used in nuclear medicine. Their preparation methods have also been frequently reported. Taking 123I as an example, its preparation technology will be briefly introduced below.

^{123}I has become the second most important radionuclide in current clinical use after ^{99m}Tc due to its excellent chemical and nuclear ($T_{1/2}$ = 13.2 h, EC ≈ 100%, E_r = 159 keV) properties. Iodine forms stable compounds for analogues of various biomolecules such as proteins and nuclear targets, and thus ^{123}I-labeled radiopharmaceuticals have become the most important drugs for cardiovascular, oncological, and receptors. These drugs are characterized by low damage, high sensitivity, and selectivity, which enable accurate early assays.

There are more than twenty ways to prepare ^{123}I. Based on the adopted nuclear reaction, the production of ^{123}I by accelerators can be divided into the direct method and indirect method. Direct methods such as ^{121}Sb(α, 2n)^{123}I, ^{124}Te(p, 2n)^{123}I, and ^{123}Te(p, n)^{123}I. Indirect methods use ^{123}Xe → ^{123}I generators to prepare ^{123}I, examples of nuclear reactions are ^{123}Te(^{3}He, 3n) ^{123}Xe → ^{123}I, ^{127}I(α, 5n) ^{123}Xe → ^{123}I.

Due to limitations in yield, impurity levels, and cost, there are six main nuclear reactions of practical significance: ^{124}Te(p, 2n)^{123}I, ^{123}Te(p, n) ^{123}I, ^{122}Te(d, n) ^{123}I, ^{127}I(p, 5n) ^{123}Xe → ^{123}I, ^{124}Xe(p, x)^{123}I, and ^{124}Xe(γ, n) ^{123}Xe → ^{123}I.

1. **Direct method of ^{123}I preparation**

The direct method of preparing ^{123}I requires medium and low energy accelerators to initiate nuclear reactions with protons or deuterium on enriched Te targets. The targets are prepared using high abundance Te isotopes such as ^{124}Te, ^{123}Te, and oxides of ^{122}Te, which are melted in Pt disks by heating to form irradiation targets. The irradiation is cooled with a thin layer of water below the disk and a large stream of water on the back of the disk.

The irradiated target needs to be chemically treated to separate ^{123}I from the target material. The chemical separation methods for ^{123}I are dry distillation and wet chemical separation. The dry distillation method is the same as that of ^{131}I described in Sect. 2.2, while the wet chemical separation method includes wet distillation, adsorption, filtration, and other methods. Using the wet chemical method to process target parts (pieces) is complicated to operate, with a longer time, lower ^{123}I total yield, and lots of radioactive waste. In comparison, dry distillation has the advantages of simple operation, short distillation time (a few minutes), high recovery rate (close to 100%), and a small amount of radioactive waste, etc. Therefore, in the production of using the direct method to prepare^{123}I, the dry distillation method is mainly adopted.

2. **Indirect method of ^{123}I preparation**

The main indirect methods developed internationally are ^{127}I(p, 5n) ^{123}Xe → ^{123}I, ^{124}Xe(p, x) ^{123}I and ^{124}Xe(γ, n) ^{123}Xe → ^{123}I. The production of ^{123}I by indirect methods requires the use of the medium- and high-energy cyclotrons or electron accelerators, and the main impurities in the product are ^{125}I with a half-life of 60d.

The (p, 5n) reaction has the highest yield of all nuclear reactions for preparing ^{123}I, but it requires a high-energy accelerator (> 60 meV) and is therefore currently used by only a few countries with high-energy accelerators to produce ^{123}I. This is also the main method for the large-scale production of ^{123}I at present.

In the 1980s, a method of producing ^{123}I by the ^{124}Xe(p, x)^{123}I reaction using highly enriched ^{124}Xe emerged. This method has developed rapidly because it only requires a medium-energy cyclotron. This method can adopt a similar separation technique to the production of ^{125}I from ^{124}Xe mentioned in Sect. 2.2. However, although the use of highly enriched ^{124}Xe can increase the ^{123}I yield and effectively reduce the ^{125}I content, the price of highly enriched ^{124}Xe is very expensive. The current price per liter of ^{124}Xe with 99.9% abundance is around CNY250,000.

^{123}I can also be prepared by the ^{124}Xe(γ, n) ^{123}Xe nuclear reaction using a highly enriched ^{124}Xe and electron accelerator. The purity of ^{123}I prepared by this method is the highest among all ^{123}I production methods.

2.4 Radionuclide Generators

The radionuclide generator is an alternative way of obtaining artificial radionuclides. It enables the periodic separation of short-lived daughter nuclides from long-lived parent nuclides through simple operations, providing favorable conditions for the application of short-lived daughter nuclides, especially in locations far away from reactors and without accelerators. Currently, the most applied field of radionuclide generators is nuclear medicine. The parent nuclide it uses is produced via a reactor or accelerator. In general, radionuclide generators are named after their parent and daughter nuclides or directly after the daughter nuclide, for example, a device with a parent of ^{99}Mo and a daughter of ^{99m}Tc is called a ^{99}Mo- ^{99m}Tc generator or a ^{99m}Tc generator. The radionuclide generator can separate the daughter nuclide from it at appropriate intervals during its lifetime, just like milking a cow, so the radionuclide generator is also called a "cow". Radionuclide generators were first used in medicine. In 1920, Failla isolated ^{222}Rn from ^{226}Ra and introduced the concept of a generator. 1951, M. W. Green and others developed the world's first artificial radionuclide generator, ^{132}Te- ^{132}I generator, by using the principle of separating ^{222}Rn from ^{226}Ra. Since then, ^{99}Mo/^{99m}Tc,^{113}Sn- ^{113}In, and other generators were developed successively. Theoretically, many such parent-daughter nuclide systems can constitute radionuclide generators. The American scientist M. Bruce did a lot of work and published an article in 1965 listing 118 potentially useful generator systems. More than 150 radionuclide generators have been reported in the literature, but only about 20 of them have been actually applied (^{28}Mg- ^{28}Al, ^{38}S- ^{38}Cl, ^{42}Ar- ^{42}K, ^{44}Ti- ^{44}Sc, ^{47}Ca-^{47}Sc, ^{68}Ge- ^{68}Ga, ^{72}Se- ^{72}As, ^{81}Rb- ^{81m}Kr, ^{83}Rb- ^{83m}Kr, ^{87}Y- ^{87m}Sr, ^{90}Sr- ^{90}Y, ^{99}Mo/^{99m}Tc, ^{103}Pd- ^{103m}Rh, ^{103}Ru- ^{103m}Rh, ^{111}Ag- ^{111m}Cd, ^{113}Sn- ^{113m}In, ^{125}Sb- ^{125m}Te, ^{131}Ba- ^{131}Cs,^{132}Te- ^{132}I, ^{137}Cs- ^{137m}Ba, ^{188}W- ^{188}Re, ^{189}Ir- ^{189m}Os, ^{194}Hg- ^{194}Au, etc.). Among these parent/daughter nuclides, ^{99}Mo/^{99m}Tc is the most widely used radionuclide generator due to the easy mass production of ^{99}Mo and the excellent nuclear properties of ^{99m}Tc. At present, ^{99}Mo/^{99m}Tc generators and their supporting drugs have become the main source of radiopharmaceuticals for nuclear medicine imaging, and the amount of $^{99\,m}$ Tc accounts for more than 80% of the total amount of radionuclides used for medical diagnosis.

2.4.1 Fundamentals

Radionuclide generators use physical or chemical means to separate the continuously generated daughter nuclides from the parent nuclide by taking advantage of the half-lives of the parent and daughter nuclides and the differences in their physical, chemical, and other properties. In practical radionuclide generators, the half-life of the daughter nuclides is short, while that of the parent nuclides is relatively long.

1. **Radioactive parent-daughter interrelationships**

Suppose that: at t = 0, there is only the number of parent nuclei ($N_{1,0}$), the number of remaining parent nuclei at time t is

$$N_{1,t} = N_{1,0}e^{-\lambda_1 t} \tag{2.8}$$

When the decay of the parent nuclide produces only a single daughter radionuclide, for the daughter nuclide there are

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 = \lambda_1 N_{1,0} e^{-\lambda_1 t} - \lambda_2 N_2 \tag{2.9}$$

From the above equation, it follows that

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_{1,0}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \tag{2.10}$$

Then, at any moment t, the activity of the daughter nuclide is

$$\lambda_2 N_2 = \lambda_1 N_{1,0} \frac{\lambda_2}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \tag{2.11}$$

$$\frac{\lambda_2 N_2}{\lambda_1 N_1} = \frac{\lambda_2}{\lambda_2 - \lambda_1}\left(1 - e^{(\lambda_1 - \lambda_2)t}\right) \tag{2.12}$$

For the case where the parent nuclide A decays to give rise to multiple daughter nuclides, since the decay branching ratio of the parent nuclide decaying to a particular daughter nuclide B is certain, the activity of the daughter nuclides is

$$\lambda_2 N_2 = F\lambda_1 N_{1,0} \frac{\lambda_2}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \tag{2.13}$$

where: F is the decay branching ratio for the decay of parent nuclide A into daughter nuclide B.

As seen in Eq. (2.11), the daughter nuclides produced by the pure parent nuclide as an initial substance is 0 when t = 0 and $t \to \infty$. At some intermediate time t_m, the activity of the daughter nuclide will reach a maximum, when the

$$\frac{d(\lambda_2 N_2)}{dt} = 0 = -\lambda_1 e^{-\lambda_1 t_m} + \lambda_2 e^{-\lambda_2 t_m} \tag{2.14}$$

Therefore,

$$\lambda_1 e^{-\lambda_1 t_m} = \lambda_2 e^{-\lambda_2 t_m} \tag{2.15}$$

So, there is

$$\frac{\lambda_2}{\lambda_1} = e^{(\lambda_2 - \lambda_1) t_m} \tag{2.16}$$

$$t_m = \frac{\ln(\lambda_2/\lambda_1)}{\lambda_2 - \lambda_1} \tag{2.17}$$

Based on Eq. (2.17), the drenching interval of the radionuclide generator can be determined.

2. **Instantaneous versus long-term equilibrium**

Since the lifetime of the parent nuclide in the generator is generally longer than that of the daughter nuclide, i.e., $\lambda_2 > \lambda_1$. According to Eq. (2.12), when $t \geq t_m$, there is

$$\frac{\lambda_2 N_2}{\lambda_1 N_1} \approx \frac{\lambda_2}{\lambda_2 - \lambda_1} = const. \tag{2.18}$$

The presence of such a constant ratio of activity as in the above equation is called transient equilibrium. In the case of transient equilibrium, the rate of decrease in the activity of the daughter is the same as that of the parent.

When $\lambda_1 \leq \lambda_2$ and t is great enough,

$$\lambda_1 N_1 \approx \lambda_2 N_2 \quad or \quad A_1 \approx A_2 \tag{2.19}$$

At this point, the nuclide activities of parent and daughter are almost equal, and this equilibrium is called long-term equilibrium.

2.4.2 Types of Radionuclide Generators

According to the separation method of parent and daughter nuclides, the main types of radionuclide generators are chromatography type generators, sublimation type generators, and extraction type generators. The chromatographic generator has become the most commonly used type of radionuclide generator due to its compact structure, simple eluting operation, and easy protection.

2.4.3 *Requirements for the Preparation of Radionuclide Generators*

When preparing a radionuclide generator, it is necessary to consider the selection of the parent nuclide, the generator structure, etc. When designing the generator structure, the separation method of the parent and daughter nuclides, the generator sizes, and radiation protection should be considered.

1. **Selection of parent nuclide**

When selecting a parent nuclide, it is usually necessary to consider several aspects such as the use and nuclear properties of the daughter nuclide (ray type, energy, half-life, etc.), the half-life of the parent nuclide, the separation of the parent and daughter nuclides, and the production capacity of the parent nuclide. For example, medicine requires short half-life nuclides with a half-life of a few hours and major γ-ray energy between 100 and 250 keV for organ imaging and medical diagnosis. ^{99m}Tc is suitable for nuclear medicine imaging because of its desirable nuclear properties (^{99m}Tc emits monoenergetic γ-rays at 141 keV with a half-life of 6.0 h and almost no β^--rays), and its parent nuclide ^{99}Mo has a relatively long half-life (66.0 h) which is easily transported over long distances, and can be produced in large quantities in a reactor by the (n, γ) nuclear reaction of ^{98}Mo or the (n, f) nuclear reaction of ^{235}U at low prices. These characteristics of parent and daughter nuclides make ^{99}Mo- ^{99m}Tc generators the most widely used type of generator.

Parent nuclides are usually obtained in three main ways: irradiation from nuclear reactors, irradiation from cyclotrons, and extraction from nuclear fission products.

2. **Design of generator structure**

The structure of radionuclide generators varies with the method of separation of the parent and daughter nuclides and the specifications of the generator. The separation method is selected according to the requirements for the separation of parent and daughter nuclides and the purity of the daughter nuclides. Efficient separation, high efficiency, speed, and ease of operation are usually required, and the daughter nuclides obtained by separation under the conditions of multiple repetitions should still maintain high nuclear purity, radiochemical purity, and specific activity of radioactivity, as well as a suitable chemical state and stable chemical composition. The commonly used separation methods are ion chromatography, solvent extraction, and sublimation, among which ion chromatography is most used. Radiation protection capability and the ease and safety of transportation are also important considerations in the design of the generator. Different types of radiation, different radioactive loadings, etc. require appropriate adjustments to the material and thickness of the protective layer of the generator to ensure the safety of the staff during the production and usage of the generator. In addition, additional sterile filters are required for generators intended for medical use.

2.4.4 Requirements for Medical Radionuclide Generators

It is generally accepted that a satisfactory medical radionuclide generator should meet the following conditions:

(1) Daughter nuclides have appropriately long half-lives, suitable types of radiation, and energies. In the past, short-lived nuclides with half-lives of a few hours to tens of hours were mostly used. In recent years, due to the improvement of detectors and operational automation programs, the clinical application of some ultra-short-lived nuclides with a half-life of minutes or seconds become possible.
(2) Daughter nuclides should have good pharmacological properties and be suitable for the study of physiological functions. This is an important condition for evaluating whether the radionuclide generator has medical value.
(3) The parent nuclide for the radionuclide generator can be easily produced in large quantities, preferably in the reactor, to reduce costs. In addition, it is required that the half-life of the parent nuclide should be as long as possible so that the generator has a long service life.
(4) Parent and daughter nuclides are easy to separate. The parent and daughter nuclides in a radionuclide generator are generally different chemical elements. The method of separating the daughter from the parent must be simple, rapid, and high-yielding. At the same time, the repeated separation must ensure that the separated daughter nuclides have high radioactive purity, radiochemical purity, and radioactive concentration. And the chemical composition of the product should be stable and preferably meet the requirements for direct application (oral or injectable).

2.4.5 Preparation of Major Radionuclide Generators

1. ^{99}Mo/^{99m}Tc generator

Since the introduction of ^{99m}Tc in 1957, the clinical application of the ^{99}Mo/^{99m}Tc generator has greatly contributed to the development of nuclear medicine imaging. ^{99m}Tc is a pure gamma photon emitter with an energy of 141 keV and a $T_{1/2}$ of 6.02 h and has multiple valence states. Therefore, it can be made into a variety of drugs that are selectively distributed in many organs of the body. Technetium is unstable in its reduced state and can interact with many organic or inorganic compounds containing oxygen, nitrogen, and sulfur to form complexes under certain pH conditions. These technetium-labeled complexes are relatively stable and non-toxic, both in vivo and in vitro. Thus, ^{99m}Tc can be used to prepare a variety of radiopharmaceuticals for organ imaging of brain, heart, liver, kidney, bone, thyroid, etc. Nowadays, there are more than 100 kinds of radiopharmaceuticals labeled with ^{99m}Tc. Most of them can be made into medicine kits for supply, which are simple to label, convenient to use,

and widely used in clinical practice, accounting for more than 80% of all clinical radionuclides, and are known as "universal radionuclides". Because of the short half-life and low energy γ-radiation, even if it is used in a large amount (7.4×10^8 Bq–3.7×10^9 Bq), the radiation dose of ^{99m}Tc received by the patient is still small. Therefore, ^{99m}Tc is very safe to use and has become the most desirable and commonly used radionuclide at present.

There are two main ways to obtain the parent nuclide ^{99}Mo in ^{99}Mo/^{99m}Tc generators, ^{235}U(n, f)^{99}Mo and ^{98}Mo(n, γ)^{99}Mo methods. The extraction of fission ^{99}Mo has the disadvantages of complex processes and a large amount of high-activity waste charged, but high specific activity carrier-free ^{99}Mo can be obtained to prepare high-quality chromatographic ^{99}Mo/^{99m}Tc generators via this method. The (n, γ) method has the advantages of simple operation and less high-activity waste charged, but the generated ^{99}Mo has low specific activity and a large amount of ^{98}Mo is present. The methods used to separate ^{99m}Tc from ^{99}Mo generated by the (n, γ) method are ion chromatography (gel method), sublimation, and solvent extraction, and their corresponding generators are called gel generators, sublimation generators, and solvent extraction generators.

Chromatography generators produced by fission ^{99}Mo have the advantages of simple generator fabrication, easy drenching, easy protection, easy meeting the requirements of sterility and no heat source, etc. They are very suitable for clinical applications and have become the most dominant type of generator at present. All countries in the world basically use fission ^{99}Mo to prepare chromatographic ^{99}Mo/^{99m}Tc generators. Therefore, this section mainly introduces the chromatographic ^{99}Mo/^{99m}Tc generator prepared by fissionable ^{99}Mo (fissionable ^{99}Mo/^{99m}Tc generator).

(1) Fission-^{99}Mo/^{99m}Tc generator

Acidic Al_2O_3 adsorbs the parent nuclide ^{99}Mo but is less able to adsorb the higher valent (+VII) ^{99m}Tc. The fission-^{99}Mo/^{99m}Tc generator takes advantage of the difference in the chemical properties of the parent and daughter nuclides to separate them. The parent nuclide ^{99}Mo is adsorbed on the Al_2O_3 column in the form of $^{99}MoO_4^{2-}$, and then the high valent (+7) ^{99m}Tc is eluted in the form of $^{99m}TcO_4^-$ with an eluent such as 0.9% NaCl, while the parent remains in the generator. The daughter nuclide grows with the decay of the parent while decreasing by its own decay, and thus can be calculated using the equation for continuous decay.

① Preparation processes and environmental area division

The preparation of a fission-^{99}Mo/^{99m}Tc generator includes the following processes: column packing pretreatment, column packing loading, cold column disinfection, cold column washing, cold generator assembly, feed solution pH adjustment, quantitative feed solution filling, pre-eluting, vacuum vial preparation, physiological saline preparation and dispensing, product inspection, packaging and delivery, etc. Since ^{99m}Tc is mainly used for labeling the injected drugs in vivo, it must meet the requirements of sterility and no heat source. Therefore, the preparation of the ^{99}Mo/^{99m}Tc

generator is required to be completed in different clean areas, and the core components and main parts of the generator should be sterilized. As different methods can be adopted for column disinfection (cold column disinfection or hot column disinfection), the preparation processes of the fission-^{99}Mo/^{99m}Tc generator will be adjusted.

② Main preparation processes

a. Pretreatment of column packing

The column packing used in fission-produced generators is mainly aluminum trioxide. The pretreatment of the column packing has a great impact on the performance of the generator. The processes of pretreatment include selection of alumina type, heat treatment and acid–base immersion (surface activation), sieving, eluting, drying, etc. One of the important factors affecting the performance of the generator is the particle size of the aluminum trioxide installed in the column. A larger particle size significantly reduces the adsorption capacity due to the reduced specific surface area, while smaller particle sizes can cause difficulties in eluting the generator. Therefore, the size of alumina for column loading selected is generally 100–200 mesh. After loading the column, wash the column packing with a low-acid HCl solution to remove the very tiny aluminum trioxide as much as possible.

b. Column packing loading

Wet-loaded is mainly used for column packing. Since the surface of alumina is positively charged under acidic conditions, it can adsorb negatively charged molybdate, so the acidity is controlled at pH = 2–3 when loading the column. When loading the column, the Al_2O_3 should be loaded as much as possible to avoid the channeling phenomenon during loading and eluting of the mother liquor, which affects the performance of the generator.

There are two ways to disinfect the generator: cold column disinfection and hot column disinfection. Cold column disinfection is generally used in the production of the generator because of the generally high radioactive dose during fission ^{99}Mo extraction, which can radiate the disinfection of the ^{99}Mo solution itself. Irradiation disinfection and high-pressure steam disinfection can be used to disinfect the cold column.

c. Fission ^{99}Mo feed solution filling and pre-eluting

An amount of fission ^{99}Mo is added to the column using pressurized or negative pressure methods. Then pre-elute with 0.9% physiological saline to check whether the generator pipeline is unobstructed.

In acidic solutions, the degree of polymerization of molybdate ions increases as the acidity of the solution increases. The positively charged alumina can only adsorb negatively charged molybdate ions under acidic conditions. Thus, column loading of molybdenum solutions under acidic conditions can effectively improve the

adsorption capacity of alumina for molybdenum. However, when the molybdenum solution is eluted with a large volume of normal saline after being put on the column in strong acidity, the degree of polymerization of molybdic acid may be reduced, which may result in molybdenum penetration. Therefore, the acidity of the molybdenum solution is generally controlled under weak acid conditions during column loading, and the pH is usually controlled within the range of 2–3.

Due to the radiation decomposition of water, some of the + VII-valent technetium may be converted to + IV-valent technetium by the radicals generated by the radiolysis of water, and the low-valent technetium is easily adsorbed by the alumina, thus reducing the eluting efficiency of the generator. Adding appropriate additives or draining the column after each eluting can effectively prevent the reduction of the generator eluting efficiency.

③ Quality control conditions for generators

a. **Eluent characters**: colorless transparent liquid.
b. **Eluting efficiency**: is calculated as follows:

$$A^{i}_{^{99m}\mathrm{Tc}} = 1.1003 A^{0}_{^{99}\mathrm{Mo}}\left(e^{-0.0204968t} - e^{-0.115116t}\right) \tag{2.20}$$

$$\eta = \frac{A^{2}_{^{99m}\mathrm{Tc}}}{A^{i}_{^{99m}\mathrm{Tc}}} \times 100 \tag{2.21}$$

where

$A^{i}_{^{99m}\mathrm{Tc}}$ ^{99m}Tc theoretical elute volume, Bq.
$A^{0}_{^{99}\mathrm{Mo}}$ ^{99}Mo loading column volume, Bq.
$A^{2}_{^{99m}\mathrm{Tc}}$ ^{99m}Tc actual elute volume, Bq.
η Eluting efficiency, %.

c. **Eluting curve**: Use 10 mL of 0.9% saline as the eluent, take samples every 1 mL, and analyze the radiation of ^{99m}Tc in every 1 mL of eluent by a gamma counter, to draw the eluent curve. The eluting volume can be determined by the eluting curve.
d. **Nuclear purity**: The content of impurity nuclides in the eluent can be measured by γ-spectrometer, requiring ^{99}Mo < 0.1%, ^{131}I < 0.005%, ^{90}Sr < 6.0×10^{-6}%, ^{103}Ru < 0.005%, ^{89}Sr < 6.0×10^{-5}%, α-radionuclides < 1.0×10^{-7}%, other β-ray and γ-ray impurities < 0.01%.
e. **Radiochemical purity**: Use paper chromatography to develop the system in acetone water for 10–15 cm at room temperature, $^{99m}TcO_4^-$ > 98%, R_f-value should be 0.9–1.0.
f. **Generator activity**: Measure the amount of radioactivity of ^{99}Mo in a certain volume of the feed liquid, and calculate the column loading volume to obtain the activity column loading of the generator.
g. **Eluent acidity**: Require a pH of 4.0–7.0.
h. **Aluminum content**: Require to be < 10 μg mL^{-1}.

i. **Biological indicators**: Endotoxin content < 2.0 EU mL^{-1}.

(2) Gel-^{99}Mo/^{99m}Tc generator

For countries with a high level of nuclear technology, fission ^{99}Mo can be produced in large quantities due to the technologies used in fission ^{99}Mo production, such as ^{235}U target preparation, fission ^{99}Mo extraction and production equipment processing, radioactive waste treatment, etc. However, for those countries and regions with a low level of nuclear technology, due to the complex process of ^{235}U target preparation and fission ^{99}Mo extraction, huge equipment investment, and the need to deal with a large amount of strong radioactive waste, especially the environmental pollution caused by adverse control of radioactive waste gas, it is impossible to produce fission ^{99}Mo. In addition, due to the short half-life of ^{99}Mo (64 h), it is not suitable for long-distance transportation, so the cost of importing fission ^{99}Mo raw materials or ^{99}Mo/^{99m}Tc generators is high. These factors limit the use of ^{99}Mo/^{99m}Tc generators in countries and regions with a low level of nuclear technology. Therefore, many developing countries have undertaken research on alternative production methods for ^{99}Mo/^{99m}Tc generators. The preparation of gel-^{99}Mo/^{99m}Tc generators by making gel-loaded columns of reactor irradiated low specific activity ^{99}Mo provides the conditions for the use of relatively inexpensive ^{99m}Tc in developing countries.

① Basic principles

The gel-^{99}Mo/^{99m}Tc generator is also a chromatographic generator. After dissolving the MoO_3 of the reactor irradiation, it can be reacted with $ZrOCl_2$ solution to form a stable zirconium molybdate precipitate ($ZrOMoO_4$), which is then filtered, dried at low temperature, crushed, and sieved to make a gel-^{99}Mo/^{99m}Tc generator column packing. When eluted with physiological saline, ^{99m}Tc is washed off, while ^{99}Mo remains in the generator column in the form of zirconium molybdate.

② Control points of production

In the production of gel-^{99}Mo/^{99m}Tc generator column packing, the most important influence on the eluting performance of the generator is the drying conditions of the gel and the particle size of the loaded gel. The dried gel must maintain certain water content and be amorphous, otherwise, the eluting efficiency will be very low. At the same time, the particle size of the gel has a great impact on the elution efficiency of the generator. The smaller the gel size, the higher the elution efficiency of the generator. But if the size is too small, the generator will be difficult to elute, and clogging is likely to occur. Therefore, choosing a suitable gel size is also an important factor to ensure the efficiency of the generator. The drying and granulation methods of gels still need further study.

③ Problem existed

Although many studies have reported that the elution efficiency of gel-^{99}Mo/^{99m}Tc generators can reach more than 80%, it is difficult to obtain stable molybdenum zirconate acyl column packing due to the difficulty in controlling the processing conditions of molybdenum zirconate acyl gels (such as the water content in the dried gel, the average particle size of the gel on the column, the utilization rate of the gel, etc.) in actual production. At the same time, because ^{99m}Tc is uniformly distributed in zirconium molybdate gel, the eluting of ^{99m}Tc is relatively difficult. Therefore, the elution efficiency of the generator is generally low, the eluting peak is wide, the volume of the eluent is large, and the specific activity of ^{99m}Tc in the eluent is low. Due to the low eluting efficiency, in order to provide the gel-^{99}Mo/^{99m}Tc generator with the activity that users required, it is necessary to load the zirconium molybdate gel packing with several times the activity. Although the volume of the column in the generator is not significantly different from that of the fission column, due to a large amount of radioactivity, in order to meet the protection requirements during transportation, the amount of radioactivity loaded into it is larger, the thickness of the protective layer must be increased to increase the total weight of the generator.

The eluate of the gel-based ^{99}Mo/^{99m}Tc generator contains chemical impurities such as Zr and Mo and the accumulation of ^{99}Tc increases due to the low elution rate. The presence of Zr, Mo, and ^{99}Tc may affect the labeling rate of ^{99m}Tc, as well as the subsequent imaging and therapeutic effects.

2. ^{188}W/^{188}Re generator

^{188}Re can be obtained from the parent ^{188}W decay (with a half-life of up to 69.4 d) whose half-life is 17.9 h. It is a radionuclide with nuclear properties well suited for the treatment of tumors, which turns into stable ^{188}Os through β^--decay. It emits β-rays with a maximum energy of 2.12 meV and 1.97 meV with a probability of 79% and 20% respectively, accompanied by 155 keV γ-rays that are well suited for imaging. It is convenient to study the pharmacokinetics of ^{188}Re labeled drugs such as biological distribution, radiation dose estimation, etc. Because of the above advantages, ^{188}Re has become a promising radionuclide for medical use. Currently, ^{188}Re labeled radioactive compounds can be used in the treatment of bone tumors, treatment of head and neck soft tissue tumors, radiation synovectomy of rheum arthritis, and radioimmunotherapy of tumors.

^{188}Re can be easily obtained from the ^{188}W/^{188}Re generator. The ^{188}W/^{188}Re generator was developed in 1998 and has been continuously improved and refined. Although it is expensive, the price of 3.7×10^7 Bq (1 mCi) ^{188}Re is lower than that of any other therapeutic radionuclide because the ^{188}W/^{188}Re generator has a lifetime of up to one year and can be eluted every three days. It can be predicted that after solving the source problem of ^{188}W, the ^{188}W/^{188}Re generator will be widely used in the field of nuclear medicine therapy as the ^{99}Mo/^{99m}Tc generator in the field of imaging.

Two times (n, γ) reactions are required to obtain ^{188}W from ^{186}W, which puts forward higher requirements for the reactor (neutron fluence rate of about 10^{15} cm^{-2} s^{-1}). Therefore, low-power reactors cannot produce chromatographic ^{188}W/^{188}Re generators.

Since W/Mo and Re/Tc have similar chemical properties, the preparation method of the ^{188}W/^{188}Re generator is similar to that of the ^{99}Mo/^{99m}Tc generator. At present, there are two main preparation methods. For ^{188}W raw material with high specific activity, the preparation method similar to the fission-^{99}Mo/^{99m}Tc generator is adopted. ^{188}W can be adsorbed on the column with alumina and ^{188}Re can be washed off the column with physiological saline or physiological saline with ascorbic acid added as eluent. This preparation method has the advantages of simple processes and good eluting performance of the generator. For low specific activity ^{188}W raw materials, a similar preparation process to that of the gel-^{99}Mo/^{99m}Tc generator can be used to produce the ^{188}W/^{188}Re generator, namely, synthesize ^{188}W into zirconium tungstate acyl gel and load it onto the column to make a gel-^{188}W/^{188}Re generator. Since the tungsten content in the gel can reach 56%, which is much larger than the adsorption capacity of aluminum trioxide, it is possible to produce ^{188}W/^{188}Re generators in reactors with a low neutron fluence rate. At present, the gel-^{188}W/^{188}Re generator is still in the research stage. Like the gel-^{99}Mo/^{99m}Tc generator, it still has problems such as difficulties to control gel synthesis conditions and unstable generator eluting efficiency.

Due to the relatively low specific activity of eluted ^{188}Re and the relatively high ^{188}W content in the eluent, the application of gel-^{188}W/^{188}Re generators is limited. To improve the specific activity of ^{188}Re, a concentration device (anion exchange column or tandem anion/cation exchange column) is usually attached to the gel-^{188}W/^{188}Re generator, which can improve the specific activity of ^{188}Re by an order of magnitude. The Shanghai Institute of Atomic Nuclei of the Chinese Academy of Sciences has conducted related research and applied for a patent in 2001—*Medical Radionuclide Generator with Concentration Device.* In this patent, the generator is characterized in that the alumina chromatographic column is connected in series with the cation/anion exchange column. The cation/anion exchange column can remove the ^{188}W eluted from the alumina column and concentrate the ^{188}Re, so that ^{188}Re with high specificity and no carrier can be obtained, which can be directly used in the clinic, and the total yield of ^{188}Re in the whole system is 65–70%.

3. ^{68}Ge/^{68}Ga generators

In recent years, the rapid development of positron emission computed tomography (PET) technology has enabled nuclear medicine imaging to move from target organ imaging (functional imaging) to tissue, cellular, and even genetic imaging (molecular level imaging). This development has promoted the production and sale of positronium nuclides. As one of the positron-emitting nuclides used in PET technology, ^{68}Ga can be easily obtained from ^{68}Ge/^{68}Ga generators, with a half-life of 68.3 min.

Being a parent nuclide, ^{68}Ge has a half-life of 288 d. It is mainly prepared by nuclear reactions such as ^{69} Ga(p, 2n) ^{68}Ge, ^{67}Zn(^{3}He, 2n)^{68}Ge, and ^{66}Zn(α, 2n)^{68}Ge. Separating Ge from Ga or Zn can generally be done by distillation, solvent extraction, chromatography, etc.

The earliest ^{68}Ge/^{68}Ga generator reported in the literature was the solvent extraction generator. The first chromatographic generator was proposed by Green and Tucker. This generator uses alumina as the adsorption material, with the parent nuclide ^{68}Ge adsorbed on the alumina and the daughter nuclide ^{68}Ga eluted down with 0.0005 M EDTA. Currently, this generator has been widely used. However, before radioactive labeling, complex and time-consuming operations are required to decompose the stable Ga-EDTA complex and completely remove EDTA, which is very inconvenient in practical clinical applications. Therefore, the development of generators that can directly elute ^{68}Ga of ionic form from the generator has become a focus of ^{68}Ge/^{68}Ga generator research. To this end, Ehrhardt and Welch proposed a solvent extraction ^{68}Ge/^{68}Ga generator. This type of generator can produce the 8-hydroxyquinoline complex which has a low complexation with Ga. However, the "open" operation of this type of generator increases the possibility of eluent contamination, and together with the need for forced discharge, the application of this type of generator is limited. Loc'h et al. developed a generator system that uses SnO_2 as the column packing with the HCl eluent of 1 mol L^{-1}. A generator system based on alumina as the column packing and NaOH as eluent has also been developed. Both of the above generators are capable of eluting ^{68}Ga in ionic form and have significant advantages over other generator systems: higher ^{68}Ga yields and lower ^{68}Ge penetration. However, it has been reported that the maximum content of Sn and Al in the eluent of the generators using these two inorganic adsorbents can be more than 2 ppm and 5 ppm respectively. Besides, due to the strong complexation between EDTA and ^{68}Ga in the SnO_2/EDTA generator system, the eluted ^{68}Ga is not suitable for the preparation of radiolabeled compounds. Research on the development of new column packing materials and the selection of eluting agents to obtain ^{68}Ge generators with low penetration and convenient clinical applications has become another focus of research on ^{68}Ge/^{68}Ga generators in recent decades. It was found that α-Fe_2O_3 is a suitable inorganic adsorbent. Using this adsorbent as the column packing, HCl solution with pH = 2 can be used as the eluent, and the penetration rate of ^{68}Ge in the eluent is 6×10^{-6}–2×10^{-4}, the content of Fe is less than 0.03 ppm, and ^{68}Ga can be eluted in ionic form, which is suitable for clinical applications.

Scholars have also studied selective organic polymers as column separation materials such as porous styrene–divinylbenzene copolymer (R-MGlu) containing N-methyl glucosamin. This polymer can effectively adsorb ^{68}Ge, while ^{68}Ga can be washed with complexing agents with low affinity with Ga such as citric acid and phosphoric acid solutions, and the penetration rate of ^{68}Ge in the eluent is less than 0.4‰. Therefore, it is convenient for subsequent clinical applications, and the radiolabeling rate of ^{68}Ga is high. It was also found that R-MGlu is highly stable to irradiation. After using the generator for 6 months, no obvious penetration of ^{68}Ge was detected, indicating that R-MGlu is not degraded. Thus, this polymer is very promising for the production of ^{68}Ge/^{68}Ga generators.

4. Other generators

In addition to the above commonly used generators, there are many other generators such as ^{133}Sn/^{113m}In generators, ^{90}Sr/^{90}Y generators, etc. These generators basically use chromatographic columns for the separation of parent and daughter nuclides.

^{133}Sn/^{113m}In generator: ^{113}Sn is prepared in the reactor by the ^{112}Sn(n, γ)^{113}Sn reaction. Because the thermal neutron reaction cross-section of ^{112}Sn is small, highly enriched ^{112}Sn wires are generally used and irradiated for a long time. Dissolved the irradiated wire with 6 mol L^{-1} HCl under heating and evaporate it to near dry. Then dissolve the residue with low acidity HCl and add bromine water to oxidize Sn(+II) to Sn(+IV). The solution is then transferred to a chromatographic column containing hydrated zirconia, on which the tetravalent tin is adsorbed to make a generator. Using 0.05 mol L^{-1} HCl as eluent and the medical ^{113m}In solution can be obtained.

^{90}Sr/^{90}Y generator: The half-life of ^{90}Sr is 29 a, which can be extracted from fission products cooled for a long time. Since ^{90}Sr is a long-lived radionuclide with high toxicity, it is necessary to strictly control the penetration rate of ^{90}Sr. The daughter nuclide ^{90}Y is a pure β^- radionuclide with a half-life of 64 h, which is well suited to be made into a radiotherapeutic agent. ^{90}Sr extracted from fission products is usually adsorbed on a cation exchange resin to make a generator, and EDTA is used as an eluent to wash ^{90}Y off from the chromatographic column.

5. Application and development trend of radionuclide generator

A radionuclide generator can safely and conveniently provide short half-life radionuclides with high nuclear purity, no carrier, high specific activity, and high radioactive concentration many times. So, it has been widely used in medical, industrial, scientific research, and many other fields. Especially in the field of nuclear medicine, radionuclide generators have greatly promoted the development of this field. Since the application of short-lived nuclides is a direction of medical examination and diagnosis, in addition to the existing medical radionuclide generators ^{132}Te/^{132}I, ^{99}Mo/^{99m}Tc, ^{113}Sn/^{113m}In, ^{87}Y/^{87m}Sr, ^{68}Ge/^{68}Ga, some new radionuclide generators with shorter half-lives need to be developed.

In recent years, with the rapid development of PET, PET/ECT, etc. and the integration of various nuclear diagnosis technologies, the development of generators for PET and diagnostic and therapeutic purposes, as well as ultra-short-lived nuclide generators for cardiovascular disease research has become the research focus of radionuclide generators. Of particular interest are radionuclides produced by twice-captured neutrons such as ^{166}Dy, ^{188}W, and ^{190}Os, and ^{82}Sr produced by high-energy accelerators.

Exercise

1. Briefly describe the source of radionuclides.
2. Briefly describe the production process of ^{131}I by dry distillation.
3. What should be aware of when preparing solid targets for accelerators?

4. Compare and contrast the methods of preparing ^{99}Mo- ^{99m}Tc generators.
5. A new ^{99}Mo- ^{99m}Tc generator with specification of 7.4×10^9 Bq:
   (1) How long is the optimal eluting time?
   (2) What is the total radioactivity on the chromatographic column 25 h after leaving the factory? Assuming that the eluting efficiency is 85%, how much ^{99m}Tc can be obtained?

Bibliography

Cheng, W. L., Lee, C. S., Chen, C. C., Wang, Y. M., & Ting, G. (1989). Study on the separation of molybdenum-99 and recycling of uranium to water boiler reactor. *International Journal of Radiation Applications and Instrumentation. Part*, *40*(4), 315–324. https://doi.org/10.1016/0883-2889(89)90224-4

Chuvilin, D. Y., Khvostionov, V. E., Markovskij, D. V., Pavshook, V. A., Ponomarev-Stepnoy, N. N., Udovenko, A. N., & Tome, L. A. (2007). Production of ^{89}Sr in solution reactor. *Applied Radiation and Isotopes, 65*(10), 1087–1094. https://doi.org/10.1016/j.apradiso.2007.05.002

Cocalia, V. A., Holbrey, J. D., Gutowski, K. E., Bridges, N. J., & Rogers, R. D. (2006). Separations of metal ions using ionic liquids: The challenges of multiple mechanisms. *Tsinghua Science and Technology, 11*(2), 188–193. https://doi.org/10.1016/S1007-0214(06)70174-2

Dasso, C. H., Pollarolo, G., & Winther, A. (1994). Systematics of isotope production with radioactive beams. *Physical Review Letters, 73*(14), 1907–1910.

Favaretto, C., Talip, Z., Borgna, F., Grundler, P. V., Dellepiane, G., Sommerhalder, A., Zhang, H., Schibli, R., Braccini, S., Müller, C., & Meulen, N. P. (2021). Cyclotron production and radiochemical purification of terbium-155 for SPECT imaging. *EJNMMI Radiopharmacy and Chemistry, 6*(1), 37.

Fiaccabrino, D. E., Kunz, P., & Radchenko, V. (2021). Potential for production of medical radionuclides with on-line isotope separation at the ISAC facility at TRIUMF and particular discussion of the examples of ^{165}Er and ^{155}Tb. *Nuclear Medicine and Biology, 94–95*, 81–91.

Glenn, D., Heger, A. S., & Hladik, W. B. (1997). Comparison of characteristics of solution and conventional reactors for ^{99}Mo production. *Nuclear Technology*. https://doi.org/10.13182/NT97-A35374

Heitzman, H., Young, B. A., Rausch, D. J., Rickert, P., Stepinski, D. C., & Dietz, M. L. (2006). Fluorous ionic liquids as solvents for the liquid-liquid extraction of metal ions by macrocyclic polyethers. In *Talanta* (Vol. 69, pp. 527–531). Elsevier. https://doi.org/10.1016/j.talanta.2005.09.046

International Atomic Energy Agency. (1998). *Management of radioactive waste from ^{99}Mo Production.*

International Atomic Energy Agency. (2003). *Manual for reactor produced radioisotopes.*

International Atomic Energy Agency. (2021a). *Production of emerging radionuclides towards theranostic applications: Copper-61, Scandium-43 and -44, and Yttrium-86*.

International Atomic Energy Agency. (2021b). *Therapeutic Radiopharmaceuticals Labelled with Copper-67, Rhenium-186 and Scandium-47*.

Knapp, F. F., & Dash, A. (2016). Reactor-produced therapeutic radionuclides. In F. F. Knapp & A. Dash (Eds.), *Radiopharmaceuticals for therapy* (pp. 71–113). Springer.

Knust, E. J., Dutschka, K., & Weinreich, R. (2000). Preparation of ^{124}I solutions after thermodistillation of irradiated $^{124}TeO_2$ targets. *Applied Radiation and Isotopes, 52*(2), 181–184. https://doi.org/10.1016/S0969-8043(99)00127-X

Legeai, S., Diliberto, S., Stein, N., Boulanger, C., Estager, J., Papaiconomou, N., & Draye, M. (2008). Room-temperature ionic liquid for lanthanum electrodeposition. *Electrochemistry Communications, 10*(11), 1661–1664. https://doi.org/10.1016/j.elecom.2008.08.005

Lepera, C. G., & Wong, W.-H. (2004). Production of isotopes. In E. E. Kim, M.-C. Lee, T. Inoue, & W. H. Wong (Eds.), *Clinical PET: Principles and applications* (pp. 31–43). Springer.

Luo, H., Dai, S., Bonnesen, P. V., & Buchanan, A. C. (2006). Separation of fission products based on ionic liquids: Task-specific ionic liquids containing an AZA-crown ether fragment. *Journal of Alloys and Compounds, 418*(1–2), 195–199. https://doi.org/10.1016/j.jallcom.2005.10.054

Mushtaq, A. (2012). Producing radioisotopes in power reactors. *Journal of Radioanalytical and Nuclear Chemistry, 292*(2), 793–802.

Ruth, T. J. (2013). Accelerator production of medical radionuclides: A review. *Nuclear Physics News, 23*(2), 30–33.

Saha, G. B. (2018). Production of radionuclides. In G. B. Saha (Ed.), *Fundamentals of nuclear pharmacy* (pp. 49–75). Springer International Publishing.

Welch, M. J., & Redvanly, C. S. (2005). *Handbook of radiopharmaceuticals: Radiochemistry and applications*. Wiley.

Chapter 3
Nuclear Analytical Techniques and Methods



The nuclear analytical technique is a modern analytical technique consisting of various methods based on particle-matter interaction, nuclear effects, and nuclear spectroscopy. The analytical technique is likened to the eye of substance composition characterization, and the nuclear analytical technique is the microscope added to this eye to understand the characteristics of atomic nuclei. Modern nuclear analytical technique is an advanced analytical technique that is developed based on nuclear physics and nuclear chemistry, using various nuclear effects, nuclear spectroscopy, nuclear electronics, nuclear detection technology, etc. It has the advantages of high sensitivity, good accuracy, high resolution, low destructiveness, and multi-element analysis, with the ability of nuclide analysis and microstructure analysis, as well as the characteristics of implementing off-line and online measurements. Therefore, it can often be used in the analysis and identification work that is difficult or even impossible to be completed by general non-nuclear analytical techniques, such as cultural relics identification, dating, origin determination, technological level analysis, and online quality monitoring. At the same time, with the development of life science, especially with the research of life science reaching the molecular level, the modern nuclear analytical technique shows an irreplaceable role.

This chapter mainly introduces the methods and principles of nuclear analysis and focuses on several commonly used nuclear analytical techniques. Readers may refer to related materials or books for more in-depth knowledge of nuclear analytical techniques.

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6_3

3.1 Overview of Nuclear Analytical Techniques and Methods

3.1.1 Classification of Nuclear Analytical Techniques

When rays or particles interact with matter, the state or parameters of the incident primary rays or particles and the target nucleus will change, and in some cases, secondary rays or secondary particles will be produced. These changes and secondary emissions largely depend on the composition and structural characteristics of the substance interacting with rays or particles. The characteristics of these secondary rays or particles can be used to qualitatively and quantitatively study the elements, nuclides, or structures of the substance. This kind of technology is generally referred to as nuclear analytical techniques. Nuclear analytical techniques mainly include ion beam analysis (IBA), hyperfine effect analysis, and activation analysis. And each of these techniques can be sub-classified. For example, activation analysis can be divided into photon activation analysis ($\boldsymbol{\gamma}$, n), neutron activation analysis (n, $\boldsymbol{\gamma}$) or (n, p), and charged particle activation analysis (d, p) according to different incident particles; ion beam analysis includes Rutherford backscattering spectrometry (RBS), elastic recoil (ERD), channeling effect, charged particle-induced X-ray emission (PIXE), mass spectrometry (MS), etc.; hyperfine interaction includes the Mössbauer effect, perturbed angular correlation technique, nuclear magnetic resonance (NMR), positron-annihilation technique (PAT), neutron scattering and neutron diffraction. These nuclear analytical techniques cover elemental analysis, nuclide analysis, and microstructure analysis, and are widely used in physics, chemistry, biology, geology, archaeology, materials, environment, life science, and other scientific fields.

Ion beam analysis is a technology in which when charged ions with certain energy bombard and interact with the target material, both the target and ion beam state change, resulting in various secondary effects. By analyzing and measuring these secondary effects, the structure and properties of the bombarded material can be studied. The ion beam analysis technique was first introduced in 1968 as an important surface analytical method. It mainly includes nuclear reaction analysis (NRA), Rutherford backscattering spectrometry (RBS), proton-induced X-ray emission (PIXE), accelerator mass spectrometry (AMS), and channeling technology (CT). These methods have been widely used in condensed matter physics and material science. The establishment of micro-beam analysis has further extended the application fields of ion beam analysis to life, environment, geoscience, archaeology, and other disciplines.

The hyperfine interaction uses the interaction between the magnetic moment and electric quadrupole moment of the atomic nucleus and the surrounding electromagnetic field to analyze the movement and division of nuclear energy level and obtain information about the surrounding environment, so as to detect the microstructure of matter. The main techniques include the Mössbauer effect, perturbed angular correlation technique, nuclear magnetic resonance, positron-annihilation technique, neutron scattering, neutron diffraction, etc. This kind of method can not only provide

information about the atomic nucleus and its adjacent atoms but also provide macro average information. Therefore, it is applied to a wider range of disciplines and has played an important role in promoting the development of many disciplines.

Activation analysis obtains the composition of the analyzed object by detecting the prompt radiation or delayed radiation generated by the bombardment of the sample with a charged neutron beam, γ photon beam, or charged particle beam. This technology was first introduced in 1934 and has developed into molecular activation analysis and in vivo activation analysis in recent years. Activation analysis mainly includes charged particle activation, γ-ray activation, and neutron activation. Among them, neutron activation analysis is highly sensitive and accurate and allows the simultaneous determination of multiple elements. These characteristics of activation analysis are particularly prominent in environmental studies. For example, for long-distance atmospheric transport problems, the chemical composition and source of atmospheric particles in polar regions, and the determination of environmental background values in some special cases, when higher sensitivity and accuracy are required, it is difficult to meet the requirements using other traditional methods. Besides, activation analysis techniques are also superior for analyzing trace elements in solid environmental samples (e.g., atmospheric dust, aerosols, plant samples, atmospheric suspended matter, etc.).

3.1.2 Principles of Nuclear Analytical Techniques

The nuclear analytical technique is based on the corresponding radiation characteristics (ray, particle, and radiation energy) generated by the measured material or sample under the action of the ray or particle beam. Some materials and samples have radiation characteristics themselves. Using the corresponding detector to measure the radiation characteristics (such as the characteristic spectral line) of a nuclide in the material or sample, the nuclide type can be determined. After the calibration of counting efficiency, the activity and content of the nuclide in the sample can be further determined. Nuclear analytical techniques can be used for both qualitative and quantitative analysis.

3.1.3 Characteristics of Nuclear Analytical Techniques

Nuclear analytical techniques have the irreplaceable characteristics of most conventional non-nuclear techniques, such as high sensitivity, high accuracy and precision, high resolution (including spatial solution and energy resolution), non-destructiveness, multi-element determination capability, specificity, etc., providing a more powerful technical means for the in-depth development of natural science.

The nuclear analysis is a non-destructive analysis (NDA). It is the most effective and widely used technology in the field of nuclear safeguards. Since uranium

and plutonium are the core materials of nuclear weapons and the main objects of nuclear safeguards, it is extremely important to develop the technology of non-destructive radiation detection and analysis of uranium and plutonium materials, which can obtain not only chemical information such as isotopic abundance and chemical components of uranium and plutonium materials but also the physical information such as mass, age, shape, thickness of packaging container materials and internal contaminated distribution of nuclear facilities. The NDA technologies related to uranium and plutonium developed from radiation detection and analysis of uranium and plutonium materials have played a positive supporting role in nuclear safety assurance, arms control verification, decommissioning of nuclear facilities, and disposal of nuclear contaminants. The n-radiation and γ-radiation detection technologies are widely used in the security of nuclear safety. Integrated waste assay system (IWAS), tomographic gamma scanning (TGS), and other NDA measurement systems for waste analysis have been widely used in nuclear material waste disposal, nuclear material accounting, radiation and protection, etc.

For chemical analysis, the adoption of inductively coupled plasma-atomic emission spectrometry (ICP-AES) and the technologies that have been used for nuclear activation analysis including spark source mass spectrometry (SSMS), X-ray fluorescence (XRF), and γ-ray spectrometry have more systematically contributed to the development of multi-element instrumental analytical methods.

The multi-element instrumental analytical method has a great advantage over the single-element analytical method, namely, it can obtain more information about a sample. For example, with inductively coupled plasma-atomic emission spectrometry, data of up to 50 or more elements can be obtained from a single sample in a matter of minutes. Compared with the costs of sampling and sample preparation, the time, manpower, and material resources spent by this method are negligible, especially in the fields of geochemistry, cosmochemistry, life chemistry, and information technology. The nuclear analytical method differs from other multi-elemental analytical methods in which the signal source is different. The objects it analyzes are isotopes rather than atoms, and the signals are elementary particles, γ-ray, or α-particle radiation. Thus, for elemental analysis, the proportion of isotopes of an element must be known or measurable. In the case of elemental analysis, one or more isotopes to be measured in the element should be converted to radionuclides by means of nuclear activation reaction before measuring the signal.

3.2 X-Ray Fluorescence Analysis

X-ray fluorescence analysis (XRF) is a method that uses primary X-ray photons or other microscopic particles to excite atoms in the sample to be measured to produce fluorescence (secondary X-rays) for material composition analysis and chemical form study.

X-ray is a kind of electromagnetic radiation, according to the traditional statement, its wavelength is between ultraviolet and γ-rays. But with the development

of high-energy electron accelerators, the energy of X-rays produced by electron bremsstrahlung may be much greater than that of γ-rays. Therefore, there's no strict boundary on the wavelength range of X-rays. For X-ray fluorescence analysis, X-ray generally refers to electromagnetic radiation with a wavelength of 0.001–50 nm. For chemical analysis, the most interested band is 0.01–24 nm, in which near 0.01 nm is the K-series spectrum of the transuranic elements and near 24 nm is the K-series spectrum of the lightest element Li.

When an atom is excited by X-ray photons (primary X-rays) or other particles that ionize the inner electrons of the atom and produce vacancies, the inner electrons of the atom will be re-coordinated. The outer electron jumps to the inner electron vacancy and emits secondary X-ray photons at the same time, known as X-ray fluorescence. The energy released by the transition from the outer electron to the inner electron vacancy is equal to the energy difference between the two electron energy levels. Therefore, the wavelength of X-ray fluorescence is characteristic for different elements.

In 1923, the Swedish chemist Gvon Hevesy proposed the application of X-ray fluorescence spectroscopy for quantitative analysis. However, due to the limitations of the level of detection technology at that time, the method was not practically applied. Until the late 1940s, with the improvement of X-ray tubes, spectroscopic technology, and semiconductor detector technology, X-ray fluorescence analysis technology entered a period of rapid development and became a very important analytical method.

According to different excitation, dispersion and detection methods, X-ray fluorescence analysis technologies can be divided into X-ray spectroscopy (i.e., using wavelength dispersion) and X-ray energy spectroscopy (i.e., using energy dispersion).

3.2.1 Principle and Characteristics of X-Ray Fluorescence Analysis

When the high-energy X-ray with an energy higher than the binding energy of the inner electron of the atom collides with the atom, the inner electron is excited and a hole appears, leaving the entire atomic system in an unstable excited state with an extremely short lifetime of about 10^{-12}–10^{-14} s. The excited atom then spontaneously jumps from the high-energy state to the low-energy state. This process is called a relaxation process. This process can be either a non-radiative transition or a radiative transition.

When the electron in the outer layer jumps to a hole, the energy released may then be absorbed within the atom to excite another secondary photoelectron in the outer layer. This is called an Auger effect, also known as the secondary photoelectric effect or the radiation-free effect. The secondary photoelectron excited is the

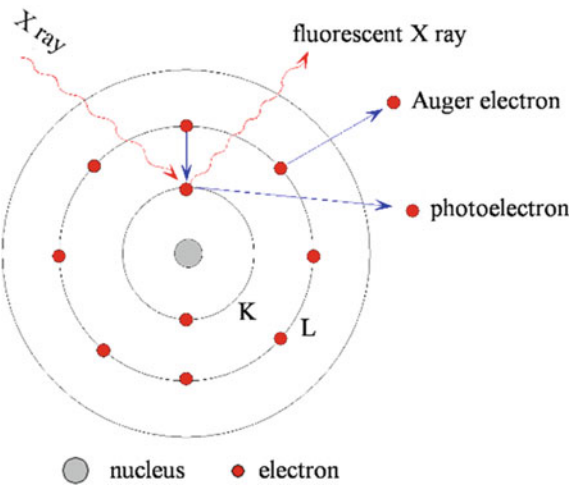


Fig. 3.1 Generation process of fluorescent X-ray and Auger electron

Auger electron, its energy is characteristic and independent of the energy of incident radiation.

X-ray fluorescence is generated when the energy released by the outer electrons jumping into the inner hole is not absorbed within the atom, but emitted in the form of radiation, with an energy equal to the energy difference between the two energy levels. Thus, the energy or wavelength of X-ray fluorescence is characteristic and has a one-to-one correspondence with the element. Figure 3.1 shows a schematic diagram of X-ray fluorescence and Auger electron generation process.

After the K-layer electrons are expelled, their holes can be filled by any electron in the outer layer, which can produce a series of spectral lines, called K-series spectral lines. The X-rays radiated by the transition from L-layer to K-layer are called K_α-rays and those radiated from the M-layer to the K-layer are called K_β-rays… Similarly, the expulsion of electrons from the L-layer can produce L-series radiation (see Fig. 3.2).

If the incident X-ray excites the K-layer electrons of an element into photoelectrons and the L-layer electrons jump to the K-layer, then there is energy ΔE released, and $\Delta E = E_K - E_L$. This energy is released in the form of X-rays, which can produce K_α-rays, K_β-rays, L-series rays, etc. H. G. Moseley found that the wavelength λ of fluorescent X-rays and the atomic number Z of the elements satisfy the following relationship, which is called Moseley's law:

$$\lambda = k(Z - s)^{-2} \tag{3.1}$$

where k and s are constants for the same set of spectral lines.

And according to quantum theory, the X-ray can be regarded as a particle beam composed of a quantum or photon that obeys the energy equation:

$$E = h\nu = hc/\lambda \tag{3.2}$$

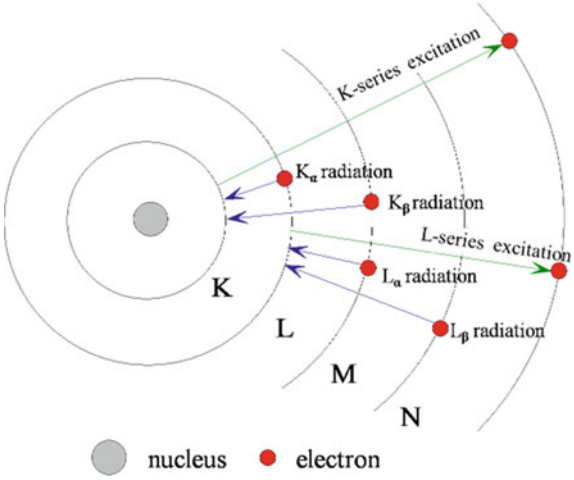


Fig. 3.2 Generation process of K-series and L-series radiation

where

E photon energy.
h Planck constant, $h = 6.63 \times 10^{-34}$ J s.
ν frequency of the rays.
λ wavelength.
c speed of light, $c = 3.0 \times 10^8$ m/s.

Therefore, as long as the wavelength or energy of the fluorescent X-ray is measured, the type of elements can be determined. This is the basis of the X-ray fluorescence qualitative analysis. In addition, the intensity of fluorescent X-ray has a certain relationship with the content of the corresponding element, according to which the quantitative analysis of the element can be carried out.

X-ray fluorescence analysis is generally used to analyze the composition of substances. It can also be used to study the basic properties of atoms such as oxidation number, ionic charge, electronegativity, and chemical bond. When used for substance composition analysis, the detection limit is usually up to 10^{-5} g g^{-1}–10^{-6} g g^{-1}, and 10^{-7} g g^{-1}–10^{-9} g g^{-1} can also be measured for many elements. When excited by protons, the detection limit can even reach 10^{-12} g g^{-1}. This analytical method has a wide range of applications and can analyze all elements with atomic number $Z \geq 3$.

The X-ray fluorescence spectrometry has the following characteristics.

(1) The range of elements analyzed is wide. From Na with atomic number 11 to U with atomic number 92 can be determined.
(2) The fluorescent X-ray spectral lines are simple with little mutual interference. Samples do not need to be separated, and the analytical method is relatively simple.
(3) The range of analytical concentration is wide. It can be analyzed from constant to trace, and the detection limit of heavy elements can reach 1 ppm.

(4) It can be used for non-destructive analysis of samples, which is fast, accurate, and highly automated.

3.2.2 Basic Structure of the X-Ray Fluorescence Spectrometer

An X-ray fluorescence spectrometer mainly consists of excitation, dispersion, detection, recording, and data processing units. The function of the excitation unit is to generate primary X-rays, it is composed of a high-voltage generator and an X-ray tube. The latter has higher power and is cooled with water and oil simultaneously. The function of the dispersion unit is to separate the X-rays of the desired wavelength. It is composed of sample chamber, slit, goniometer, analytical crystal, etc. By rotating the analytical crystal and detector at the speed of 1:2, X-rays of different wavelengths can be measured at different positions of Bragg angle through a goniometer for qualitative analysis of elements. The function of the detector is to convert X-ray photon energy into electrical signals, commonly used detectors include the Geiger-Müller counter tube, proportional counter tube, scintillation counter tube, semiconductor detector, etc. The recording unit consists of amplifier, pulse amplitude analyzer, and display section. The signal of pulse analysis of scaler or pulse amplitude analyzer can be directly input into the computer for online processing to obtain the content of measured elements.

The X-ray fluorescence spectrometer has a simple structure with no complex spectroscopic system. X-ray excitation source can be an X-ray generator or radionuclide. The detector and recorder of the pulse amplitude analyzer for energy dispersion are the same as those of the X-ray fluorescence spectrometer.

X-ray fluorescence spectrometer and X-ray fluorescence energy spectrometer have their own advantages and disadvantages. The former has a high resolution, it has wide adaptability to the determination of light and heavy elements, and its sensitivity to the determination of both high and low content elements can meet the requirements. The geometric efficiency of X-ray detection of the latter can be improved by 2–3 orders of magnitude, it has high sensitivity and can simultaneously perform energy resolution (i.e., qualitative analysis) and quantitative determination for X-rays with a wide energy range, but it has a poor resolution for energy spectrum with energy less than 20 keV.

3.2.3 *Qualitative and Quantitative Analytical Methods*

1. **Sample preparation**

X-ray fluorescence spectroscopy is a relative analytical method that needs to determine the content of the sample by determining the standard sample. The basic requirements for the sample include no water, oil, or volatile components, especially corrosive solvents. The form of the sample can be solid (block, powder) or liquid. The situation of preparing the sample has a significant effect on the uncertainty of the determination result, therefore, the sample preparation methods and processes are important aspects of analyzing samples by the X-ray fluorescence spectrometry.

Liquid samples can be determined either directly in a liquid sample cup or by dropping them onto filter paper, Mylar film, or PTFE substrate and drying the solvent with an infrared lamp.

Solid samples often need to be processed into a certain shape that can be placed in the sample box of the instrument for determination. The methods of preparing solid samples are complex and many factors should be considered. For example, for metal samples, attention should be paid to the errors caused by component segregation. Samples with the same chemical composition and different heat treatment processes may have different counting rates. Metal samples with uneven composition should be remelted and processed into discs after rapid cooling. Samples with uneven surfaces should be polished. For powder samples, grind the sample to 300–400 mesh, then press it into discs, which can also be placed in the sample box for determination. If the solid sample cannot obtain a uniform and flat surface, the sample can be dissolved with acid and then precipitated into salt for determination. If the sample to be determined is not allowed to be destroyed, but the surface of the sample is not flat (such as precious metal jewelry), using a special correction algorithm can also achieve satisfactory results.

2. **Qualitative analysis**

The fluorescent X-rays of different elements have their specific wavelengths or energies. Therefore, the composition of elements can be determined according to the wavelength or energy of fluorescent X-rays. In terms of the wavelength-dispersive spectrometer, for a crystal with a certain interplanar spacing, the wavelength λ of X-ray can be calculated from the 2θ angle of the detector rotation, and thus the element composition can be determined. For the energy dispersive spectrometer, the energy can be differentiated by the channel to determine the type and composition of the element. In fact, in qualitative analysis, the automatic qualitative identification algorithm can be used to automatically identify spectral lines and give qualitative results. However, if the element content is too low or there is spectral line interference between elements, manual identification is still required to find and confirm the existence of characteristic spectral lines and to judge and identify the interference. In manual identification, the characteristic X-rays of the X-ray tube target and the adjoint line of the strong peak should be identified first, and then the remaining

spectral lines should be labeled according to the energy. When analyzing unknown spectral lines, factors such as the source and nature of the sample should be considered for comprehensive judgment.

3. **Quantitative analysis**

The basis for quantitative analysis of X-ray fluorescence spectroscopy is that the fluorescence X-ray intensity I_i of an element is directly proportional to the content C_i of the element in the sample. The conversion of the measured characteristic X-ray fluorescence spectral intensity into concentration is affected by four factors.

$$C_i = K_i I_i M_i S_i \tag{3.3}$$

where

C_i concentration of the element to be measured, the subscript *i* is the element to be measured.
K_i correction factor of the instrument.
I_i measured X-ray fluorescence intensity of the element to be measured, the net intensity obtained after correction of background, spectral overlap, and dead time.
M_i correction factor of interelement absorption-enhancement effects.
S_i factors related to the physical form of the sample, such as homogeneity, thickness, the surface structure of the sample, etc.

The factors K, I, M, and S cannot be eliminated by mathematical calculation or experiments, and the effect of these factors is usually minimized using sample preparation.

After eliminating the background and interference and obtaining the net intensity of the spectral line of the analyzed element, an intensity-concentration quantitative analysis equation can be established between the intensity of the analyzed spectral line and the concentration of the analyzed component in the standard sample to calculate the concentration of the unknown sample.

Quantitative analysis can be carried out by the standard curve method, incremental method, internal standard method, etc. All these methods require that the composition of the standard sample and the sample should be the same or similar as much as possible, otherwise, the matrix effect of the sample or the effect of coexisting elements will cause significant deviation in the determination results. The so-called matrix effect refers to the effect of the basic chemical composition and physicochemical state of the sample on the X-ray fluorescence intensity. The change of chemical composition will affect the absorption of the sample to the primary X-rays and X-ray fluorescence, as well as change the fluorescence enhancement effect. For example, in the determination of Fe, Ni, and other elements in stainless steel, NiK_α fluorescence X-rays will be generated due to the excitation of the initial X-ray. In the sample, NiK_α may be absorbed by Fe, causing Fe excitation to produce FeK_α. When determining Ni, the result is lower than the actual value because of the absorption effect of Fe. When

determining Fe, a relatively high result will be shown because of the fluorescence enhancement effect. Therefore, for the sample matrix with complex composition and structure, various methods are required to correct the result in order to achieve an accurate analysis of the sample.

X-ray fluorescence spectrometry is characterized by a simple sample preparation technique, but complex matrix correction is required to obtain data for quantitative analysis.

4. **Thickness quantitative analysis**

The basis for thickness quantitative analysis by X-ray fluorescence spectrometry is that the fluorescence X-ray intensity I_T (primary fluorescence intensity) of a thin film of an element with thickness T has the following relationship with the fluorescence X-ray intensity I_∞ of an element in infinite thickness (just need to reach the saturated thickness in real case) thin films:

$$I_T / I_\infty = 1 - e^{-\mu_s^* \rho T} \tag{3.4}$$

where

μ_s^* mass absorption coefficient of the sample to incident light.
ρ density of the sample.

$\mu_s^* \rho$ is a constant related to the thin film. According to the above relationship, the film thickness can be determined by the fluorescence intensity of the spectral lines of the elements in the film sample. When analyzing the thickness of single-layer films, both the primary fluorescence intensity and the secondary fluorescence intensity (with a more complex calculation) should be taken into account. For the analysis of multi-layer film thickness, the absorption effect of the outer film on the fluorescence of the inner film needs to be considered, the calculation is more complex and will not be introduced in detail here. The theoretical formula for calculating the primary fluorescence intensity of the thin film has been applied to quantitative analysis software such as LAMA III and TFFP, so the results can be modified by the relevant software, that is, the film thickness can be calculated by applying formula (3.4).

3.3 Neutron Activation Analysis

Activation analysis is one of the important analytical methods in nuclear analysis technology. With the construction of various reactors and accelerators, the development of nuclear physics, and the establishment of γ-spectroscopy, especially the development of high-purity germanium detectors and computer technology, activation analysis has become an advanced trace analysis technique with high sensitivity, fast and non-destructive for simultaneous analysis of multiple elements.

3.3.1 Principle and Characteristics of Activation Analysis

As a nuclear analytical method, activation analysis is based on nuclear reactions. This method is to bombard the sample to be determined with neutrons, charged particles, or high-energy γ photons with a certain energy and current intensity, and then determine the delayed radiation emitted during the decay of the radioactive nuclei generated in nuclear reactions, or directly determine the prompt radiation emitted in nuclear reactions, so as to realize the qualitative and quantitative analysis of elements. When neutrons are used to bombard the nucleus of the sample, the nucleus will absorb the neutrons and in most cases form unstable radioactive isotopes, which is called "activation". The "activated" nuclide will decay according to its own laws and emit γ-rays at the same time. Since a specific correspondence exists between the γ-rays emitted by nuclides and the nuclide, by determining the energy and intensity of the radiation, the qualitative and quantitative analysis of the element can be realized. This is the basic process of "activation analysis".

Activation analysis is based on the radionuclide produced in nuclear reactions, whose activity is given by Eq. (3.5).

$$A_t = f\sigma N\left(1 - e^{-0.693t/T_{1/2}}\right) \tag{3.5}$$

where

$T_{1/2}$ half-life.
f particle fluence rate.
σ nuclear reaction cross-section.
N number of the target nucleus.
t duration of irradiation.
A_t Total activity of the radionuclide produced at irradiation time t.

Generally speaking, in activation analysis, radioactivity measurement is not performed immediately after irradiation, but the radioactive sample is allowed to "cool down" (i.e., decay) for a period of time. Therefore, the activity $A_{t'}$ at time t' after the end of radiation is:

$$A_{t'} = A_t e^{-\lambda t'} = f\sigma N\left(1 - e^{-0.693t/T_{1/2}}\right)e^{-0.693t'/T_{1/2}} \tag{3.6}$$

t' is the cooling time, N is the number of target nucleus, $N = 6.023 \times 10^{23}\theta\frac{W}{M}$, θ is the natural abundance of target nucleus, W is the mass of the target element, M is the relative atomic mass of the target element, and 6.023×10^{23} is the Avogadro's number. Substitute the value of N into Eq. (3.6):

$$A_{t'} = 6.023 \times 10^{23} f\sigma\theta\frac{W}{M}\left(1 - e^{-0.693t/T_{1/2}}\right)e^{-0.693t'/T_{1/2}} \tag{3.7}$$

Equation (3.7) is the most basic activation equation in activation analysis. In principle, activation analysis is an absolute analytical method. However, in practice,

$A_{t'}$ the absolute measurement of radioactivity $A_{t'}$ is complicated, the value of σ and f is not easy to be measured accurately. Therefore, absolute methods are rarely used in activation analysis, and the relative method is mostly used. The so-called relative method is to prepare a standard sample containing a known amount of elements W_{ss} to be measured, irradiate and measure the standard sample under the same conditions as the sample, from which:

$$A_{t'_{ss}} = f\sigma N_{ss}\left(1 - e^{-0.693t/T_{1/2}}\right)e^{-0.693t'/T_{1/2}} \tag{3.8}$$

$$A_{t'_s} = f\sigma N_s\left(1 - e^{-0.693t/T_{1/2}}\right)e^{-0.693t'/T_{1/2}}. \tag{3.9}$$

From Eqs. (3.8) and (3.9), it can be deduced that

$$\frac{A_{t'_s}}{A_{t'_{ss}}} = \frac{N_s}{N_{ss}} = \frac{W_s}{W_{ss}} = \frac{n_{t'_s}}{n_{t'_{ss}}} \tag{3.10}$$

where

$n_{t'_s}$ counting rate of the nuclide to be measured in the sample measured at time t′.
$n_{t'_{ss}}$ counting rate of the nuclide to be measured in the standard sample measured at time t′.

Thus, the concentration of the element to be measured in the sample is

$$C = \frac{n_{t'_s} \cdot W_{ss}}{n_{t'_{ss}} \cdot m} \tag{3.11}$$

where

m mass of the sample, g.

Equation (3.11) is the mo basic formula of the relative method of activation analysis.

In the field of radioanalytical chemistry, neutron activation analysis has always been a widely valued analytical method. It has high sensitivity and can determine many elements at the same time, which has been widely used in production and scientific research. This section will briefly describe the technological base of activation analysis.

Neutron activation analysis has the following advantages:

(1) High sensitivity. The sensitivity of the neutron activation method for analyzing most elements in the periodic table is between 10^{-6} and 10^{-13} g. A wide range of sampling amounts (can be as little as 1 μg, up to more than 10 g) is extremely valuable for the analysis of some rare and precious samples.
(2) High accuracy and precision. Due to the strong penetrability of neutrons, the changes in the neutron fluence rate of the reactor are small, and the resolution

of the detector is high, which can quantitatively give the analysis error. Therefore, neutron activation analysis is one of the trace element analytical methods with high accuracy, which can be used for arbitration analysis. The accuracy of neutron activation analysis can generally be controlled within 5%, and its precision can be controlled within 1–2%.

(3) Multi-element analysis capability. Thirty to forty elements can be determined simultaneously in a single sample by long-time and short-time irradiation, with a maximum analytical capacity of 68 elements.

(4) No reagent blank and no need for sample pretreatment, which allows for "non-destructive" analysis in many applications. Other elemental analytical methods often require various forms of chemical treatment of the sample, while neutron activation analysis generally does not need any chemical treatment before irradiation. This avoids possible loss and contamination (especially for ultra-low content elements) caused by sample preparation and sample dissolution. Besides, the sample used in activation analysis can be used for other purposes after its radioactivity decays to a certain degree. Even for radiochemical activation analysis, chemical treatment is carried out after the activation of the sample, and additive pollution has no effect on the elements to be measured.

(5) Small matrix effect. Except for the matrix whose main component is the element with a high absorption cross-section, activation analysis is suitable for a variety of samples with complex chemical components such as nuclear materials, environmental samples, biological tissues, geological samples, etc.

(6) In vivo analysis, which is difficult to be achieved by other methods.

Neutron activation analysis in reactors has been continuously developing for 80 years due to its various advantages. At present, more than 90% of the world's research reactors are equipped with neutron activation analysis facilities. Importantly, the accuracy of this method is still difficult to surpass by many modern analytical methods.

However, neutron activation analysis also has some drawbacks.

(1) The sensitivity of the analysis varies considerably from element to element.

(2) The equipment used for neutron activation analysis is complex and expensive, and irradiation devices are not easy to obtain. In addition, certain radioactive protection facilities are also required.

(3) The chemical state and structure of the elements cannot be determined.

Since many methods can be used for neutron activation analysis, the above advantages and disadvantages vary with conditions. For example, when determining the content of elements in seawater or matrix with high sodium content, the measurement of other elements will be greatly affected by the strong radioactivity of ^{24}Na produced after activation. If nuclides with a short half-life are measured, radiochemical separation against the irradiated sample is required, and the advantages of non-destructive analysis will no longer exist. However, this situation does not affect the measurement of long half-life nuclides because the radioactivity of ^{24}Na that can be detected is close to the natural background after 10 days of cooling. The cycle of neutron activation analysis is generally long, but if activation analysis of only short-lived nuclides

is carried out, the speed of analysis can be greatly increased, and only a few minutes will be taken at a time.

In recent years, another multi-element analytical method - inductively coupled plasma mass spectrometry (ICP-MS) has developed rapidly, which greatly improves the sensitivity of the analysis. The popularization of ICP-MS brought severe challenges to neutron activation analysis. However, after comparing these two methods, scholars generally believe that both of them have their own advantages and that neutron activation analysis will not be completely replaced by ICP-MS. For example, when analyzing solid samples (including particulate matter), activation analysis does not require sample dissolution, which can avoid possible loss and contamination caused by sample preparation and dissolution. This shows obvious advantages compared with ICP-MS.

3.3.2 Classification of Activation Analysis

The basis of activation analysis is to irradiate the sample with neutrons, photons, or other charged particles (e.g. protons, etc.) to convert some isotope of the element into a radioisotope. According to the half-life of the generated isotope and the nature and energy of the characteristic rays emitted, the existence of the element to be measured can be determined. By measuring the radioactive intensity of the generated radioisotope or the rays emitted during the reaction, the content of that element in the sample can be calculated. Based on different irradiated particles, activation analysis can be mainly divided into three categories: neutron activation analysis, charged particle activation analysis, and photon activation analysis, among which the neutron activation analysis is the most widely used.

The main nuclear reactions utilized in neutron activation analysis are the (n, γ), (n, p), and (n, α) reactions. Thermal neutron and epithermal neutron reactions are almost (n, γ) reactions with generally large reaction cross sections and few side reactions. Thus, the (n, γ) reaction has been holding an important position in neutron activation analysis. For (n, p) and (n, α) nuclear reactions, the neutrons are fast neutrons. In principle, neutron activation analysis can be used to determine 77 elements among the elements with an atomic number from 1 to 83.

The nuclear reactions mainly used in charged particle activation analysis are (p, n) reaction, (d, n) reaction, (d, p) reaction, (α, n) reaction, etc. The range of charged particles is very short, and the nuclear reactions mainly occur on the surface of the sample, which is suitable for surface analysis. The reaction cross-section of charged particles to elements is smaller than that of thermal neutrons, and the activation reaction is more complex. But it has the advantage of being able to determine lithium, beryllium, and other light elements which are difficult to be determined by other activation analytical methods.

For photon activation analysis, the main reaction used is (γ, n), and for light elements with small atomic numbers, the (γ, p) reaction is also important. Compared with thermal neutron activation analysis, it has higher sensitivity in the determination

of light elements such as carbon, nitrogen, oxygen, and fluorine, and medium and heavy elements such as titanium, iron, zirconium, thallium, and lead. The interference reaction of photon activation analysis is less than that of charged particle activation analysis.

3.3.3 History of Neutron Activation Analysis Techniques

In 1936, chemists G. Hevesy and H. Levy carried out the first neutron activation analysis (NAA) in history. They determined the dysprosium in yttrium oxide (Y_2O_3) through the ^{164}Dy (n, γ)^{165}Dy reaction (activation cross-section of 3900 $\pm$ 300 bar, and half-life of 139.2 min for the nuclei produced) using a 200–300 mL Ra-Be neutron source (about 3×10^6 s^{-1} of neutron yield). The result of the quantitative analysis was 10^{-3} g g^{-1}. At that time, the main indicators of activation analysis level were the isotope source and a detector based on gas ionization.

In 1942, a team led by the famous scientist Fermi built the world's first manually controlled reactor at the University of Chicago, which can provide a much higher neutron fluence rate than the isotope neutron source. In 1948, the NaI (Tl) scintillation detector appeared. These two inventions then advanced activation analysis to a new stage. In 1951, thermal neutron activation analysis was first carried out in the reactor, making neutron activation analysis an analytical method with the highest sensitivity at that time.

Since the 1960s, neutron activation analysis has developed rapidly. The first driving force for the development was the emergence of semiconductor detectors in the early 1960s. The resolution of this type of detector was dozens of times higher than that of NaI (Tl) scintillation detectors, which led to a significant change in the way of working in activation analysis. Simple group separation started to replace the complicated radiochemical separation operation, and the possibility of achieving the analysis without destroying the sample emerged. In addition, the application of Ge(Li) detectors fully exploited the potential of activation analysis for multi-element determination—one irradiation can simultaneously determine 30–40 elements, thus improving the competitiveness of activation analysis compared with other analytical methods. The second driving force came from the introduction of computers. In 1959, Fetter et al. first used the computer for activation analysis and resolved the mixed γ spectra of five components. In the same year, the automatic activation analysis device matched with a computer was designed, which can control the irradiation time, cooling time and counting time, and control sample delivery, and the drift of the spectrometer. With the development of computers, the industrial sector was equipped with small special computers for activation analysis so that automatic data acquisition and processing can be realized.

The development of neutron activation analysis has a history of more than 80 years since its birth in 1936. The operation of reactors, the emergence of semiconductor detectors, the use of computers, and the development of specific radiochemical

separation methods for neutron activation analysis have all greatly promoted the improvement of neutron activation analytical methods.

Since the 1970s, the development trend of neutron activation analysis worldwide clearly shows that its methodology has become mature. Its applications in various disciplines are also booming, especially in environmental science, biology, and geoscience. With the characteristics of high sensitivity, high accuracy, no damage to samples, simultaneous determination of multiple elements and small matrix effects, neutron activation analysis has become one of the most important analytical methods for major, minor, trace, and even ultra-trace elements, and one of the most important methods in modern nuclear analysis technology.

3.3.4 Neutron Activation Source

In neutron activation analysis, neutrons used to induce nuclear reaction can come from reactors, accelerators, or isotope neutron sources, thus neutron activation sources can be divided into reactor neutron source, accelerator neutron source, and isotope neutron source.

The reactor is a device that causes a chain fission reaction of fissile material (e.g. ^{235}U). In the reactor, fission materials capture neutrons and produce fission, releasing a large amount of energy and a large number of neutrons. The neutron energy spectrum produced by the reactor is very broad (1 keV–15 meV).

As an activation source, reactor neutrons have the following characteristics:

① High thermal neutron fluence rate.
② Large activation cross-section for most elements.
③ Simple reaction channel [mostly (n, γ) reactions].
④ The neutron influence rate has good spatial uniformity and temporal constancy (steady-state reactor). The former determines its high sensitivity, while the latter implies good qualitative selectivity and quantitative accuracy.

Reactor neutron activation analysis accounts for more than 95% of all neutron activation analysis, thus, reactor neutron activation analysis has always been the mainstream of activation analysis.

The accelerator neutron source is obtained by the interaction between the high-speed charged particles produced by the accelerator with some target material. Bombard the tritium target when the deuteron is accelerated to about 150 keV by the accelerator and a strong neutron beam will be generated through the (d, T) reaction. Therefore, the accelerator neutron source can perform many activation analyses with good sensitivity. However, many factors can affect the neutron energy produced by the accelerator and its yield, such as the energy of the incident particles, the stability of the target material, etc.

Isotope neutron source is the source of neutrons produced by nuclear reaction (use the ray emitted by radionuclides to bombard a target material) such as the Am-Be neutron source, or the spontaneous fission neutron source such as ^{252}Cf. Compare

with the reactor neutron source, an isotope neutron source has lower thermal neutron output. One Curie isotope neutron source usually provides a sample with a neutron fluence rate of only 10^5 cm^{-2} s^{-1}. However, it is small and can be made into a portable neutron source, thus it is convenient to use. In addition, spontaneous fission neutrons of ^{252}Cf can also be used for activation analysis. This type of fission neutron source does not require target material and has a high neutron yield, which has also been widely used.

3.3.5 Process of Neutron Activation Analysis

The sample is usually sent into the irradiation channel of the reactor using a pneumatic device "rabbit". According to the properties of the element to be analyzed, different neutron fluence rates and irradiation times are selected. After irradiation, the "rabbit" device will be used to transfer the sample out of the irradiation channel. After cooling for a certain time, analyze the content of elements in the activated sample using a gamma spectrometer.

Neutron activation analysis can be mainly divided into the following six steps:

(1) Determination of irradiation conditions: Determine the irradiation time and cooling time according to the matrix of the element, approximate content estimation, activation analysis parameters, and the neutron fluence rate at the irradiation position.
(2) Preparation of samples and standards: Prepare samples and standards of the elements to be analyzed and certified reference materials for analytical quality control according to the safety requirements of the irradiation process. During sample preservation and preparation, attention should be paid to prevent the samples from being contaminated and the elements to be measured from being lost.
(3) Neutron irradiation: Seal the samples and standards in the irradiation container. Send the container into the reactor, accelerator, or isotope source through the transmission device for activation. Note that samples and standards should be irradiated under the same conditions. During the activation process, the self-shielding effect, radiation decomposition of the sample, and gamma heat should be prevented.
(4) Radiochemical separation: In some special cases, irradiated samples require radiochemical treatment to remove interfering radionuclides or to extract elements to be measured. Common methods include precipitation, ion exchange, extraction, distillation, etc.
(5) Radioactivity measurement: According to different conditions, Geiger-Müller counter tube, proportional counter, NaI (Tl) scintillation detector, Si (Li) and HPGe semiconductor detector, and their related instruments (e.g. multi-channel analyzers, etc.) are used to measure samples, standards, and quality control

reference materials. Modern neutron activation analysis is mainly based on HPGe gamma spectrometers, other detectors are not frequently used.

(6) Data processing: Based on the spectral data obtained by the detector, the energy, area, error, and related parameters of the peak can be calculated, and the content of the element to be measured in the sample can then be calculated. This process is usually performed by computers and related software.

3.3.6 Application of Neutron Activation Analysis

Activation analysis is a valuable method that is widely applied in many fields. In the 1950s, activation analysis was used to solve the analytical problems in the atomic energy industry and ultrapure materials. In the 1970s, it was applied in environmental science, biology, medicine, archaeology, geological science, and other fields on a larger scale.

In terms of environmental science, the application of activation analysis can be divided into applications in water environment, soil environment, atmospheric environment, etc. See Chap. 7 for details.

In geochemistry and cosmochemistry, activation analysis can be used to study the crustal rock and ore sample geochemistry, marine geochemistry, etc.

In biomedical, activation analysis can be applied for:

(1) Study the normal concentration of trace elements in biological tissues and their metabolic processes.
(2) Use stable isotope tracers that can be activated to study the regularity of the absorption of elements by various organ tissues in vivo over time.
(3) In vivo activation analysis.
(4) Study the relationship between various diseases and trace elements.

Take the isotope tracer technique as an example, the application of neutron activation analysis in biomedicine will be briefly discussed below. Isotopic tracing can be divided into radio isotopic tracing and activatable stable isotopic tracing. Radioactive tracers have been successfully used to study the behavior of elements in living tissues, drug efficacy, and nutrition. However, this method has the disadvantage of causing irradiation damage. Therefore, it does not apply to sensitive groups such as infants, adolescents, and gravidas, which are precisely the key research objects of some diseases (e.g. iron deficiency anemia). To avoid the harm of using dangerous radioactive tracers, an "activatable stable isotopic tracer technique" has been developed in recent years as an alternative to the radioactive tracer technique. The activatable tracer technique introduces the stable enriched isotope (as a tracer) into the organism, and then uses the activation analytical method to determine the content of the isotope in samples of blood, hair, nails, urine, and stool of the organism, to understand the absorption and metabolism processes of the element in the body. In this kind of tracer experiment, the introduction of a small amount of tracer can cause significant changes in the content of this nuclide in the organism without exceeding

the allowable intake of the element. Therefore, stable nuclides used for tracing shall meet the following requirements:

(1) Natural abundance must be low, preferably less than 10%.
(2) Inexpensive, and can obtain their high enrichment form, preferably 10 times higher than their natural abundance.
(3) The cross-section of nuclear reaction should be high.
(4) The rays of generated products are easy to detect.

For example, Chevallier used ^{18}O-labeled compounds to study the rate of cholesterol synthesis in the human body. The natural abundance of ^{18}O is 0.02%, but it can be concentrated to more than 90%. After being added to the human body, ^{18}O-labeled compounds can be determined by the ^{18}O(n, p) ^{18}F reaction.

Bethard et al. used ^{46}Ca with a concentration of 31% to study calcium metabolism in children. Although the detection sensitivity of this isotope is not as high as that of ^{48}Ca, the chemical operation is simplified due to the ^{47}Ca with a half-life of 4.5 d can be produced by the ^{46}Ca(n, γ)^{47}Ca reaction.

Neutron activation analysis is widely applied in many fields with great potential for development. By continuously improving the technology itself, the sensitivity of the analysis, and the ability to analyze more elements simultaneously, it can be applied to more industries. For example, in the online analysis system of coal, the neutron-induced prompt γ-ray technology is used to detect ash and various elemental components such as carbon, hydrogen, and oxygen; and the prompt γ-neutron activation analysis (i.e. PGNAA) can be used to detect ash, ash composition, and sulfur content, if combined with a water meter, it can also determine moisture, calorific value, and other indicators.

3.4 Isotopic Tracer Technique

The isotopic tracer method is a microanalytical method that uses radionuclides as tracers to label objects of study. In 1923, Hevesy first established the isotopic tracer experiment to study the distribution and transfer of lead salts in legumes by using the natural radionuclide ^{201}Pb. In 1934, the Curies discovered artificial radioactivity. The subsequent establishment of accelerators, reactors, and other production facilities and equipment provided material conditions for the rapid development and wide application of radionuclide tracer methods.

3.4.1 Principles and Characteristics of Isotopic Tracing

The radionuclides (or stable nuclides) and their compounds used for isotopic tracing have the same chemical and biological properties as the corresponding isotopes and their compounds in nature but have different nuclear physical properties. Therefore,

isotopes can be used as a label to make labeled compounds containing isotopes (such as labeled food, drugs, metabolites, etc.) to replace the corresponding non-labeled compounds. Using the nuclear physical properties of radionuclides that constantly emit characteristic rays, their position, quantity, and transformation in vivo or in vitro can be tracked at any time by nuclear detectors. Although stable isotopes do not emit rays, the mass difference between these isotopes and ordinary corresponding isotopes can be determined by a mass spectrometer, gachromatographyph, nuclear magnetic resonance, and other analytical instruments. Both radionuclides and stable isotopes can be used as tracers, but when the latter is used as a tracer, its sensitivity is lower, the types available are few, the price is expensive, and its application is limited. In comparison, using radionuclides as tracers is not only highly sensitive but also simple and easy to measure, which can accurately quantify and locate, and meet the physiological conditions of the research object.

Radioisotope tracer techniques have the following characteristics.

(1) High sensitivity.

The radioactive tracer method can measure the level of 10^{-11}–10^{-18} g, that is, one radioactive atom can be detected from 10^{15} non-radioactive atoms. It is 10^{7}–10^{8} times more sensitive than the current sensitive gravimetric analytical balances, and the most accurate chemical analytical method so far is difficult to measure the level of 10^{-12} g.

(2) Simple methods.

Radioactivity determination is not interfered with by other non-radioactive substances, which can omit many complex chemical separation steps. When tracing in vivo, some radionuclides can be used to emit penetrating γ-rays, and the results can be obtained by in vitro determination. This greatly simplifies the experimental process and achieves non-destructive analysis. With the development of liquid scintillation counting techniques, radionuclides emitting soft β-rays such as ^{14}C and ^{3}H have been more and more widely used in medical and biological experiments.

(3) Accurate positioning and quantification.

Radionuclide tracer methods can accurately and quantitatively determine the transfer and transformation of metabolic substances. Combined with some morphological techniques (such as pathological tissue section techniques, electron microscopy techniques, etc.), the quantitative distribution of radioactive tracers in tissues and organs can be determined, and the positional accuracy can reach the cellular level, subcellular level, and even molecular level.

(4) Meet the physiological conditions.

In radionuclide tracer experiments, the chemical quantity of the radiolabeled compound is extremely small, which has little effect on the content of the corresponding substances in the body. During the experiment, the physiological processes in vivo remain in a normal balance. Therefore, the analytic results

obtained not only conform to the physiological conditions but also better reflect the nature of the objective existence.

The radionuclide tracer method also has some shortcomings. For example, the personnel engaged in radionuclide work shall receive certain special training, the operation shall have corresponding safety protection facilities and conditions, and some elements (such as oxygen, nitrogen, etc.) do not have appropriate radionuclides at present, etc. When conducting tracer experiments, attention must also be paid to the isotope effect and radiation effect of the tracer. The so-called isotope effect refers to the significant difference in individual properties caused by the small differences in chemical properties between radionuclides (or stable isotopes) and the corresponding common element. For light elements, the isotope effect is more significant because the mass discrimination between isotopes is multiplicative. For instance, the mass of ^{3}H is three times that of ^{1}H, and the mass of ^{2}H is twice that of ^{1}H. When tritiated water ($^{3}H_2O$) is used as a tracer, its content in ordinary H_2O cannot be too large, otherwise, the physical constants of water, the infiltration to cell membranes, and cytoplasmic viscosity will be changed. But generally speaking, in tracer experiments, the error caused by isotope effects is often considered within the experimental error and can be ignored. The rays emitted from radionuclides are conducive to tracking and measurement. When the radiation that interacts with the organism reaches a certain dose, it may cause a change in the physiological state of the organism, which is the radiation effect of radionuclides. Therefore, the amount of radionuclides used should be less than the safe dose and strictly controlled within the allowable range of the biological organism, so as to avoid the wrong results due to radiation damage to the measurement object.

3.4.2 Application of Isotope Tracer Techniques in Life Science

Radionuclide tracing is widely used in the field of biochemistry and molecular biology. It plays an important role in revealing the mystery of physical and chemical processes in vivo and intracellular and clarifying the material basis of life activities. In recent years, based on the original technology, isotope tracing has achieved many new developments such as dual (or even multi-label) nuclide tracer techniques, stable isotope tracer techniques, activation analysis techniques, electron microscopy techniques, the combination of isotope technology and other new techniques, etc. The development of these technologies has driven biochemistry from static to dynamic, from cell level to molecular level. They clarified a series of difficult problems including the genetic code, membrane receptor, RNA–DNA reverse transcription, etc., which opened a new way for human beings to understand the fundamental phenomena of life.

In life sciences, isotope tracer techniques are mainly used to determine the composition of trace substances in biological samples and study the transfer, metabolism, and transformation of substances in organisms.

1. **Determination of trace substances in biological samples**

The sensitivity of nuclide analysis is much higher than that of the common chemical analytical methods. The most sensitive chemical analysis can detect substances with a content of around 1 μg, whereas radioactive substances that can be detected by nuclide analysis can sometimes reach the order of 10^{-8} μg or even 10^{-11} μg. The following methods are commonly used.

(1) Isotope dilution method

The isotope dilution method is applicable to the analysis of trace substances or the determination of substances that are difficult to be quantitatively isolated from other substances. In biochemistry, the isotope dilution method can be used to quantitatively determine a component of a mixture without quantitative separation, which can solve the difficulty of separating the mixture composed of substances with similar chemical properties. For example, to determine tyrosine in protein hydrolysate, add radioactive ^{14}C-tyrosine to the hydrolysate. After fully mixed, isolate and purify part of the tyrosine solution to determine its radioactivity. The relationship between the weight B of the original tyrosine in the hydrolysate and the weight A of the added ^{14}C-tyrosine is

$$B = (a_0/a - 1) \times A \tag{3.12}$$

where

a_0 Specific activity of the ^{14}C-tyrosine added.
a Specific activity of the tyrosine isolated.

With the same method, the contents of other amino acids in the hydrolysate can also be determined.

The isotope dilution method can also be used to determine water content in the human body in the diagnosis of edema, dehydration, wasting diseases, and post-traumatic convalescence. The concrete method is to first inject water containing deuterium or tritium into the human body, after the body fluid reaches equilibrium with the water, extract the blood sample and determine the isotopic content. The whole-body water content is

$$V_2 = V_1 \times c_0/c \tag{3.13}$$

where

V_1 Volume of water containing deuterium or tritium injected.
V_2 Volume of whole-body water content.

c_0 Isotopic concentration.
c Isotope concentration after dilution.

(2) Competitive radioassay

Competitive radioassay is a special isotope dilution method with high sensitivity, strong specificity, low samples and reagents dosage, relatively simple and rapid operation, and a wide range of applications, which can be used for routine diagnosis, disease screening, and medical research, as well as for the determination of very small amounts of bioactive substances in body fluids.

Three reagents are usually required for competitive radioassay:

(1) Standards: purified products of the substance being determined.
(2) Labels: substances with the same chemical composition and structure as the substance being determined, but with radioactivity.
(3) Binding reagents: reagents that can specifically bind to the substance being determined.

There are many kinds of binding reagents, thus, this method can be used to determine almost all bioactive substances. All competitive radioassay methods that use naturally occurring proteins in plasma as binding reagents are called the competitive protein binding assay, which does not involve immunological reactions. For example, when determining cortisol, a globulin that can bind to corticosteroids in plasma can be used as a binding reagent.

Radioimmunoassay (RIA) is a competitive radioassay using the antigen–antibody reaction. It is an ultramicro analytical method that has been increasingly used in recent years. It can determine more than 300 substances, most of which are hormones, including steroid hormones, polypeptide hormones, non-peptide hormones, etc. In addition, it can also determine proteins, cyclic nucleotides, enzymes, tumor-related antigens/antibodies, pathogens, trace drugs, and other substances.

If the substance being determined is a protein or other antigen, the antiserum containing the corresponding antibody can be used as the binding reagent. The basic principle of plasma insulin radioimmunoassay is that both the labeling antigen and the non-labeled antigen bind to the antibody, and the probability of binding is the same. When the content of the antibody is limited, the labeled insulin added to the plasma and the insulin in the plasma compete with each other to bind with the antibody (see Fig. 3.3).

Obviously, the more non-labeled antigens, the less labeled antigens in the antigen–antibody complex, and the lower the specific activity of radioactivity. By determining the radioactivity of the binding (or free) fraction, the content of plasma insulin can be known.

(3) Whole-body counting

The whole-body counter can quickly and sensitively determine the total radioactivity in the human body. It can determine radioactivity much lower than the allowable doses and other natural radioactivity in the human body such as ^{40}K. Even if there is only

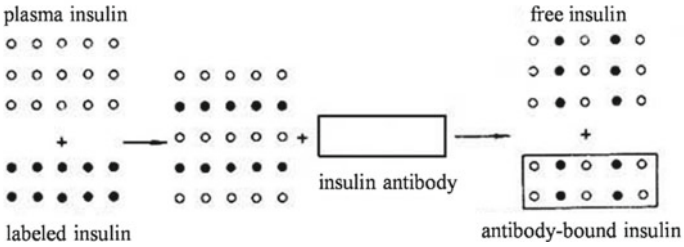


Fig. 3.3 Schematic diagram of the principle of plasma insulin determination by radioimmunoassay

10^2 Bq gamma radioactivity per kilogram of body weight, it can still be determined. Since the proportion of ^{40}K in the total body potassium (0.0118%) is constant, the total body potassium can be calculated by determining the content of ^{40}K in the body. This method can be used to determine the severity of disease in patients with muscular atrophy.

Using the combination of activation analysis and whole-body counting, the contents of iron, cobalt, sodium, calcium, cadmium, nitrogen and many other elements in the human body can be determined.

2. **Transfer of substances in organism**

By labeling the substances to be studied, it is possible to track the situation and speed of transfer of these substances in the body and study the distribution, concentration, uptake, absorption, secretion, excretion, permeability, blood flow rate, tumor localization, inner molecular reaction sites, principles of drug action, etc. For example, make ^{32}P-labeled Mycobacterium tuberculosis into an aerosol and let the mice inhale it. By determining the radioactivity of the lung, esophagus, liver, kidney, and other parts at different times, the regularity of the distribution and retention of the bacterium infected through the respiratory tract in the body can be understood.

The rays produced by radionuclides can sensitize photographic films. The technique of using film to examine, determine, and record radioactivity is called autoradiography. Autoradiography can not only be used to understand the distribution of radioactive substances in certain tissues, organs, whole animals, or other samples, but also the only method to determine the radioactivity in biological samples at the cellular level. It has been used to study issues including cell structure, cell physiology, cell pathology, cell physicochemical properties, etc. At present, the adoption of electron microscope radioautography is more beneficial for conducting experimental studies at the subcellular level.

3. **Metabolism and transformation of substances in organism**

By using appropriate isotopes and their labels as tracers to analyze the changes of isotopic content in substances, the relationship between their mutual transformation in different tissues, organs, cells, and molecules in the organisms can be known,

the precursors and products can be distinguished, the accurate position of isotopic tracers on the molecules can be given, and then the mechanisms of metabolism and transformation between various substances can be further inferred.

In the past, in vitro enzymology was generally used in the study of material transformation. However, the results of in vitro enzymology may not represent the overall situation. The application of isotopic tracer techniques has dramatically shortened the experimental cycle and can be applied in the case of in vitro, whole, and cell-free systems. Since the operation is simplified and the sensitivity of determination is improved, isotope tracing can be applied not only for qualitative analysis but also for quantitative analysis.

For example, to study the biosynthesis and metabolism of cholesterol, the method of labeling precursors can be used to reveal the pathway and steps of cholesterol production. Studies have shown that all compounds that can be converted into acetyl coenzyme A in vivo can be used as raw materials for cholesterol production. The entire biosynthetic process from acetic acid to cholesterol includes at least 36 steps of chemical reactions, and there are 20 intermediates from squalene to cholesterol. The biosynthetic pathway of cholesterol can be simplified as acetic acid → methyl-dihydroxy valeric acid → cholesterol. For another instance, when studying the source of liver cholesterol, the radionuclide label ^{3}H-cholesterol is used in the tracer experiments of intravenous injection. The results showed that most of the radioactivity first enters the liver and then appears in the feces. This process can be accelerated by thyroxine, indicating that the liver is the main organ for processing plasma cholesterol. The thyroid gland can reduce the content of cholesterol in the blood, the mechanism is that thyroxine can accelerate the transfer of plasma cholesterol to the liver.

In the study of clarifying the conversion of ribonucleotide to deoxyribonucleotide, the double-label method can be used. The purpose can be achieved by directly determining the double-labeled products or separately determining the radioactivity after chemical separation. Introduce ^{14}C to the base and ribose of guanine nucleotide (GMP). Then, mix it with deoxyguanine nucleotide (dGMP) in the in vitro system. After performing acid hydrolysis and chromatography on the original label and the product (a mixture of labeled GMP and dGMP), determine the radioactivity of their respective bases and pentose. It can be found that the radioactivity ratio of the two parts is essentially equal, which can prove that the pentose of the product dGMP is the pentose of the original label (without other sources). Otherwise, a significant difference must be seen in this ratio. The results show that pentose deoxygenation is taken place without the decomposition of base and pentose. Therefore, deoxyribonucleotides are directly converted from ribonucleotides, rather than form by connecting the base (decomposed by ribonucleotides) with deoxyribose.

Cell-free tracer experiments can analyze the transfer conditions of substances in cells. A typical example is to use ^{3}H-dTTP as a precursor for the tracer experiment of DNA incorporation. After adding ^{3}H-dTTP according to a certain experimental design, the radioactivity of the product DNA is determined as a detection index of the newly synthesized DNA.

3.5 Neutron Diffraction

The neutron scattering technique is an experimental technology that uses the scattering effect of low-energy neutrons to obtain relevant information about substances. It is an important means to study the microstructure and law of motion of matter at the atomic and molecular scales and has been widely used in many fields such as physics, materials, chemistry, energy, environment, and life science. Based on the interaction between neutrons and matter, neutron scattering can be divided into elastic scattering, which is used to measure the static structure of matter, and inelastic scattering, which is used to study the dynamic process of matter. Elastic scattering includes neutron diffraction, neutron small-angle scattering, and neutron reflectometry, among which neutron diffraction is the earliest studied and most widely used branch.

The study of neutron diffraction originated in 1945. After more than 60 years of development, it has become an indispensable method for structural analysis. It complements X-ray diffraction and electron diffraction so that more complete information can be obtained for structural studies.

3.5.1 Principle and Characteristics of Neutron Diffraction

Neutrons have wave-particle duality. When neutrons pass through crystalline substances, the orderly arranged atoms are equivalent to a three-dimensional grating for the neutron wave, and the diffraction phenomenon will occur when the neutron wave passes through. The scattered wave will form interference enhancement at some specific scattering angles, that is, the formation of diffraction peaks. The position and intensity of the peak are related to the position and arrangement of atoms in the crystal and the type of atoms at each position. For magnetic substances, the position of the diffraction peak is also related to the size, orientation, and arrangement of the magnetic moment of atoms. According to the de Broglie relation, for thermal neutrons, the wavelength is about 0.1–1 nm, which is equivalent to the atomic spacing of general substances, making neutron diffraction an ideal means to study the microstructure of substances.

The differences between neutron diffraction and X-ray diffraction are as follows:

(1) X-ray interacts with electrons, thus its scattering intensity on the atom is proportional to the atomic number Z. Neutron interacts with nuclei, its scattering intensity on different nuclei is not a monotonic function of Z-value. Therefore, neutrons are particularly suitable for determining the position of light elements in the point lattice (the sensitivity of X-ray is insufficient) and the position of elements adjacent to the Z-value (the resolution of X-rays is not high enough).
(2) For the same element, neutrons can distinguish different isotopes, which makes neutron diffraction show special advantages in some aspects, especially in the use of the hydrogen–deuterium difference to label and study organic molecules.

(3) Neutrons have magnetic moments, which can interact with atomic magnetic moments to produce neutron-specific magnetic diffraction. Through the analysis of magnetic diffraction, the magnitude and orientation of magnetic moments of magnetic atoms in the lattice of magnetic materials can be determined. Therefore, neutron diffraction is an important technical means to study the magnetic structure.
(4) Generally speaking, neutrons have stronger penetrability than X-rays. Thus, they are more suitable for structural studies of thick containers under high and low temperatures, high pressure, and other conditions.

The main disadvantage of neutron diffraction is the need for a special strong neutron source. In addition, due to the insufficient neutron source strength, larger samples and longer data collection times are often required.

3.5.2 Neutron Diffraction Device

The neutron diffraction device is similar to the X-ray diffraction device. Figure 3.4 is the schematic diagram of a biaxial neutron diffractometer.

The thermal neutron beam extracted from the nuclear reactor channel is emitted to the monochromator through the collimator. After being reflected by the single crystal, the single wavelength neutrons obtained will be incident on the sample again. Then, the intensity of the diffracted beam is determined from all angles by a neutron detector rotating around the sample. Through data processing methods similar to those used for X-ray diffraction, the nuclear density distribution at different positions of the

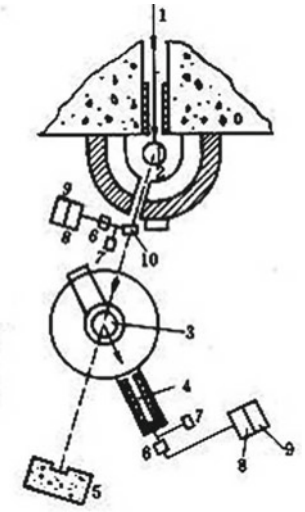


Fig. 3.4 Schematic diagram of a two-axis neutron diffractometer. 1—neutron beam, 2—monochromator, 3—sample and sample stage, 4—neutron detector, 5—neutron trapper, 6—preamplifier, 7—high voltage power supply, 8—amplifier, 9—scaler, 10—monitor

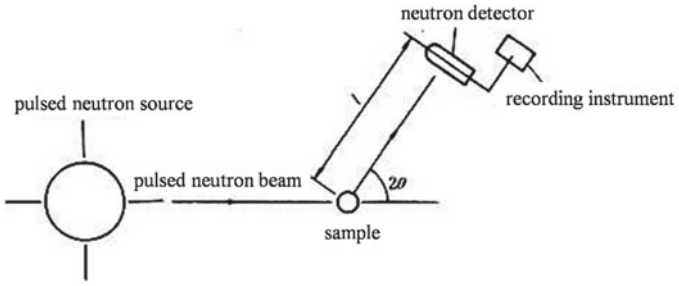


Fig. 3.5 Schematic diagram of time-of-flight neutron diffraction

lattice can be obtained. In addition, in terms of experimental technology, the time-of-flight diffraction method (it determines the energy spectrum of neutrons by measuring its flight time, which is the main method to determine the neutron energy spectrum at present) established by using neutrons of different wavelengths with different velocities (and energies) is different from the traditional method. This method is mainly used in intense pulsed neutron sources such as accelerators. Figure 3.5 shows the schematic diagram of time-of-flight neutron diffraction.

3.5.3 Applications of Neutron Diffraction

The applications of neutron diffraction are mainly in the following five aspects:

(1) Molecular structure studies. The purpose of molecular structure studies is to determine the position of light atoms, especially hydrogen atoms. For example, the positions of light elements in the structures of various inorganic carbon, hydrogen, and oxide (such as WC, MoC, ThC, UC, NaH, TiH, ZrH, HfH, PdH, PbO, $BaSO_4$, SnO_2) are mainly determined by neutron diffraction. At present, structure studies have been extended to organic molecules (e.g., amino acids, vitamin B, and even more complex macromolecules such as myoglobin).
(2) Alloy material studies. Alloy systems often need to distinguish between those atoms whose atomic numbers are very close, as their scattering amplitudes to X-rays are very similar. This problem does not exist with neutron diffraction.
(3) Magnetic material studies. For atoms with magnetic moments, additional scattering of neutrons will occur.
(4) Studies of vibration, including magnetic vibration, by inelastic scattering.
(5) Studies of amorphous structure—liquids, gases, and defects.

1. **Molecular structure studies**

The position of light elements can be determined by neutron diffraction. Since the X-ray scattering amplitude of an element is proportional to its atomic number, it

is impossible to obtain accurate information by using X-ray to study hydrogen-containing substances or oxides and carbides of heavy elements. In this case, for the absolute predominance of the amplitude of recombinant elements, very high-intensity measurement accuracy is required to detect the weak effect of light elements, which is generally impossible in practice. For neutrons, however, light elements are usually not a prominent problem. For example, oxygen has a scattering amplitude of 5.8×10^{-13} cm, when it is mixed with heavy metals such as tungsten (4.8×10^{-13} cm), gold (7.6×10^{-13} cm), or lead (9.4×10^{-13} cm), it is easy to be detected. Hydrogen has a scattering amplitude of -3.7×10^{-13} cm, which, compared with most other elements, the value is not too small.

When studying the structure of compounds, one or more space groups can be obtained to describe the symmetry of heavy elements when the X-ray method is used to determine the position of unit cells and other atoms except for hydrogen and some light elements. As long as the additional spectrum does not appear on the neutron diffraction pattern, it is certain that the unit cell found by X-rays is indeed the true unit cell including the hydrogen atom. Modern X-ray crystal structure studies, which include high-accuracy intensity measurements, will be able to approximately determine the position of hydrogen atoms. The measurement accuracy of the position and motion of hydrogen atoms is close to the corresponding accuracy of X-rays or neutrons to heavy atoms. Generally speaking, the standard procedure for this kind of work is to first collect three-dimensional intensity data of single crystals and then carry out the least square method and Fourier analysis.

2. **Structural identification of atoms with similar atomic numbers**

As mentioned above, the atomic scattering amplitude of X-rays increases regularly with the atomic number. Therefore, it is impossible to identify elements with similar atomic numbers (such as iron and cobalt) in the same compound only based on X-ray diffraction. However, the scattering amplitudes to neutrons by these elements may vary greatly. In this case, they can be identified according to the data of neutron intensity. This method can improve the structural information given by X-ray studies.

For transition metal alloys (e.g., Fe-Co and Cu–Zn), the scattering amplitudes of the two components to the X-ray are very close, thus, the corresponding superlattice spectral lines cannot be detected. For substances with different scattering amplitudes of A and B atoms in A-B alloys, it is very simple to determine their superstructure by neutrons. Table 3.1 shows the scattering amplitudes of X-rays and neutrons of some elements and isotopes, and the quoted X-ray amplitude values correspond to $(\sin \theta)/\lambda = 0.3 \times 10^8$ cm^{-1}. In 1949, Shull and Siegel use neutron diffraction to prove that the FeCo material changes orderly as it cools very slowly from 1023 K. Figure 3.6 shows the results of their experiments. For ordered samples, in addition to the appearance of distinct superlattice lines (100), (111), and (210), the background scattering is also reduced by 20%, which is consistent with the prediction.

In terms of the study of adjacent elements, the degree of order of 3d transition alloy (e.g. Fe–Co–V, Fe–Cr, Ni–Mn, Ni–Cr, etc.) samples is difficult to be determined by X-rays but can be easily identified with neutron diffraction.

Table 3.1 X-ray and neutron scattering amplitudes for some elements and isotopes

Atom or isotope	X-ray ($(\sin\theta)/\lambda = 0.03$ nm) $\times 10^{-12}$ cm	Neutron $\times 10^{-12}$ cm
Mn	4.2	− 0.39
Fe	4.4	0.95
^{54}Fe	4.4	0.42
^{56}Fe	4.4	1.01
^{57}Fe	4.4	0.23
Co	4.6	0.25
Ni	4.8	1.03
^{58}Ni	–	1.44
^{60}Ni	–	0.28
^{52}Ni	–	− 0.87
Cu	5.1	0.76
^{65}Cu	–	1.11
Zn	5.3	0.57
Au	16.1	0.76

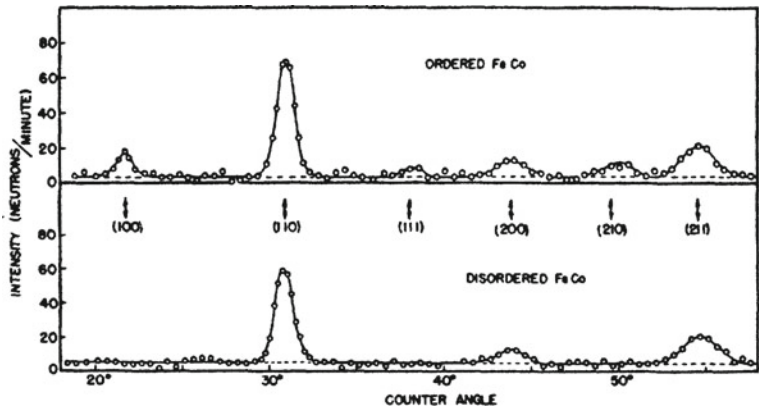


Fig. 3.6 Neutron diffraction patterns of Fe–Co ordered (**a**) and disordered (**b**) samples

3. **Magnetic material studies**

The greatest contribution of neutron diffraction to the study of solids is in the study of magnetic materials. In 1949, Shull and Smart first applied neutron diffraction technology to the study of antiferromagnetic oxides. They determined the antiferromagnetic structure of MnO at liquid-nitrogen temperature and thus determined that the adjacent magnetic moments of Mn atoms in the (111) plane are in the opposite direction. In the 1950s, many antiferromagnets (such as FeO, NiO, CoO, α-Fe_2O_3, etc.) were studied by neutron diffraction, and spinel-type ferrites (such as Fe_3O_4 and $MnFe_2O_4$) and garnet-type ferrites (such as $Y_3Fe_5O_{12}$, etc.) were also been

determined, which proved that the magnetic structure model proposed by Nair was correct. In the late 1950s, helical magnetic structures were first found in MnO, and then various such structures were found in rare earth and its alloys. In recent years, noncollinear antiferromagnetic structures have also been found in some antiferromagnets. In addition, neutron diffraction methods are also used to study the size of magnetic moment, the density distribution of magnetic electrons, the structure of magnetic domains, etc. Neutron diffraction has also been applied to the study of other fields such as structural phase transition, preferred orientation, crystal morphology, dislocation defects, amorphous state, and so on.

In the years since the first investigation of powder samples by low-fluence neutrons, many elements and compounds have been studied. In addition to the transition elements themselves, the most extensive research has been carried out on the magnetic structure of iron group compounds of transition metals, followed by rare earth element compounds. Detailed information can be found in *Neutron Diffraction* prepared by G. E. Bacon.

4. **Studies on inelastic incoherent scattering**

The inelastic scattering of slow neutrons and X-rays is essentially different. The inelastic scattering of monochromatic X-rays is usually the diffuse scattering of X-rays. If X-rays and neutrons have the same wavelength, the energy of X-ray light quantum will be 10^5 times greater than that of neutrons. In inelastic scattering, the energy loss of X-ray is negligible compared with the energy of crystal vibration, and the scattered quantum can be considered to have the same energy as the incident quantum. On the other hand, the change of the slow neutron energy is of the same order of magnitude as the incident energy. Therefore, unlike X-rays, inelastically scattered neutrons have significantly different wavelengths from incident wavelengths. In 1951, Egelstaff first experimentally proved the energy gain of neutrons in inelastic scattering in the experiment by using a long-wave neutron beam that passes through a lead filter. This characteristic is very important for the study of solids because it is possible to determine the details of the crystal energy spectrum by analyzing the energy spectrum of neutrons after scattering in detail (i.e. acoustic vibrations in crystal).

Compared with the general infrared absorption spectroscopy and Raman spectroscopy, the results of inelastic incoherent scattering are of great significance. Infrared measurements can only detect vibrations that incorporate changes in molecular dipole moments. Raman spectroscopy can only observe movements that involve changes in molecular polarizability. But neutron spectroscopy is not subjected to these "selection rules", it mainly focuses on showing the vibrations and rotations of those molecules in which hydrogen atoms participate.

5. **Study of amorphous structure**

In amorphous materials and liquids, the arrangement of atoms is not long-range ordered but short-range ordered. No obvious Bragg peaks appear on the scattering

curve, only a few short and wide peaks reflecting short-range order can be found. Such curves are called the radial distribution function, from which the nearest-neighbor atomic coordination number and the distance between atoms can be obtained. For example, the measurement of amorphous material TbFe2 shows that the atomic number of the nearest-neighbor Fe–Fe is 60 and the distance between atoms is 0.252 nm, the nearest-neighbor Tb–Tb has an atomic number of 9.2 and an interatomic distance of 0.349 nm, the nearest-neighbor Tb-Fe has an atomic number of 7.6 and the distance between atoms is 0.306 nm.

3.6 Neutron Radiography

Neutron radiography is a new non-destructive method of observing objects. Visible light can be used to observe the surface of an object, X-ray radiography can be used to observe the interior of an object and provide information about the density, while neutron radiography can provide a deeper insight into the internal structure of an object and provide information about the differences in the properties.

3.6.1 Principles and Characteristics of Neutron Radiography

1. **Principle of neutron radiography**

When neutrons pass through matter, they interact with the nucleus of matter, and their intensity is therefore weakened. From a macro perspective, the following mathematical relationship exists between the intensity of transmitted neutrons and the intensity of incident neutrons:

$$I = I_0 e^{-\Sigma t} \tag{3.14}$$

where

I Intensity of the Transmitted Neutron.
I_0 Intensity of the incident neutron.
t Thickness of the sample in the direction of the neutron beam, cm.
Σ Attenuation coefficient of the sample to neutrons (macroscopic cross-section), cm^{-1}.

If the sample is inhomogeneous or defective, the intensity of transmitted neutrons will change. Recording these changes can reflect the internal information of the sample.

2. Characteristics of neutron radiography

Compared with X-ray radiography, neutron radiography has its unique advantages. X-rays interact with electrons outside the nucleus, while neutrons interact with the nucleus. The attenuation capacity of matter to X-rays increases with the increase of the atomic number of matter, making X-ray radiography most suitable for imaging materials with high atomic numbers. Unlike X-rays, the attenuation capacity of matter to neutrons depends on the nuclear properties of elements or nuclides, thus, neutron radiography can image some materials with low atomic numbers as image those with high atomic numbers. For example, the attenuation capacity of heavy metals such as Fe, Pb, and Bi to neutrons with energy below 1 meV is much smaller than that of light substances such as H, Li, and B. Thus, neutron radiography can be used to inspect the structure of hydrogen-containing objects in the iron shell. Figure 3.7 shows photographs of bullets obtained by X-ray radiography (top) and neutron (bottom) radiography The attenuation coefficients of X-rays to isotopes of the same element are equal, while the values of neutrons differ greatly. The principle of X-ray radiography is to use the density difference of materials, while neutron radiography uses the difference of nuclear absorption cross-section. Therefore, neutron radiography can be used for the photography of materials with high and low atomic numbers, materials with small reaction cross-sections, materials with large reaction cross-section elements, and materials with varying isotopic contents, and appropriate energy can be selected to obtain the best neutron radiography effect. Another special application of neutron radiography is to photograph highly radioactive objects without being affected by the radioactive gamma and X-ray background of the sample. Neutron radiography can be used as a complement to X-ray radiography in non-destructive inspection of materials, which has been widely used in the military industry, nuclear industry, aerospace industry, aircraft manufacturing industry, agriculture, medicine, and other fields.

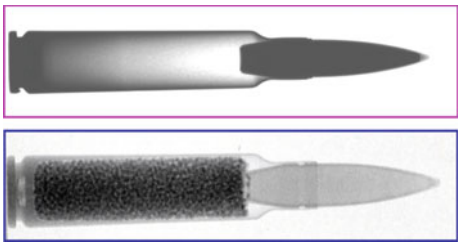


Fig. 3.7 Photographs of bullets obtained by X-ray (Top) and neutron (Bottom) radiography

3.6.2 Classification of Neutron Radiography

Neutron radiography is a technique that uses the attenuation of neutron beam when penetrating an object to show the internal structure of some objects. According to the energy of neutrons used, neutron radiography can generally be divided into cold neutron radiography ($E < 0.005$ eV), thermal neutron radiography (0.005 eV $< E < 0.5$ eV), epithermal neutron radiography (0.5 eV $< E < 10$ keV) and fast neutron radiography (10 keV $< E < 10$ meV).

Neutron radiography has two imaging methods. One is the direct exposure method, in which the conversion screen and film are exposed and imaged in the neutron beam simultaneously. The other is the indirect exposure method—after being exposed to the neutron beam, the potential radiograph with appropriate life will be formed on the conversion screen, and the radiograph will be transmitted to other places and the film will be exposed and imaged.

The advantages of the direct exposure method are the short photographic process, high sensitivity, and high image resolution. The disadvantage is that the film simultaneously records the γ-rays in the neutron beam and those emitted by other objects during neutron irradiation, forming a large background, which affects the clarity of the image. In comparison, the indirect exposure method avoids the interference of γ-rays, but the photographic process is long, which is suitable for objects with high radioactivity such as reactor fuel elements.

3.6.3 Neutron Photographic Device

Figure 3.8 shows a neutron radiographic device. It mainly consists of a neutron source, collimator, and detector. These three parts are called the three elements of neutron radiography, which have an impact on the sensitivity, resolution, and penetration of neutron radiographic imaging.

The neutron source is composed of a source, moderator, and shielding layer, which produces the neutron radiation beam suitable for neutron radiography. The reactor neutron source is the most suitable neutron source for neutron radiography, but other neutron sources can also be used. If thermal neutron radiography is to be carried out, appropriate moderating substances should be surrounded the source to slow down fast neutrons to thermal neutrons.

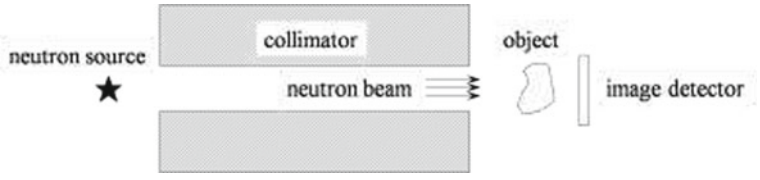


Fig. 3.8 Schematic diagram of the neutron radiographic device

The function of the collimator is to collimate and shape the neutron beam produced by the neutron source, improve the parallelism of the neutron beam, and guide the neutron beam to the illuminated object. The quality of the collimator directly affects the resolution of imaging.

Commonly used imaging detectors are mainly X-ray photographic films. Since the efficiency of film exposure directly by neutrons is too low, it's necessary to use a conversion screen. Neutrons interact with the conversion screen and emit alpha, beta, or gamma rays to sensitize and image the film. Conversion screens are divided into two categories. One is the screen made of materials such as Gd, Li, B, Cd, etc., which absorb thermal neutrons and emit prompt radiation to expose the film. When using this kind of screen, the direct exposure method is needed, that is, stick the screen close to the film, put them into a cassette, and expose them together to the neutron beam. The other is made of In, Dy, Ag, and other materials, which form radioactive nuclei with a certain life after capturing thermal neutrons. The indirect exposure method is required when using this kind of screen.

3.6.4 Factors Affecting Image Quality of Neutron Radiography

A conventional index to measure the image quality of neutron radiography is the sensitivity of neutron radiography. The sensitivity is affected by the image contrast and resolution of neutron radiography. And the resolution is related to the definition (the degree of mutation and smoothness of blackness conversion). In addition, misoperation during the process of exposure and development will also adversely affect the image quality. Table 3.2 lists various factors that affect the sensitivity of neutron radiography.

Table 3.2 Factors affecting neutron photographic sensitivity

Image contrast		Image definition	
Contribution of objects to contrast	Contribution of films to contrast	Geometric factors	Grain factors
Thickness of sample	Film type	Collimation ratio	Film type
Quality	Time and intensity of development	Sample-film distance	Screen type
Scattering ability	Disturbance and blackness	A sudden change in sample thickness	Quality
	Activity of developer	Screen-film contact	Development

3.6.5 Applications of Neutron Radiography

Neutron radiography is a non-destructive detecting technology that has been widely used. This section will introduce some main application examples, which are conducive to a clearer understanding of the characteristics and advantages of neutron radiography.

1. **Study on gas–water two-phase flow in the metal tube**

Dynamic real-time neutron radiography allows the study of gas–water two-phase flow in metal tubes, while methods such as X-ray radiography and optical method cannot be used to achieve the study. A typical example is a study of gas–water two-phase flow in the rectangular aluminum alloy tube and water flow between the three-layer concentric aluminum tube by high frame rate neutron radiography. Neutron radiography clearly recorded the two-phase flow patterns such as slug flow, emulsion flow, and annular flow, measured the three-dimensional distribution and lacunarity of cavities, and validated the theoretical model of fluid mechanics. In addition, neutron radiography can also be used to detect the refrigeration process of refrigerators and study the single-phase and two-phase flow of heavy metals.

2. **Study on porous materials**

Neutron radiography can be used to study porous materials such as concrete and brick. The establishment of underground oil depots and offshore oil platforms needs to consider the water and oil seepage of concrete. In the past, the study of the infiltration process required cutting the specimen into many samples, and the data was scattered due to the difference between samples. Neutron radiography can be used to continuously observe the whole process of infiltration and obtain accurate and reliable data. Concrete produces microcracks under the action of mechanical force, and microcracks will slowly develop into larger cracks. The resolution of neutron radiography is much higher than that of X-ray radiography. Neutron radiography can detect cracks of 0.6 μm, which is 25 times higher than the X-ray detection limit. Therefore, using neutron radiography to detect microcracks is important in engineering.

3. **Detection of moisture and corrosion**

Water trapped by aircraft components and aluminum corrosion can cause serious flight accidents, thus, their detection and maintenance play an important role in the safety and prolonging the life of aircraft. Neutron radiography allows early detection of these problems and provides accurate maintenance information. The aircraft wing itself is a fuel tank, the fuel contains water, and long-term operation will lead to aluminum corrosion. The inner surface of corroded aluminum will generate $Al(OH)_3$ spots, which contain hydrogen. When the wing fuel tank is emptied, the mobile neutron radiography—electric imaging method can be applied for detection. Due to the high contrast sensitivity, this method can easily detect corrosion spots, with

a detection accuracy of up to 0.1 mm. In comparison, X-ray radiography cannot undergo such detection of moisture and corrosion. Although other methods might be feasible, the components need to be removed, which is costly, time-consuming, and laborious. The removable neutron radiographic system can carry out non-destructive online inspection of aircraft without removing parts, and the inspection is fast, reliable, and sensitive.

4. **Detection of structural materials containing radioactive substances**

Radioactive materials can sensitize the film, so general photographic methods cannot be used for photography of radioactive substances. By using the transfer method and conversion screens that are insensitive to γ (e.g., the In screen) track detectors, neutrons can photograph structural materials containing strong radioactive substances. Neutron radiography plays an important role in the nuclear industry. The United States, Japan, and many European countries have neutron radiographic systems on the reactors to detect nuclear fuel. Although nuclear fuel elements contain a lot of radioactivity, neutron radiography can be used to detect the deformation, fracture, melting, and other conditions of uranium cores in nuclear fuel elements. For the newly processed nuclear fuel, neutron radiography can give data on impurities, voids, uniformity, density, and agglomeration. And for used nuclear fuel, neutron radiography can give information on cracks, enrichment, swelling, creep, etc. Countries like Japan and Germany use movable neutron cameras to take photographs directly in the spent fuel pit of power reactors. Neutron radiography can detect the loss of B_4C absorbers of the reactor control rod.

5. **Neutron radiography of explosive devices**

The shell of explosive devices is generally metal, and the explosive material inside contains hydrogen. The mass absorption coefficient of neutrons in hydrogen is very large, while that in heavy elements is very small. Taking advantage of this feature, neutron radiography can be used to detect artillery shells, bullets, detonators, and safety fuses, the uniformity and porosity of the internal explosives can be detected through the metal shell. Tsinghua University detected the rocket detonating cord with neutron radiography to study the density change of the explosive in the detonating cord and found explosive cracks with a minimum of 0.2 mm. The French Saclay Nuclear Research Centre uses neutron radiography to detect the signal device of the Ariane launching system. Neutron radiography has been used in the control and verification of weapons, such as detecting fissile materials, detecting missiles (to confirm whether they are nuclear weapons or general missiles), etc.

6. **Other applications of neutron radiography**

Neutron radiography can be used for non-destructive detecting of the characteristics of substances in sealed metal containers, which helps to identify antiquities and works of art, such as the authenticity and age of oil paintings. It can also be used for

the detection of electronic components, such as the detection of material moisture and its distribution and changes and the measurement of material macroscopic cross-sections. In addition, neutron radiography also has potential in the applications of biology and medicine, which can be used to check the function or pathological changes of human soft tissues containing hydrogen and to detect or diagnose bone tumors.

Exercise

1. Describe the basic principle of x-ray fluorescence analysis.
2. What are the specific requirements for samples when using X-ray fluorescence analytical methods for sample analysis?
3. What is the principle of neutron activation analysis?
4. What are the principles and characteristics of neutron diffraction?

Bibliography

Bacon, G. E., Curry, N. A., & Wilson, S. A. (1964). A crystallographic study of solid benzene by neutron diffraction. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences, 279*(1376), 98–110. https://doi.org/10.1098/rspa.1964.0092

Beck, J. N., & Lamberty, C. M. (2007). Thermal neutron activation analysis—An important analytical tool. *Applied Spectroscopy Reviews, 37*(1), 19–55. https://doi.org/10.1081/asr-120004372

Bogdanović Radović, I., Steinbauer, E., & Benka, O. (2000). Elastic recoil detection analysis for large recoil angles (LA-ERDA). *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 170*(1–2), 163–170. https://doi.org/10.1016/s0168-583x(00)00077-x

Choukem, S.-P., & Gautier, J.-F. (2008). How to measure hepatic insulin resistance? *Diabetes Metabolism, 34*(6), 664–673.

Chu, W. K., & Liu, J. R. (1996). Rutherford backscattering spectrometry: Reminiscences and progresses. *Materials Chemistry and Physics, 46*(2–3), 183–188. https://doi.org/10.1016/s0254-0584(97)80012-0

Fujimoto, F. (1991). Ion-beam analysis. *Bunseki Kagaku, 40*(11), 577–597.

Greenberg, R. R., Bode, P., & De Nadai Fernandes, E. A. (2011). Neutron activation analysis: A primary method of measurement. *Spectrochimica Acta Part B: Atomic Spectroscopy, 66*(3–4), 193–241. https://doi.org/10.1016/j.sab.2010.12.011

Han, X., Zhuo, S., & Wang, P. (2006). Analysis of films by X-ray fluorescence spectrometry. *Spectroscopy and Spectral Analysis, 26*(1), 159–165.

Jang, C., Chen, L., & Rabinowitz, J. D. (2018). Metabolomics and isotope tracing. *Cell, 173*(4), 822–837.

Martin, A. P., Brunton, A. N., Fraser, G. W., & Abbey, A. F. (2001). Imaging X-ray fluorescence spectroscopy: Laboratory measurements. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 460*(2–3), 316–325. https://doi.org/10.1016/s0168-9002(00)01076-7

Miller, S. D., Bilheux, J. C., Gleason, S. S., Nichols, T. L., Bingham, P. R., & Green, M. L. (2011). Large-scale user facility imaging and scattering techniques to facilitate basic medical research. In *Medical Imaging*. InTech. https://doi.org/10.5772/28419

Segebade, C., Starovoitova, V. N., Borgwardt, T., & Wells, D. (2017). Principles, methodologies, and applications of photon activation analysis: A review. *Journal of Radioanalytical and Nuclear Chemistry, 312*(3), 443–459. https://doi.org/10.1007/s10967-017-5238-6

Shikano, K., Yonezawa, H., & Shigematsu, T. (1993). Charged particle activation analysis of light elements at sub-ppb level. *Journal of Radioanalytical and Nuclear Chemistry Articles, 167*(1), 81–88. https://doi.org/10.1007/bf02035465

Shull, C. G., & Siegel, S. (1949). Neutron Diffraction Studies of Order-Disorder in Alloys. *Physical Review, 75*(7), 1008–1010. https://doi.org/10.1103/PhysRev.75.1008

Strobl, M., Manke, I., Kardjilov, N., Hilger, A., Dawson, M., & Banhart, J. (2009). Advances in Neutron radiography and tomography. *Journal of Physics D: Applied Physics, 42*(24), 243001.

Chapter 4
Nuclear Instrumentation



All detection instruments with radionuclide sources or radiation sources and nuclear radiation detectors are collectively referred to as radionuclide instrumentation (also known as nuclear instrumentation or isotope instrumentation). Nuclear instrumentation is generally composed of a radioactive source or radiation source, a nuclear radiation detector, an electrical converter, secondary instrumentation, and other components.

For most professionals, nuclear instrumentation is generally classified into instruments for detecting nuclear radiation, equipment for generating radiation, and applications of these two types of equipment according to IEC (International Electrotechnical Commission) 60050-395:2014: International Electrotechnical Vocabulary (IEV)—Part 395: Nuclear instrumentation—Physical phenomena, basic concepts, instruments, systems, equipment, and detectors. According to the characteristics, nuclear instrumentation is divided into active nuclear instrumentation and passive nuclear instrumentation. Based on the radiation type, nuclear instrumentation can be divided into alpha, beta, gamma, etc., and energy spectrum instrumentation. According to the international standardization classification, the application system of nuclear instrumentation is divided into nuclear power plants operation, measurement, control and safety protection system, nuclear safety and radiation protection monitoring systems, and general nuclear instrumentation system (nuclear technology research, development, application, etc.). According to different application fields, nuclear instrumentation is divided into basic nuclear instrumentation, nuclear instrumentation for industrial use, nuclear instrumentation for agriculture, nuclear medicine instrumentation, nuclear instrumentation for resource development, nuclear instrumentation for nuclear power and reactors, nuclear instrumentation for environmental protection and radiation protection, etc.

Non-contact nondestructive testing is the greatest feature of nuclear instrumentation, which is especially suitable for measuring and controlling high temperature, high pressure, explosive, toxic, and other corrosive objects and environments that

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6_4

are difficult or unable for other instruments to work. Therefore, under certain conditions, nuclear instrumentation has become the key equipment in some systems. The application of nuclear instrumentation is mainly concentrated in metallurgy, mining, energy development, petrochemical industry, paper making, and other industries. It is currently an indispensable new detection means in many fields of national economic construction.

This chapter mainly introduces the development, basic components, and general classification of nuclear instrumentation, as well as major nuclear instrumentation and its applications.

4.1 Overview of Nuclear Instrumentation

4.1.1 Characteristics and Application of Nuclear Instrumentation

Nuclear instrumentation utilizes the interaction between nuclear radiation and matter and the absorption, scattering, ionization, excitation, and other effects to obtain macroscopic and microscopic information about the matter. Nuclear instrumentation has the following characteristics:

(1) It is a non-destructive detection tool without direct contact with the detected object.
(2) It can control the non-electrical parameters of materials in non-closed and well-closed containers under various harsh conditions (such as high temperature, high pressure, high viscosity, high corrosive, and high toxicity).
(3) High detection sensitivity, stable and reliable performance, fast response speed, and long service life.
(4) It can continuously output electrical signals to realize closed-loop automatic control of the production process.
(5) Small size, lightweight, easy to carry and install.
(6) The penetration depth of rays in the material varies depending on the type of ray, generally between 0.01 and 1 m.

Due to the above characteristics, nuclear instrumentation has a wide range of objects and environments in terms of application, which are shown in Table 4.1.

Table 4.1 Application of nuclear instruments

Field	Applications
Agriculture and forestry	(1) Measure the areal density of plant leaves; (2) Measure the density of feed; (3) Measure the density of tree stems, wood, and plant products; (4) Measure water permeability of mud columns; (5) Measure the density change of wood during dry distillation; (6) Measure the moisture content of wood, grain, and living trees; (7) Measure the density and humidity of soil; (8) Measure the composition of soil and fertilizer; (8) Measure the distribution of soil moisture
Coal	In terms of exploration: (1) Measure the position, thickness, and ash content of the coal seam; (2) Determine the content of ash and other associated elements in the coal core In terms of mining: distinguish coal and rock In terms of washing: (1) Automatic gangue sorting; (2) Measure the concentration of the heavy medium; (3) Measure the concentration of flotation feed slurry In terms of mine transportation and hoisting: control the loading capacity of mine cars, coal bunkers, coal hoppers, and belt conveyors In terms of mine safety: measure gas pressure and dust content of underground air and fire alarm
Metallurgy	(1) Measure the thickness of hot rolled and cold rolled plates; (2) Measure the thickness of coatings; (3) Measure the diameter of drawing wires; (4) Measure the thickness of each part of special-shaped materials; (5) Measure the wall thickness of pipes, and the loss of fireplace and pipe wall; (6) Measure the density of billets, powders, slurry, and sintered materials; (7) Measure the material level of liquids, solids, solid–liquid mixtures, and powder; (8) Measure the moisture of sintered material or coke; (9) Determine the oxygen content in steel, the content of oxygen, silicon, and iron in materials, the composition of various ores, and analyze the iron content and alkalinity of the slag
Petroleum, chemical, paper, rubber	(1) Determine gas layers, oil layers, and water layers and their interfaces in petroleum exploration; (2) Measure the thickness of plastics, rubber, paper, and various coatings; (3) Measure the wall thickness of plastic pipes and rubber pipes; (4) Measure the fiber density in the tire; (5) Measure the wear of the tire; (6) Measure the density or temperature of pulp, rubber pulp, emulsifier, and various acid, alkali and salt solutions; (7) Measure the level of various solutions and powders in storage tanks; (8) Measure the composition and humidity of various slurries and products; (9) Measure the flow of various slurries and powders

(continued)

Table 4.1 (continued)

Field	Applications
Glass, cement, and other non-metallic mineral processing industry	(1) Measure the thickness of sandpaper, abrasive cloth, glass plate, asbestos plate, cement plate, and refractory brick; (2) Measure the density of sand, cement, loess, and slurry; (3) Measure the level of molten glass and the level of sand, clay, and cement in the silo and hopper; (4) Analyze the content of calcium and magnesium in cement and concrete, and the content of boron, potassium, lead and silicon in the glass
Food	(1) Measure the thickness, density and moisture of bread, snacks, cigarettes, etc.; (2) Measure the density of paste food made of fish, meat, eggs, milk, etc.; (3) Measure the material level and loading capacity of paste food, solid food, wine, oil, and vinegar; (4) Measure the water content of solid food, and analyze the constituent elements and their contents in various food
Textile	(1) Measure and control the thickness of blankets, oilcloths, artificial leather, gauze, etc.; (2) Measure and control the linear density and humidity of cotton yarn and other fibers
Civil engineering and hydrology	(1) Measure the density and humidity of pavements and foundations; (2) Measure the sand content of river water; (3) Measure the density of silt in reservoirs and harbors; (4) Measure the density and composition of seabed sediments; (5) Measure the mud density in the mud pipe of the dredger; (6) Measure the concentration of suspended matter in seawater; (7) Inspect the irrigation effect of dam foundation; (8) Measure the water permeability of the embankment body; (9) Measure the moisture content of the concrete
Aeronautics and aerospace	(1) Measure the fuel storage in spacecraft and aircraft; (2) Measure the density and pressure of the atmosphere; (3) Measure the wear of the spacecraft skin; (4) Measure the freezing point; (5) Measure the altitude, speed and pitch angle of the aircraft during takeoff or landing; (6) Control the helicopter formation; (7) Recovery of rockets; (8) Indication of missile miss distance to the target

4.1.2 Historical Development of Nuclear Instrumentation

In 1951, the United States first used radionuclide thickness gauges in rubber production. After that, it took about 15 years for western countries to make the use of nuclear instrumentation exceed 600,000 sets from the late 1960s to the early 1970s. The output value accounted for 0.04–0.05% of the total national economic output value, the output value profit ratio exceeded 2, and the investment benefit ratio reached 1:9. The historical development of nuclear instrumentation has roughly experienced the following three stages:

1. **Initial stage (late 1940s ~ early 1960s)**

This stage was the pioneering period of industrial nuclear instrumentation. Several developed industrial countries, led by the United States, carried out a great deal of research and development. The results were mainly shown in the two Geneva International Conferences on the peaceful uses of atomic energy held in 1955 and 1958. The general characteristics of this stage were that the development technology of nuclear instrumentation was not fully mature, and the quality was still difficult to fully meet the needs of industrial site conditions. In addition, the development of instrumentation existed with certain blindness, which led to slow development and extremely limited promotion.

2. **Mature stage (late 1960s ~ mid-1970s)**

The development of electronic technology such as transistors and large-scale integrated circuits and the emergence of new nuclear radiation detection devices brought nuclear instrumentation into a new stage. During this stage, western countries were in a period of rapid economic development. Various high and new technologies were continuously applied to production and technological transformation. Nuclear instrumentation developed rapidly and gradually matured with its unique technical advantages. Its stability and reliability were greatly enhanced, and its performance was significantly improved. The objects of usage were gradually clear, the application fields of nuclear instrumentation were constantly expanded, and significant economic benefits were obtained.

3. **High-level stage (mid-1970s ~ present)**

With the rapid development of electronic computers and integrated circuit electronic technology, nuclear instrumentation has been updated based on mass popularizations and applications and is developing in the direction of high level and high technology. The sensitivity and accuracy of the instrumentation are increasing improved, the reliability and stability are getting better, and the functions and application fields are greatly expanded. At present, some intelligent large-scale multi-functional nuclear instrumentation in countries with developed industries has appeared to solve the difficult and comprehensive problems encountered in practical work. In addition, some special miniature nuclear instrumentation has also been greatly developed.

The application of nuclear instrumentation can not only improve the quality and output of products but also save raw materials and reduce energy consumption, which has brought great economic benefits to the industry. According to the statistics of the United States in 1978, the average price of nuclear instrumentation was $12,000, and the annual maintenance fee was about $250. Generally speaking, all expenses incurred by the enterprise in purchasing the required instrumentation can be recovered within 2–3 months, and only individual expenses need to be recovered after 5–6 months. The cycle from development to production of a new nuclear instrumentation product is generally 1–3 years. When using such nuclear instrumentation, it is generally not necessary to make major changes to the original equipment and

Table 4.2 Development of nuclear instrumentation in the United States

Year	1960	1965	1970	1975	1980	1985
Number of instrumentations	4650	11,000	31,500	103,000	215,000	350,000

processes. Once connected with the control equipment, nuclear instrumentation can realize continuous production. Therefore, it has the characteristics of less investment, high efficiency, quick effect, etc. According to the report of the International Atomic Energy Agency (IAEA) in 1981, the economic benefit coefficients of various nuclear instrumentation are 1:3 for the plastic film thickness gauge, 1:9 for paper thickness and the hygrometer, 1:30 for zinc coating thickness, 1:10 for the sulfur analyzer in the desulfurization workshop, and 1:20 for the blast furnace coke hygrometer.

In terms of the application scope of nuclear instrumentation, almost all industrial sectors are involved. It has been widely used in many industrial fields such as tobacco, food, textile, building materials, paper making, printing, rubber, mining, mineral processing, coal, petroleum, chemical industry, metallurgy, machinery, transportation, transportation, etc. The popularization and utilization of nuclear instrumentation have greatly improved the economic benefits of many countries worldwide. A comprehensive economic benefit survey conducted by the United States Atomic Energy Commission (AEC) on the application of nuclear instrumentation in various industries in the United States shows that the use of nuclear instrumentation brings benefits of more than $400 million to nine industries every year. Nowadays, the nuclear instrumentation industry in industrialized countries is in a period of rapid growth. The technical indicators of the products are able to meet the highest requirements put forward by the industry. Technological progress is mainly manifested in the adoption of new nuclear radiation detectors and new technologies, the renewal of structures and the enhancement of functions, and the development of functional assembly.

Table 4.2 lists the overview development of nuclear instrumentation in the United States from the 1960s to the mid-1980s. It can be seen from the data that nuclear instrumentation in the United States developed quite rapidly at that time. While generating great socio-economic benefits, nuclear instrumentation also played an important role in promoting scientific and technological progress and driving the development of related industries.

4.1.3 Technical Advantages and Economic Benefits of Nuclear Instrumentation

In recent years, the functions of nuclear instrumentation are becoming more and more perfect, the application fields are expanding, and the unique role in industrial production is also increasingly prominent. It has become indispensable and important

testing equipment in the industrial sector. The significance of nuclear instrumentation in production is mainly shown in the following aspects:

(1) Meet production development and social needs

Take Japan as an example. From the mid-1960s to the early 1970s, with the development of the economy, the use of industrial nuclear instrumentation (mainly thickness gauges and level meters) also increased rapidly, which promoted the advancement of relevant scientific research and the rapid development of relevant industries.

(2) Solve certain major technical problems in industrial production

Nuclear instrumentation has been frequently used to solve comprehensive problems such as accurate, rapid, and large-scale geological survey, nondestructive testing of materials or parts, closed-loop automatic detection, and control of production processes, analysis, and determination of high-purity substances and environmental, health, and nutritional evaluation.

(3) Strengthen production processes and accelerate the progress of industrial technology

At present, large sets of complete equipment are generally equipped with nuclear instrumentation to realize automatic detection, adjustment, and control (even optimal control) of the production process to ensure product quality, raise labor productivity, improve labor conditions, reduce energy consumption and raw material consumption, and ultimately reduce product costs. For example, the world's largest blast furnace (~ 5000 m^3) built by the former Soviet Union was equipped with more than 100 nuclear instrumentation, and more than 450 nuclear instrumentation was installed in the Chimkent phosphate fertilizer plant.

(4) Significant economic benefits

The International Atomic Energy Agency (IAEA) believes that nuclear instrumentation is of great significance to the transformation of basic industries and the acceleration of industrial modernization in developing countries. Nuclear instrumentation has the advantages of small investment, quick effect, and remarkable economic benefits. This is also the motivation and starting point for the industrial and mining enterprises in developed countries to widely use nuclear instrumentation. The advantages of nuclear instrumentation are mainly shown in the following aspects:

① Save raw materials

At present, transmission beta or gamma thickness gauges are commonly used in the production of metal plates, chipboard, plastic sheet, (film), and paper. In the production of galvanized plates, tin plates, and other products with plating (coating), the thickness is controlled by a beta backscatter meter or an isotope X-ray fluorescence

analyzer. Accurate thickness control can save coating materials, especially precious metal raw materials. In the textile industry, radioactive static eliminators are used to eliminate static electricity generated during the production process, which can save raw materials by reducing flying hair.

② Improve product quality

When producing paper, plastic film, and various plates, beta projectors can be used to automatically control the thickness to reduce the occurrence of defective products. For tobacco production, beta density meters can be used to improve the quality of cigarettes by controlling the quantity of cut tobacco. In cement production, neutron activation analysis or X-ray fluorescence analysis can be used to rapidly analyze Si and Al content online, which can improve the grade of cement. When welding, gamma flaw detectors can be used for weld inspection, which improves the quality of welding.

③ Reduce rejects and defective products

In the production process of paper, chipboard, and plastic film, beta or gamma projection instrumentation can be used to continuously scan and check the whole material, and the measured signal can be fed back to the feeding controller in time. If the product is too thin, the feeder outlet will be expanded or the control plate will be raised to increase the feeding; if the product is too thick, the feed will be automatically reduced. This method is faster and more accurate than conventional monitoring methods, which reduces the rate of rejects and defective products. In addition, this technology can also be used in strip production to control the width. The width of transparent materials is difficult to control with ordinary transmittance comparison, but it is easier to be realized using an isotope thickness gauge.

④ Improve the running speed and working efficiency of the machine

The use of nuclear instrumentation can raise the working efficiency of equipment, thus creating higher economic value. For example, installing a thickness gauge on a paper machine can quickly change the size of the product paper; the use of radioactive static eliminators in the textile and printing industries can improve the running speed of machines; using an isotope level meter and thickness gauge can effectively control the work of continuous casting and rolling mills, reduce heat loss and improve work efficiency; the use of nuclear scales can achieve fast on-site measurement of the objects in the running car; using isotope density meters can quickly measure the density of materials and shorten the working time.

4.2 Classification and Principle

Nuclear instrumentation has a wide variety of applications with different principles of operation and modes of action. Thus, it is difficult to classify them comprehensively. According to different principles (methods), nuclear instrumentation can be divided into different types.

1. **Based on the basic principle and action mode**

According to the basic principle and mode of action, industrial nuclear instrumentation can be divided into intensity type, energy spectrum type, digital image processing type, and other types.

(1) Intensity type

The intensity measuring instrumentation mainly uses the absorption, scattering, and (neutron) moderation of rays by matter to change the intensity of the ray, so as to reflect certain relevant macroscopic physical parameters of the measured object. Examples include isotope level meters, density meters, thickness gauges, concentration meters, sediment meters, neutron moisture meters, nuclear scales, etc.

(2) Energy spectrum type

The energy spectrum analytical instrumentation determines the composition and content of the substance by measuring the secondary energy spectrum generated by the interaction between the ray and the substance to be measured, which is used for field analysis and on-site analysis. Such as X-ray fluorescence analyzers, nuclear loggings, and instruments for online activation analysis.

(3) Digital image processing type

Digital image processing instrumentation mainly uses film photography technology, two-dimensional or three-dimensional array detection technology, digital image reconstruction, and processing technology to determine the spatial or planar distribution of rays to reflect the relevant information of the detected object. This type of instrumentation is mainly used for non-destructive testing (i.e. radiographic testing). Commonly used instruments mainly include X-ray radiographic inspections, gamma ray radiographic inspections, neutron radiography, and industrial CT devices.

(4) Other types

Most of these types of instrumentation use the ionizing effect produced by radiation emitted by radionuclides to realize monitoring, such as radioisotope fire alarm devices, electrostatic eliminators, radioisotope dischargers, radioactive lightning rods, radioisotope ionization vacuum gauges, etc.

2. Based on the type of interaction between the ray before incidents on the detector and the matter

According to the type of interaction between the ray before incidents on the detector and the matter, nuclear instrumentation can be divided into transmission type, scattering type, ionization type, and isotope X-ray fluorescence type.

The radioactive source constantly emits invisible rays (alpha, beta or gamma rays). When these rays are incident on the measured object, some of them pass through the object, and some will collide with atoms in the measured object and scatter. When the rays meet atoms in some substances, ionization or excitation may also occur. The instrumentation designed based on the relationship between the number of rays passing through the measured object and some parameters of the object is called transmission instrumentation, including transmission thickness gauges, transmission density meters, and transmission level gauges. The instrumentation designed based on the relationship between the backscattering of rays and some parameters of the scatter is called scattering instrumentation, which includes scattering thickness gauges and scattering density meters. The instrumentation designed by using the ionization effect of rays on gas is called ionization instrumentation, such instrumentation includes gas pressure gauges, gas flowmeters, gas composition analyzers, etc. The instrumentation designed on the basis of the principle that the excitation of the material by the rays will produce characteristic X-rays is called isotope X-ray fluorescence instrumentation, such as isotope X-ray fluorescence analyzers and isotope X-ray fluorescence coated thickness gauges. The instrumentation designed according to the principle that neutrons emitted from neutron sources interact with substances to produce nuclear reactions is called neutron instrumentation, and neutron hygrometers are the most widely adopted.

(1) Transmission instrumentation

The transmission instrumentation is designed taking the advantage of the relationship between the intensity of the ray after passing through the substance and the thickness or density of the measured object. Research has shown that when a beam of parallel ray passes through the measured object, the intensity of the ray after passing through the object is related to the thickness and density of the object under the condition of certain material composition. When the density is constant, the thickness of a substance can be measured, and the intensity of the ray after passing through the substance will decrease with the increase of the thickness. Similarly, the density of a substance can also be measured while keeping the thickness constant. This is encountered in many production processes. For example, in the process of producing the plastic film, the density of the film can be kept constant while its thickness often fluctuates during the calendaring process. Another example is that when the slurry is transported in a pipeline, the pipeline can be filled to keep its thickness unchanged, while its density varies with time.

When passing through a substance, the intensity of a ray will decrease with the increase of thickness or density of the substance, which is due to the interaction

between β-rays and γ-rays when they pass through the substance. When β-rays pass through matter, ionization, reflection, and absorption mainly occur. The so-called absorption is the incident beta particles are absorbed by the substances. Beta particles have no fixed range in the substance. When particles of the same energy pass through a substance, due to different paths, some beta particles are reflected or absorbed within a relatively short range, while others are not, and those that are not absorbed continue to move forward. As the thickness or density of the substance increases, more particles are absorbed, and thus fewer particles pass through. For γ-rays, its interaction with matter mainly includes the photoelectric effect, Compton effect, and electron pair production. When a gamma photon enters the substance, it interacts with atoms in the substance and produces the photoelectric effect. As the energy of the incident gamma photon increases, the energy loss is mainly in the form of Compton scattering. With the increase of the incident gamma photon energy, the energy loss is mainly reflected by Compton scattering. When the energy of gamma photons reaches a certain value, electron pairs can be generated, that is, an electron–positron pair is formed, and gamma photons lose all their energy. When the energy of gamma photons is relatively large, the motion direction of electrons and positrons is almost the same as that of photons, with only a small angle difference. Due to the photoelectric effect, Compton effect, and electron pair production, the intensity of γ-rays gradually decreases.

(2) Scattering instrumentation

The scattering instrumentation is designed by using the backscattering phenomenon that occurs when the ray passes through the substance. That's to say when the ray is irradiated on the measured object, due to the collision with the atoms in the measured object, some rays change their original direction. Among the scattered rays, some of them will be backscattered. There is a certain relationship between the number of backscattered rays and some parameters of the measured object. In the case of constant material composition, the number of backscattered rays is related to the thickness and density of the substance. When the density is constant, the number of backscattered rays is related to the thickness of the substance. Using this rule, a scattering thickness gauge can be made within a certain thickness range. If the material thickness exceeds a certain value, the change in the number of rays cannot be measured. This value is called saturated thickness. For substances whose thickness is greater than the saturated thickness and whose density is changing, the number of backscattered rays is related to the material thickness. Using this relationship, the density of the substance can be measured.

(3) Ionization instrumentation

The ionization instrumentation is designed based on the ionizing effect of rays on the matter. When ionization occurs, if the energy obtained by the bound electrons is gained from the incident particles, the ionization is called direct ionization. If the

energy is obtained from the higher energy electrons ejected from the incident particles, the ionization is called indirect ionization. According to such ionization effect, gas pressure gauges, gas composition analyzers, and gas flowmeters can be made. There are several types of instrumentation using ionization, which follows different principles of detection. The gas pressure gauge is designed using the principle that the gas pressure in the ionization chamber is proportional to the ionization current. The gas composition analyzer is designed according to the principle that if the gas composition changes under constant gas pressure, the ionization current will also change. The gas flowmeter is designed on the basis of the characteristic that ionized gas ions move with the gas, and the gas flow can be measured by detecting the time required for the ions to move a certain distance.

(4) Isotope X-ray fluorescence instrumentation

The isotope X-ray fluorescence instrumentation can be developed by using the excitation of substances by radiation. This instrumentation mainly includes the isotope X-ray fluorescence analyzer. When using an appropriate primary radiation source to irradiate the sample, the atoms of the sample will be in an excited state. Atoms in the excited state are extremely unstable and will emit characteristic X-rays. The so-called characteristic X-ray means that the energy of this X-ray can characterize the elements that emit X-rays so that the elements contained in the sample can be known by measuring the energy of the characteristic X-rays emitted by the sample. Besides, the intensity of the characteristic X-rays of an element in the sample is proportional to the content of the element in the sample.

4.3 Core Components—Radioactive Source and Detector

Nuclear instrumentation generally consists of a radioactive source, nuclear radiation detector, electric converter, secondary instrument, etc., among which radioactive source and nuclear radiation detector together make up a parameter converter, which is the core component of nuclear instrumentation. This section will introduce them respectively.

4.3.1 Radioactive Sources

Alpha particles, beta particles, gamma photons, and neutrons emitted by the radioactive source will produce various effects when interacting with substances. In this process, the energy of the ray is transferred to the substance, and the substance will undergo physical or chemical changes accordingly. Nuclear instrumentation is to detect the interaction between the rays emitted by the radioactive source and the

substances, and then determine the position, thickness, density, concentration, defect, and composition of the measured object.

1. **Basic conditions for radioactive sources used in nuclear instrumentation**

Although there are many kinds of radionuclides, not many radioactive sources can be used in nuclear instrumentation. This is because the radioactive sources used in nuclear instrumentation need to meet the following conditions:

(1) Long half-life

The sensitivity, measurement error, and response time of nuclear instrumentation are greatly related to the intensity of the radioactive source used in the instrumentation. When the radioactive source with a short half-life is used, the intensity of the source tends to decay rapidly, resulting in an increase in the measurement error, a decrease in sensitivity, and a deterioration in response time of the instrumentation, requiring frequent replacement of the radioactive source and regular calibration of the instrumentation. Therefore, radioactive sources are required to have a long half-life, generally more than one year. In this way, the radioactive source can have sufficient strength over a long period of time, thus ensuring that the instrumentation has better performance indicators and extending the replacement cycle of the radioactive source used in the instrumentation.

(2) Capable of emitting rays with appropriate energy and energy spectrum

The probability of interaction between rays with different energies and matter is different. Appropriate energy and energy spectrum can ensure an increase in the probability of achieving the desired effects. In addition, the appropriate energy and energy spectrum of the rays enables the instrumentation to obtain the minimum measurement error and the highest sensitivity with the minimum source intensity.

(3) High specific activity

The amount of radionuclides (i.e., radioactivity) contained in a unit mass of a radioactive substance is called the specific activity. Generally speaking, the volume of strong radioactive sources with low specific activity is relatively large, thus, the self-absorption effect of a large radioactive source is more serious than that of a small one. Additionally, when the spatial distribution of a certain quantity is measured with such a large radioactive source, the geometric resolution will be reduced accordingly. Therefore, selecting a radioactive source with high specific activity can be a good choice to obtain better measurement results.

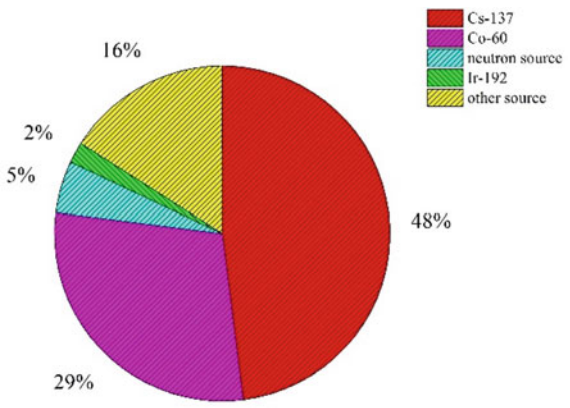


Fig. 4.1 The proportion of common radioactive sources

(4) Moderate price (or low price) and easy to obtain

It is required that the source of the radioactive source should be convenient, and the price should be low. This is because if the source is inconvenient to obtain, difficult to prepare, and unbearable to afford, the cost of using radioactive sources will rise, which is not conducive to the promotion, and thus the usage of radioactive sources will be limited in relevant nuclear instrumentation.

To meet the above requirements, only a few radionuclides can become radioactive sources suitable for nuclear instrumentation. The usage ratio of several commonly used radioactive sources is shown in Fig. 4.1. It can be seen that ^{137}Cs accounts for the largest share. It is widely used in conventional nuclear instrumentation such as nuclear scales, thickness gauges, and density meters. ^{60}Co takes second place, which is mainly used for flaw detectors, level meters, well exploration equipment, etc.

2. **Classification of radioactive sources**

Radioactive sources used in nuclear instrumentation are generally divided into five categories, including alpha radioactive sources, beta radioactive sources, gamma radioactive sources, neutron radioactive sources, and composite radioactive sources.

(1) Alpha radioactive sources

The main radionuclides used to prepare alpha radioactive sources are ^{210}Po, ^{226}Ra, ^{228}Th, ^{239}Pu, ^{241}Am, and ^{242}Cm. These nuclides have strong toxicity, so when preparing this kind of radioactive source, while ensuring that alpha rays can be effectively emitted, it is also necessary to make sure that the prepared materials do not leak. The most used alpha radioactive sources are ^{210}Po and ^{239}Pu sources. ^{210}Po belongs to the uranium-radium series in the natural radioactive series. Its content in

nature is very small, and it is usually obtained by artificial methods. ^{210}Po hardly emits gamma rays and can be regarded as a pure alpha emitter, emitting alpha particles with an energy of 5.3 meV and decaying into stable ^{206}Po. However, ^{210}Po has a short half-life of only 138 d. ^{239}Pu is generated by ^{238}U capturing one neutron in the reactor, which has the following reaction equation:

$$^{238}_{92}\mathrm{U} + n \rightarrow {}^{239}_{92}\mathrm{U} \xrightarrow[23.5\ \mathrm{min}]{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow[2.33\,\mathrm{d}]{\beta^-} {}^{239}_{94}\mathrm{Pu}$$

^{239}Pu can emit alpha particles of three different energies (i.e., 5156.59, 5144.3, and 5105.8 keV) and gamma rays of two energies (i.e., 51.624 and 38.661 keV). ^{239}Pu has the advantage of a long half-life of 2.4×10^4 a.

The application of alpha radioactive sources in nuclear instrumentation is shown in Table 4.3.

(2) Beta radioactive sources

There are many kinds of beta radionuclides, but many of them are not pure beta emitters. This is because in most cases beta radionuclides also emit gamma rays at the

Table 4.3 Main applications of alpha radioactive sources in nuclear instrumentation

Principle	Application	Features and uses
Ionization	Static eliminator	Eliminate static electricity on the surface of the object without a power supply and auxiliary facilities
	Negative ion generator	Generate ions without high-frequency discharge
	Radioactive lightning rod	Expand the scope of lightning protection
	Discharge ionization source in electronic devices	Increase the working stability of electronic devices and prolong the service life
	Ion smoke detector	Fire alarm
	Electronic capture evaluator	Analysis of gas components
Excitation	Ultra-low-energy X-ray generator	Generate ultra-low energy (several keV) quantized X-rays, X-ray fluorescence analysis of low atomic number materials
Absorption	Alpha transmission thickness gauge	Measure the thickness of the thin layer material
	Dew point meter	Measure dew point
	Gas pressure gauge, density meter	Measure gas pressure and density

same time, i.e., beta-gamma emitters, which brings inconvenience to the utilization of beta rays.

The radionuclides currently used for beta source preparation include ^{3}H, ^{14}C, ^{32}P, ^{60}Co, ^{85}Kr, ^{90}Sr, ^{90}Y, ^{204}TI, ^{147}Pm, ^{63}Ni, ^{22}Na, etc., among which ^{3}H, ^{14}C, ^{90}Sr, etc. are commonly used pure beta emitters.

^{3}H has a long half-life of 12.35 a. The maximum energy of beta particles emitted by ^{3}H is 18.6 keV, and the average energy is 5.7 keV. It has the advantages of low energy, no gamma-ray emission, and high specific activity, which is often adsorbed on metal titanium or zirconium for utilization. But unfortunately, it is relatively expensive.

^{14}C has a half-life of 5730 a. It emits beta particles with a maximum energy of 156.467 keV. Since the range of beta particles emitted by ^{14}C in the air is about the same as that of the alpha particles emitted by ^{239}Pu, ^{14}C and ^{239}Pu are sometimes used as a mixed radioactive source of alfa and beta sources.

Table 4.4 lists the main applications of beta radioactive sources in nuclear instrumentation.

Among all beta sources, ^{90}Sr is relatively easy and cheap to obtain. It has the advantage that the beta particle emitted has high average energy and shows a wide flat part on the energy spectrum curve.

Table 4.4 Major applications of beta radioactive sources in nuclear instrumentation

Principle	Application	Radioactive source	Uses
Ionization	Static eliminator	^{3}H, ^{147}Pm, ^{85}Kr, ^{90}Sr	Eliminate static electricity from object surfaces and dust
	Discharge ionization sources in electronic devices	^{3}H, ^{14}C, ^{63}Ni	Increase the stability of electronic device work and prolong the service life
	Ion smoke detector	^{63}Ni	Fire alarm
	Electron capture evaluator	^{3}H, ^{63}Ni	Analysis of gas components
Excitation	Bremsstrahlung source	^{3}H, ^{147}Pm, ^{85}Kr, ^{90}Sr	Generate secondary X-rays
Radiation effect	Medical applicator	^{90}Sr	Treat skin diseases
	Irradiator	^{90}Sr	Chemical coating polymerization, breeding, stimulating growth
Absorption	Isotope transmission instrument	^{147}Pm, ^{85}Kr, ^{90}Sr, ^{106}Ru, ^{204}Tl	Measure material thickness, density, and material level
Scattering	Isotope backscatter meter	^{147}Pm, ^{90}Sr, ^{106}Ru, ^{204}Tl	Measure coating thickness and pipe wall thickness

In actual work, in order to solve certain problems, beta sources with a specific energy spectrum are often needed. But sometimes no beta source can just emit this energy spectrum. In this case, the method of mixing several beta radionuclides in a certain proportion can be used to obtain a mixed source that meets the need.

(3) Gamma radioactive sources

Most radioisotopes emit several groups of gamma rays with different energies at the same time, only very few of them can emit gamma rays of a single energy. Gamma radioactive sources emitting multiple groups of different energies can be used as both high-energy gamma radioactive sources and low-energy gamma radioactive sources. When only high-energy gamma rays are needed, an absorption sheet can be added to the source so that the low-energy rays can be absorbed. On the contrary, when only low-energy gamma rays are required, the counts of high-energy gamma rays can be eliminated by using a single-channel pulse height analyzer. Generally speaking, considering the cost of use and ease of operation, when low-energy gamma rays are needed, it is better to directly select a low-energy gamma-ray source.

Radionuclides that are commonly used to prepare gamma radioactive sources include ^{60}Co, ^{137}Cs, ^{192}Ir, ^{170}Tm, ^{241}Am, ^{169}Yb, ^{238}Pu, ^{55}Fe, etc.

The application of gamma radioactive sources in nuclear instrumentation is shown in Table 4.5.

Table 4.5 Major applications of gamma radioactive sources in nuclear instrumentation

Principle	Application	Radioactive source	Feature
Absorption	Nuclear instrumentation that measures thickness, density, material level, and weighing	^{137}Cs, ^{60}Co, ^{170}Tm, ^{241}Am	Non-contact measurement and fast
	Radiation flaw detection	^{192}Ir, ^{137}Cs, ^{60}Co, ^{170}Tm	Simple and accurate
Scattering	Logging	^{137}Cs, ^{60}Co	Simple and fast
	Measuring tube wall thickness and coating thickness	^{137}Cs, ^{60}Co, ^{241}Am	Simple and non-contact measurement
Radiation effect	Radiation breeding, radiation preservation, sterilization, disinfection, radiation processing, tumor treatment	^{137}Cs, ^{60}Co	Good effect, simple operation, and maintenance
Photovoltaic, trigger secondary X-ray effect	X-ray fluorescence analysis	Low energy photon source	Non-destructive, fast

(4) Neutron sources

The equipment that can generate neutrons is called a neutron source. The main applications of neutron sources in nuclear instrumentation are shown in Table 4.6. Most neutron sources produce neutrons through nuclear reactions. According to the incident particles that bombard the target nucleus, the types of reactions that generate neutrons mainly include (α, n), (p, n), (d, n), etc. Neutron sources produced by (α, n) reaction have low intensity, which cannot meet the needs of strong sources. In this case, a neutron generator can be used. It uses protons or deuterons produced by light proton accelerators or deuteron accelerators (which can be easily started and shut down) to obtain neutrons through (p, n) reaction or (d, n) reaction. The neutron generator can provide a fast neutron beam with high intensity and single energy, and the intensity of the neutron beam can be adjusted at will.

In addition to the above methods for obtaining neutrons, some transplutonium elements have also been found to have the property of spontaneous fission, the neutrons emitted during fission can also be used for the preparation of neutron sources. Among them, ^{252}Cf is the most remarkable. One gram of ^{252}Cf can emit 2.34×10^{12} neutrons every second, which is comparable to a low flux (about 10^{12} cm^{-2} s^{-1}–10^{13} cm^{-2} s^{-1}) reactor. Its volume is less than 1 cm^3, which is smaller than the size of the (α, n) reaction neutron source mentioned above, and it is particularly suitable for making a point source. In the past, such spontaneous fission neutron sources were relatively expensive because they were difficult to produce. At present, the production technology of ^{252}Cf spontaneous fission neutron sources from microgram level to several hundred micrograms level (which can be used for nuclear instrumentation) has been mature and commercialized.

(5) "Composite" radioactive sources

The so-called "composite" radioactive source is the source that can produce more than one kind of particle. For example, ^{252}Cf is a composite source of neutrons and gamma rays, which has the advantages of high yield and high neutron emission rate (10^6 μg^{-1} s^{-1}). This is incomparable to any other isotope neutron source. In many countries, ^{252}Cf has gradually replaced the (α, n) reaction neutron source. It is mainly used in isotope industrial instrumentation (e.g. neutron moisture meter, compensated neutron logging tool, etc.) for neutron activation analysis, neutron radiography, and multi-parameter joint measurement. However, the price of this kind of instrumentation is still relatively high.

Table 4.6 Major applications of common neutron sources in nuclear instrumentation

Commonly used neutron sources	Detection items	Uses
^{210}Po–Be ^{238}Pu–Be ^{239}Pu–Be ^{241}Am–Be ^{242}Cm–Be ^{252}Cf	Thickness, material composition, liquid level, temperature, flow rate, etc.	Measurement of water content, elemental analysis of materials, exploration of petroleum and solid minerals

3. **Preparation of radioactive sources**

Many methods can be used to classify radioactive sources. Based on the type of rays emitted by radionuclides, they can be divided into alpha sources, beta sources, gamma sources, neutron sources, etc. According to the use, they can be divided into instrumentation sources, medical sources, standard sources, scale sources, etc. Considering the preparation method of the source, they can also be divided into powder metallurgy sources, enamel ceramic sources, electroplating sources, gas sources, etc. The mainstream classification method is to divide radioactive sources into sealed sources and unsealed sources. Normally, the radioactive sources applied in nuclear instrumentation are sealed sources, while unsealed sources are meaningful only in rare cases. Therefore, the radioactive sources generally involved are sealed sources.

When designing and preparing radioactive sources, it is necessary to consider whether the radiation type, energy, and intensity of the source can meet the requirements of use, as well as the efficiency of the useful radiation and the safety performance. Based on these principles, the radionuclides used can be determined, and the preparation process can be determined according to the physical and chemical properties of the radionuclide and the requirements of use.

(1) Basic principles of radioactive source design

The basic principles of radioactive source design are high safety, high applicability, and high radiation emissivity.

The safety of radioactive sources is the fundamental guarantee of their applicability, which depends on the process of source production and suitability of use. The International Organization for Standardization has specially formulated the ISO-2919 recommended standard for this purpose, which specifies the quality requirements and safe use of sealed radioactive sources, and provides an objective basis for the safety design of radioactive sources.

When designing and preparing the radioactive sources, the radiation intensity of the source and the amount of radioactive substance used should be reduced as much as possible on the premise of ensuring the availability of the source. This will also improve the safety of the source in use. In some countries, regulations have been formulated to restrict the use of high-activity radioactive sources and encourage the use of low-activity sources. In addition, stipulating the service life of radioactive sources is also an important aspect to ensure safety.

The applicability of the radioactive source includes radiation type, energy, radiation intensity, and size of the source. These properties mainly depend on the type and content of radionuclides in the source and the preparation process of the source. Of the more than 2000 radionuclides that have been discovered, only more than one hundred can be used to prepare radioactive sources, while only 40–50 are commonly used. These nuclides include alpha, beta, gamma, and spontaneous fission radionuclides. The radionuclide selected for the preparation of radioactive sources should have a long half-life, high specific activity, applicable radiation type and energy, as

well as being inexpensive and easy to obtain. In addition, undesired radiation should not affect the use of the source.

The radiation emissivity of a radioactive source is the proportion of effective radiation emitted when radionuclides decay in the source. When designing the radioactive source, it is required that this ratio should be as high as possible to improve the efficiency of the radioactive source. At the same time, this is conducive to reducing production costs, saving raw materials, and improving safety.

(2) Basic parameters of radioactive sources

For the user of radioactive sources, the following basic parameters are of great significance: radiation type, radiation energy, radiation intensity, activity of radionuclides, size of the external structure of the source, service life of the source, and cost of the source.

(3) Preparation of radioactive sources

The preparation of the radioactive source mainly includes the preparation of the active block in the radioactive source core, the sealing of the source core, and the quality inspection of the product source. The type of rays emitted by radionuclides, and the physical and chemical properties of radionuclides can all determine the preparation method of radioactive sources. After years of development, the main technologies for preparing radioactive sources include enamel ceramic method, glass method, powder metallurgy method, electrochemical method, direct activation method, adsorption method, etc., and other less commonly used methods such as vacuum sublimation method and electric sputtering method, etc.

① Ceramic, enamel, glass method

Mix the oxides of radionuclides with ceramic, enamel, glass, and other auxiliary materials. Then, place the mixed material into the mold and press it into shape. By high-temperature sintering, the material can be made into ceramic, enamel, and glass disc or cylinder containing radionuclides to obtain radioactive active blocks. Many methods can be used to prepare ^{137}Cs sources, one of which is the glass method. The ^{90}Sr–^{90}Y source can be prepared by the ceramic method. When preparing gamma sources and high-energy beta sources, radionuclides are usually mixed into the surface glaze rather than directly mixing the radioactive substance with ceramic, enamel, and glass. This is because the absorption of radiation in the active area can be minimized by this method.

For example, ^{137}Cs sources can be used for thickness gauges, level meters, density meters, and nuclear scales, which can be prepared by the glass method. Add ^{137}Cs into the raw glass and sinter the material into the glass body. Seal the source core in the double-layer stainless steel ($CrNi_{18}Ti_9$) source shell with argon arc welding. Its structure is shown in Fig. 4.2.

Due to the use of ceramic, enamel, and glass, the prepared radioactive sources have the advantages of high-temperature resistance and radiation resistance.

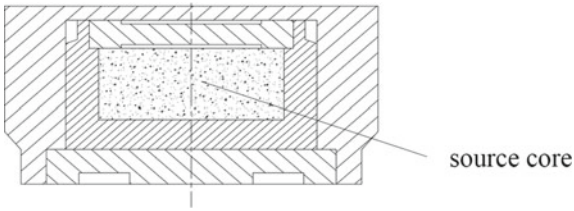


Fig. 4.2 Schematic diagram of the ^{137}Cs gamma source structure

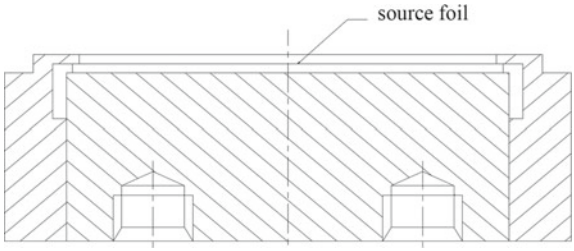


Fig. 4.3 Structural diagram of the ^{147}Pm radioactive source

② Powder metallurgy method

^{147}Pm and ^{241}Am can be made into powders in the form of stable oxides or other compounds, such as $^{147}Pm_2O_3$, $^{241}Am_2O_3$, and other stable compounds. When preparing the powder, adding alkali solution to the acidic solution containing Pm or Am to control the pH of the solution and the settling speed of hydroxide is conducive to the preparation of smaller and more uniform particles. Mix the particles with gold or silver powder, and sinter the mixed material into a blank. Clamp the blank in the metal material and roll it into a foil source. Generally speaking, the thickness of the source is 0.1–0.2 mm, and the length is more than 1 m. The rolled foil source strip should be sheared according to actual needs, and cold welding is required at the notch. Sometimes, a protective film is necessary to fix the foil source in the source holder. Figure 4.3 is a structural diagram of a typical ^{147}Pm source.

③ Electrochemical method

Electrochemical methods include electroplating (including molecular plating) and co-electrodeposition. The electroplating method is to prepare radioactive materials into the electroplating solution. The radioactive metal ions contained in the electroplating solution move to the cathode under an appropriate voltage and are reduced to the metal on the cathode surface, or deposited on the cathode surface in the form of a compound, becoming a radioactive source. The quality of the radioactive source depends on the composition, property, and temperature of the plating solution, as well as current density, plating voltage, etc. The radionuclides used for electroplating are mainly ^{235}U and ^{63}Ni.

The co-electrodeposition method is to add Au or Ag to the aqueous solution containing Am, Pu, or U so that Am, Pu, or U can be co-deposited on the cathode surface to prepare a standard source or calibration source with a high specific activity.

④ Direct activation method

^{60}Co and ^{192}Ir radioactive sources are generally prepared by the direct activation method. The method is to directly process metal cobalt and iridium into the final shape of the source such as needle, plate, disc, cylinder, etc. by machining. After cleaning the greasy dirt and oxides, dry the material, put it into the aluminum barrel, weld and seal it, and put it into the reactor for irradiation after leakage detection. According to the activity requirements of the product source, the irradiation time can be determined based on the theoretical calculation and the specific parameters of the reactor. Place the material in the channel with high thermal neutron flux for irradiation. After irradiation, the radioactive source can be made after cooling, cutting, cleaning, drying, assembling, welding and sealing, leakage detection, and quality inspection.

⑤ Chemical adsorption and replacement

A typical radioactive source prepared by this method is the ^{125}I seed source for medical brachytherapy. The process is to adsorb ^{125}I onto a source core made of silver wire, iridium wire, or ceramic beads, and then seal the source core in a titanium tube. Two common methods for the silver wire to adsorb ^{125}I include direct adsorption of ^{125}I by silver wire and oxidizing and chlorinating the silver wire with hydrogen peroxide and hydrochloric acid system before adsorbing ^{125}I. However, these two methods have the disadvantages of long adsorption time and limited adsorption capacity. In order to overcome these problems, the silver wire can be specially treated to enhance the adsorption capacity for ^{125}I (Fig. 4.4).

⑥ Preparation of gaseous radionuclide sources

Some radionuclides such as ^{85}Kr exist in a gaseous state, and special processes are required for the preparation of radioactive sources. The standard structure and main process of the ^{85}Kr source are labeled in Fig. 4.5. The main process is to vacuum the container that has a source window and filled it with ^{85}Kr gas. Then, sealing, welding, and leakage detection will be done to produce the ^{85}Kr source. In addition,

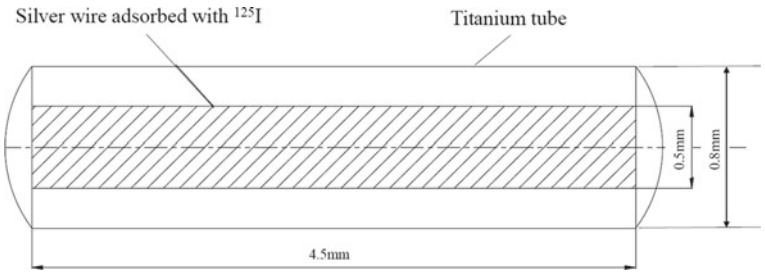


Fig. 4.4 Schematic of a standard ^{125}I seed source structure

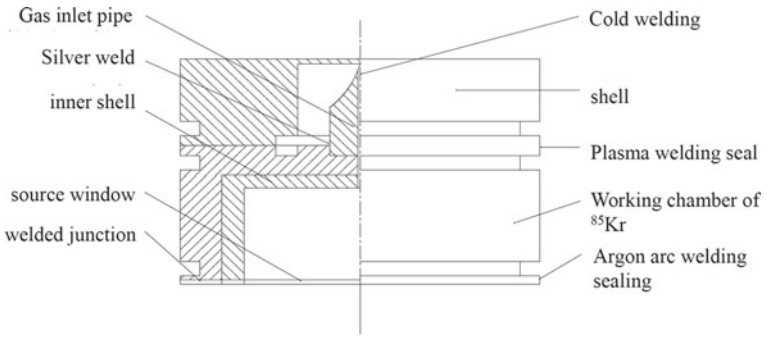


Fig. 4.5 Standard ^{85}Kr source structure schematic and main process labeling diagram

^{85}Kr can also be adsorbed on activated carbon to prepare a radioactive source with high specific activity and small volume.

⑦ Other methods

There are other methods for preparing radioactive sources, such as organic synthesis and vacuum evaporation sublimation. The preparation of ^{3}H, ^{14}C, ^{15}N, and other radioactive sources is through the organic synthesis method, that is, first prepare the organic thin film, and then prepare the film into the standard source and the radioactive source. The operation process of the vacuum evaporation sublimation method is to heat and evaporate the radionuclide in a vacuum, sublimate it to the substrate with a lower temperature, and become radioactive sources.

4. **Radioactive sources in several types of nuclear instrumentation**

(1) Transmission nuclear instrumentation

The transmission nuclear instrumentation places the source chamber and the detector on both sides of the substance to be measured. When the incident ray penetrates a substance, the intensity of the ray decreases. At this time, the detector can measure the radiation counting rate (or dose rate) after penetrating the substance, so as to detect the macroscopic non-electrical parameters of the substance to be measured. Through an exponential decay formula (to be introduced in Sect. 4.4), the density and thickness of the substance through which the rays pass can be obtained. This type of instrumentation mainly includes density meters, thickness gauges, level meters, etc.

The activity of beta sources used in transmission nuclear instrumentation is usually in the range of 40 MBq–40 GBq, while the activity of gamma sources is usually in the range of 0.4–40 GBq. Radioactive sources commonly used in transmission instrumentation are shown in Table 4.7.

Table 4.7 Radioactive sources commonly used in transmission nuclear instrumentation

Radioactive source	Type of ray	Application
^{147}Pm	β^-	Density of paper
^{85}Kr	β^-	Thickness of paper
$^{90}Sr/^{90}Y$	β^-	Thickness of metal sheet; tobacco content in cigarettes
^{60}Co	γ	Contents of coke ovens, brick kilns, etc.
^{55}Fe	x	Steel plates thinner than 20 mm, liquid level in cans
^{241}Am	γ	Steel plates thinner than 10 mm, contents of the bottle
^{137}Cs	γ	Steel plates thinner than 100 mm, contents of pipes and tanks

Table 4.8 Radioactive sources commonly used in scattering nuclear instrumentation

Radioactive source	Type of ray	Application
^{147}Pm	β^-	Density of paper, thin metal coating
^{201}Tl	β^-	Thickness of thin rubber and textiles
$^{90}Sr/^{90}Y$	β^-	Thicknesses of plastic, rubber, glass, and thin light alloy
^{241}Am	γ	Glass thinner than 10 mm and plastic thinner than 30 mm
^{137}Cs	γ	Thickness of glass over 20 mm, rock, and coal
^{241}Am–Be	n	Hydrocarbons in rocks

(2) Scattering nuclear instrumentation

The so-called scattering nuclear instrumentation is to place the source chamber and the detector on the same side of the substance to be measured. Commonly used scattering nuclear instrumentation includes hygrometer, highway nucleometer, and porosity nucleometer. In scattering imaging, since the radiation source and the detector are on the same side of the workpiece, the Compton scattering line scattered from the object can be measured, and the information about the detected object can be obtained from the change in the radiation intensity.

The activity of beta sources used in scattering nuclear instrumentation is usually in the range of 40–200 MBq, and the activity of gamma sources can reach 100 GBq. Commonly used radioactive sources in scattering nuclear instrumentation are shown in Table 4.8.

4.3.2 Detectors

The detector is also a key component of nuclear instrumentation. Its role is to convert the nuclear radiation that enters it and has a functional relationship with the measured parameters into an electrical signal. A functional relationship still exists between this electrical signal and the measured parameters and will be transmitted to the next level circuit. There are usually four main performance indicators used to measure the radiation detectors:

(1) Detective quantum efficiency. Detective quantum efficiency refers to the ratio of the number of photon events generated by photons and detectors in the initial process of action to the number of incident photons. It describes the ability of the detector to receive and record information. Incident photons may penetrate or be reflected by the medium. Sometimes, the medium needs to absorb several photons to cause a photon event, and sometimes the generated photon event is not detected, so the quantum efficiency of a detector is generally less than one.
(2) Responsiveness. Responsiveness, also known as sensitivity, is equal to the ratio of the output signal of the detector to the incident radiation power. When the radiation power increases, the output signal increases proportionally. Such detectors are called linear detectors, otherwise, they are non-linear detectors.
(3) Spectral response. Spectral response is also known as spectral sensitivity, which refers to the sensitivity of the detector when monochromatic radiation is applied. It is used to characterize the response characteristics of the detector to different wavelengths of radiation. The detector whose spectral response varies with the wavelength is called a selective detector, and conversely, it is called a non-selective detector. The spectral response in units of the response at the most sensitive wavelength of the detector is called the relative spectral response.
(4) Detectivity. The detectivity is equal to the reciprocal of the minimum radiated power that can be detected by the detector. Any detector has noise, signal that is smaller than the average value of noise fluctuation cannot be detected. The radiation power required to generate a signal as large as the noise is called the minimum radiation power that the detector can detect, or the noise equivalent power. Sometimes, detectivity can be used to describe the sensitivity of the detector.

Traditionally, detectors are divided into scintillation detectors, gas detectors, and semiconductor detectors. Commonly used detectors include:

① Scintillation detector: sodium iodide single crystal scintillation counter, plastic scintillation counter, liquid scintillation counter, etc.
② Gas detectors: ionization chamber, proportional counter, Geiger-Müller counter, etc.
③ Semiconductor detectors: HPGe (high purity germanium detector), etc.

1. **Scintillation detector**

The interaction between rays and matter will excite the medium atoms. When these excited atoms are deexcited to their ground state, they will emit light pulses, which is called scintillation. The device for detecting nuclear radiation based on this phenomenon is called a scintillation detector. In the early twentieth century, Rutherford had already used this detection method to complete the experiment of observing the scattering of alpha particles by foils composed of different elements, and successfully established the nuclear structure model of the atom. However, the scintillation detector used by Rutherford at that time was only a ZnS powder screen, which could only know the number of nuclear radiation particles hitting the ZnS

screen, but could not detect the energy of alpha particles, nor could it determine that the incident particles were alpha particles.

Although the same physical processes can be seen in both old and modern scintillation detectors, due to the great progress of science and technology, modern scintillation detectors have undergone fundamental changes in many aspects. They can be used not only to determine the existence and intensity of nuclear radiation but also to detect the energy or energy distribution of incident particles and even to identify the types of particles. Nowadays, scintillation detectors have become one of the most effective and widely applicable nuclear radiation detectors, which can be used in almost every situation and for the detection of various nuclear radiation.

At present, scintillation detectors are widely used in level meters, density meters, thickness gauges, and X-ray instrumentation. In the late 1970s, companies in West Germany, the United States, and Japan successively solved the stability problem of scintillation counters, making a breakthrough in the accuracy of scintillation detectors and reaching the technical level of the constant temperature ionization chamber. In recent years, the plastic scintillation counter has also made great progress. The improved plastic scintillator can shorten the scintillation decay time to 1 ns, which is especially suitable for the measurement of high counting rates (10^{-10} s^{-1}) and has been widely used for thickness measurement and level detection of industrial rolling material.

A scintillation counter is composed of a scintillator and photomultiplier tubes. The scintillator is a substance that can convert the energy of rays into light energy. The photomultiplier tube has two functions: one is to it receive the photons emitted by the scintillator and convert them into electrons, and the other is to multiply and amplify these electrons into measurable pulses. The photomultiplier tube consists of three parts: photocathode, dynode, and anode. With the aid of the voltage divider, a voltage of several tens to more than one hundred volts will be applied between the photocathode and the first dynode, between each dynode, and between the last dynode and the anode.

The working principle of the scintillation counter is that when the ray enters the scintillator, it directly or indirectly excites the molecules or atoms of the scintillator. When these excited molecules or atoms return from the excited state to the ground state, they emit photons. These photons generated by the scintillator are collected by the photocathode of the photomultiplier tube, from where photoelectrons are emitted. These photoelectrons are accelerated when passing through the electric field between the photocathode and the first dynode in the photomultiplier tube. Each electron emits several electrons on the first dynode, and these electrons are again accelerated by the electric field between the first dynode and the second dynode. Each electron emits several electrons on the second dynode…. This process continues, multiplying dynode by dynode. Finally, the electrons are collected by the anode of the photomultiplier tube. The anode collects a large number of electrons so that a current pulse flows through the load resistance and generates a voltage pulse. This voltage pulse is recorded by the connected electronic circuit, and the intensity of the rays can be known from the measured pulse count rate.

A good photomultiplier tube should have the following indicators:

① The photocathode should have high sensitivity.
② The spectral response of the photocathode and the spectral characteristics of the scintillator should have a good fit.
③ The linear range of the photocathode should be large.
④ Should with small background pulses and dark current.
⑤ The flight time of the electron should be short and the fluctuation should be small.
⑥ The stability and reproducibility of each parameter of the photomultiplier tube should be good.
⑦ Should withstand large luminous fluxes, and the sensitivity should not vary with load.
⑧ Should have poor sensitivity to electromagnetic fields and strong radiation fields.

As some indicators are mutually restricted, it is almost impossible to fully meet the above eight indicators. Therefore, the configuration should be optimized according to the actual needs to select the appropriate photomultiplier tube.

2. **Gas detectors**

Gas detectors belong to a very old type of detectors, which have some outstanding advantages that cannot be replaced by other detectors, including almost unlimited size and shape, no nuclear radiation damage, very easy to recover, economic and reliable operation, etc. Although there was a tendency to be replaced by scintillation detectors and semiconductor detectors, gas detectors have made great progress since the 1970s, and are widely used in the studies of high energy physics and intermediate energy heavy ion nuclear physics.

Gas detectors usually include three types of detectors in different operation states: ionization chamber, proportional counter, and Geiger-Müller counter. The common feature of these detectors is that they obtain information about nuclear radiation by collecting the electron-positive ion pairs generated when the rays pass through the working gas. Among these three types of gas detectors, ionization chambers have developed relatively rapidly, and many types of ionization chambers have been successfully developed. For example, the types used for density meters are mostly constant temperature ionization chambers, new titanium alloy constant temperature ionization chambers that are portable, drift-free, and have high detection efficiency, high-pressure ionization chambers, and vacuum ionization chambers.

An ionization chamber is essentially formed by installing a pair of mutually insulated electrodes in an inflatable container. The operating state of the ionization chamber can be divided into two categories. One is to measure single incident particles one by one, which is called a pulse ionization chamber. The other is to measure the average effect of a large number of incident particles, which is called a current ionization chamber. The output signal of the pulse ionization chamber is amplified, recorded, and analyzed by the pulse amplifier and corresponding instruments, while the output signal of the current ionization chamber is measured by the direct current amplifier.

Currently, pulse ionization chambers are mainly used to measure neutrons. An example of a pulse ionization chamber for measuring neutrons is a fission ionization

chamber. It is characterized in that fissionable material is coated on the inner side of the electrode. When neutrons are incident, neutrons and nuclei of fissionable materials undergo fission reactions, and the generated fission fragments will ionize the gas. Due to the large energy of fission fragments, a large number of positive and negative ions can be generated, and therefore a large pulse can be output.

Compared with the current ionization chamber, the pulse ionization chamber has no fundamental difference in the mechanism of generating output signals. However, significant differences can be seen in the range of measurable radioactivity, the selection of output circuit parameters, and the support structure of the internal electrode in the ionization chamber. It is because of these differences that the current ionization chamber can measure the average effect of a large number of incident particles, while the pulse ionization chamber can only measure the effect of a single incident particle.

The current ionization chamber is widely used. It can measure the intensity of various types of nuclear radiation, which has a wide range of measurements, high stability, and long service life. However, it has the disadvantage that it is difficult to produce. A qualified current ionization chamber must be produced according to the specific use conditions, and the electronic circuits are also complex.

The Geiger-Müller counter was used in intensity instrumentation such as the level switch, which is currently being phased out.

3. **Semiconductor detectors**

The design of semiconductor detectors is also based on the ionization effect of nuclear radiation in the medium. Its working principle is very similar to an ionization chamber with a solid medium. Since the late 1950s, the application of semiconductor detectors has revolutionized the measurement of nuclear radiation. Whether for charged particles or gamma rays, compared with gas detectors and scintillation detectors, the energy resolution achieved by semiconductor detectors can be improved by 1–2 orders of magnitude. The fundamental reason is that in semiconductor materials such as Si and Ge, the average energy loss of an electron–hole pair generated by nuclear radiation is only 3–5 eV. In contrast, the corresponding physical quantity in the gas detector is about 30 eV, while that in the scintillation detector is about 300 eV. In addition, the semiconductor detector has good output linear response, small volume, fast response, and very convenient and flexible use, and the external electromagnetic field has little impact on its operation. Semiconductor detectors are widely used in almost all fields related to nuclear radiation measurement, mainly for γ-ray detection, X-ray fluorescence analysis, etc., which can realize the rapid qualitative and quantitative analysis of material composition and energy spectrum measurement. However, because the sensitive volume of the semiconductor detector is limited (100 cm^3), it cannot completely replace the gas detector and the scintillation detector. This limits its application in the detection of high-energy nuclear radiation and the need for large detecting solid angles. In addition, its sensitivity to radiation damage also greatly limits its service life.

4.4 Application of Nuclear Instrumentation

Since the introduction of γ-ray density meters, thickness gauges, and level meters at the first International Conference on Nuclear Energy in the 1950s, neutron moisture meters and nuclear scales have been rapidly added to the nuclear instrumentation team. These five types of instrumentation all belong to the intensity nuclear instrumentation, which has been widely used in industry, agriculture, and water conservancy projects. Subsequently, image-based industrial CT and radiation imaging instrumentation were developed, and energy spectrum nuclear analytical instrumentation such as X-ray fluorescence analyzers and activation analysis instrumentation, which are mainly used for nuclear logging and material activation analysis. Taking activation analysis as an example, since the 1950s, it has been used to solve analytical problems in the atomic energy industry and ultrapure materials. In the 1970s, activation analysis was applied to military, environmental science, biology, medicine, archaeology, and other fields on a large scale. The principles and applications of X-ray fluorescence analysis and activation analysis will be introduced in Chap. 7.

In recent years, as an advanced means of obtaining information, nuclear instrumentation has been combined with electronic computers that can efficiently process information, which greatly improves its level of performance. This has made valuable contributions to promoting the technological transformation and technological progress of the world's traditional industries, realizing the on-site real-time control and production automation of industrial processes, and has achieved remarkable social, economic, and environmental benefits.

This section will introduce the working principles and use of several common nuclear instrumentations in detail.

4.4.1 Intensity Nuclear Instrumentation

Intensity nuclear instrumentation mainly refers to level meters, nuclear scales, thickness gauges, density meters, concentration meters, etc. The principle is that when the gamma-ray generated by the radioactive source passes through the substance to be measured, the rays will be absorbed by the medium with different heights, thicknesses, densities, and concentrations, and the intensity of the rays will be attenuated due to absorption. The thicker the thickness, the higher the density, and the higher the concentration, the greater the attenuation of γ-rays. The γ-ray passing through the object will be received by the detector, which converts the received ray into the electrical pulse signal proportional to the height, thickness, density, and concentration of the substance and send it to the host machine. In this way, the corresponding information such as the level, thickness, density, concentration, etc. in the container can be accurately obtained.

The intensity nuclear instrumentation obeys the following exponential decay law:

$$I = I_0 e^{-\mu\rho d} \tag{4.1}$$

where

I the intensity of rays after passing through the substance.
I_0 the intensity of the ray before passing through the substance.
ρ the density of the substance.
d the thickness of the substance through which the ray passes.
μ mass absorption coefficient of the substance.

The mass absorption coefficient μ of the substance depends not only on the type of the radioactive source but also on the nature of the substance (atomic number or effective atomic number), that is, μ depends on the energy of the ray E and the atomic number of the substance been penetrated Z (Z_{eff}). To simplify the calculation, μ can be regarded as a constant for a given radioactive source. If the radioactive source and the path of ray absorption are unchanged, the measured value is only related to the density and thickness of the unit material, and all other physical properties such as pressure, temperature, viscosity, color, etc. do not affect the measured value. Therefore, this method of measuring radiation is very reliable.

1. **Level meter**

The level meter mainly uses the Compton scattering effect of the interaction between the gamma rays generated by the radioactive source and the substance. In the Compton effect, gamma photons collide inelastically with the electrons outside the nucleus of the atom. Part of the energy is transferred to the electrons, making them break away from the atom and become recoil electrons, and the energy and motion direction of the scattered photons change. The Compton effect always occurs on the outer electron with the most loosely bound, and the binding energy of the outer electrons can be completely ignored compared with the incident gamma energy. So, the outer electrons can be regarded as "free electrons". In this way, according to the conservation of energy and momentum of the theory of relativity, the energy of scattered photons can be obtained as:

$$E'_\gamma = \frac{E_\gamma}{1 + \frac{E_\gamma}{m_0 c^2}(1 - \cos\theta)} \tag{4.2}$$

where

E'_γ the energy of scattered photons.
E_γ the energy of incident photons.
θ the angle between the directions of the scattered photon and the incident photon, which is called the scattering angle.
m_0 the static mass of the electron.
c speed of light.

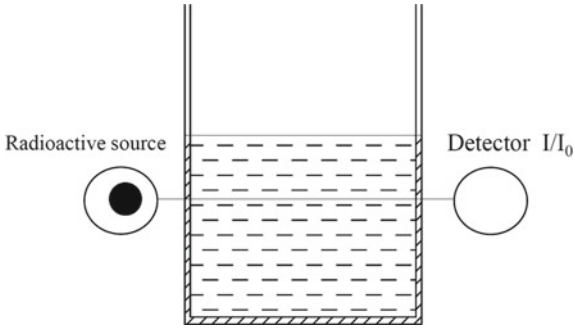


Fig. 4.6 Measurement principle of the level meter

When $\theta = 0°$, $E'_\gamma = E_\gamma$; when $\theta = 180°$, $E'_\gamma = \frac{E_\gamma}{1+\frac{2E_\gamma}{m_0c^2}}$.

The principle of measuring the level meter is shown in Fig. 4.6. When the liquid level drops to the level composed of the radioactive source and the detector, the count of the detector will suddenly change (generally increase), indicating that the liquid has dropped to the required height. In practical application, the system composed of the radioactive source and the detector can be moved up and down horizontally, and the container can also be moved up and down horizontally to achieve the purpose of measuring the level of the material.

This instrumentation can realize the non-contact online measurement of the liquid level in sealed tanks, silos, reactors, and other containers, which is independent of the physical and chemical properties of the materials to be measured in the containers. It is especially suitable for measurements in high temperature, high pressure, strong corrosion, high viscosity, crystallization, high dust, and other environments.

An actual radioactive material level measurement system is shown in Fig. 4.7, which mainly consists of a radioactive source, detector, container, and host machine. Among them, the radioactive source is an important part of the system, and the following two types of sources are usually used:

① ^{60}Co source. ^{60}Co has relatively high energy and is mainly used when the equipment wall is thick.
② ^{137}Cs sources. ^{137}Cs has lower energy of 0.661 meV, it has a better measurement effect than ^{60}Co, and is easy to shield, which is commonly used when the equipment wall is thin.

The detector is also an indispensable part of the system. Commonly used detectors include ionization chamber and scintillation detector.

① Ionization chamber. The ionization chamber has high firmness and reliability with a wide range of measurements.
② Scintillation detector. The scintillation detector has high sensitivity and low radioactive source dose. The "flexible" detector is a kind of scintillation detector. In addition to all the characteristics of the scintillation detector, it also has the

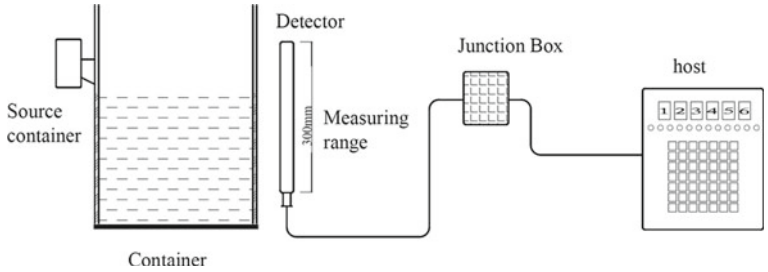


Fig. 4.7 Level meter measurement system diagram

feature of flexibility, a longer measuring range, and convenient installation, especially suitable for the measurement of irregular containers and environments with large measuring ranges.

In addition, the microprocessor as the host machine of the radioactive level meter is also an important feature. The microprocessor has a strong calculation function, continuous self-diagnosis function, and data protection function, with high accuracy and easy operation.

2. **Thickness gauge**

The two main methods used for detecting the thickness of a substance are the contact method and the non-contact method. The contact method is easy to scratch the surface of the substance. The traditional non-contact methods such as capacitive or infrared detection are easy to be affected by factors such as ash, moisture, and density of substances, leading to low accuracy. The radioactive thickness gauge measures the thickness of substances by absorbing or reflecting the rays. It can measure and control the thickness changes of wood, steel, glass, cloth, and other media online, independent of the physical and chemical properties of the substance. The material to be measured can be liquid, powder, granule, plate, etc., and the accuracy can reach 0.5%.

Radioactive thickness gauges can be divided into transmission thickness gauges and reflective thickness gauges according to the difference in principles. The principle of transmission thickness gauges is shown in Eq. (4.1) and Fig. 4.8. The principle of the reflective thickness gauge is relatively complex, the relationship curve between backscatter and measured thickness can be obtained from experiments. The general trend is that with the increase of the measured thickness, the backscattering intensity also increases, and then gradually reaches saturation. Before saturation, the measured thickness can be known as long as the backscattering intensity can be measured.

Radioactive thickness gauges include alfa thickness gauges, beta thickness gauges, gamma thickness gauges, X-ray fluorescence thickness gauges, etc. The rays are easily absorbed and scattered by the air, resulting in large interference. Therefore, the X-ray fluorescence method with the advantages of less interference, wide range, and high accuracy is more widely used than other methods.

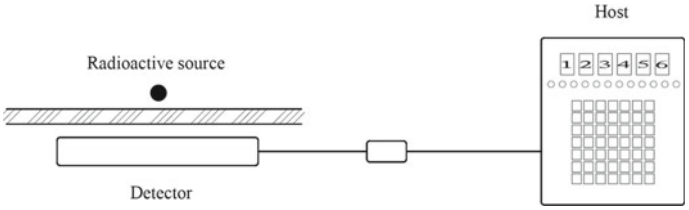


Fig. 4.8 Principle of the transmission thickness gauge

Three methods can be used for thickness measurement by X-ray fluorescence method: (1) emission: the radioactive source can excite the X-ray fluorescence of the surface layer, and the X-ray is directly recorded by the detector; (2) absorption: the source excites the X-ray fluorescence of the bottom layer, and the X-ray fluorescence is absorbed by the surface layer and then recorded by the detector; (3) backscattering: directly record the scattered rays of the primary rays of the radioactive source.

The measurement principles of the commonly used absorption and backscattering methods will be described below.

(1) Characteristic fluorescence absorption method

The characteristic X-rays of light elements (C, H, O, Si, Al, etc.) are not easy to be excited and detected, and they will not have a characteristic absorption effect on medium- and high-energy X-rays. Thus, the thickness of a thin layer of light material (such as paper) can be measured by the absorption of X-rays through the thin layer. In this case, the radiator may be an alloy containing Fe or Zn.

The measurement principle is shown in Fig. 4.9. After the primary rays of the radioactive source are absorbed by the thin layer, the elements in the radiator are excited, and the characteristic fluorescence is generated. The characteristic X-ray fluorescence generated by the radiator then passes through the substance and is recorded by the detector. The basic equation is

$$I_A = \frac{K I_0 C_A}{\frac{\mu_{02}}{\sin\alpha} + \frac{\mu_{22}}{\sin\beta}} \cdot e^{-\left(\frac{\mu_{01}}{\sin\alpha} + \frac{\mu_{21}}{\sin\beta}\right)d} \tag{4.3}$$

where

I_A the characteristic fluorescence counting rate recorded by the detector.
K constant of proportionality.
I_0 the counting rate of the primary rays of the source on the surface of the thin layer sample.
C_A the target element content of the characteristic X-ray fluorescence.
μ_{01} the linear absorption coefficient of the incident radiation by the thin layer.
μ_{02} the linear absorption coefficient of the incident radiation by the radiator.
μ_{21} the linear absorption coefficient of the characteristic fluorescence of the target element in the radiator by the thin layer.

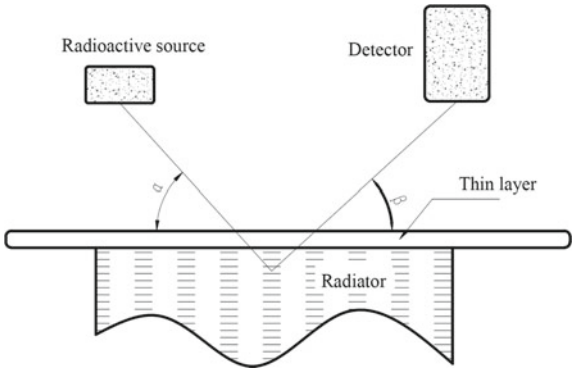


Fig. 4.9 Principle of thickness measurement by characteristic fluorescence absorption

μ_{22} the linear absorption coefficient of the characteristic fluorescence of the target element in the radiator by the radiator.
d thickness of the substance being measured.
α the incident angle of the primary ray of the source.
B the emergence angle of the characteristic fluorescence.

(2) Backscattering method

The measurement principle of the backscattering method is shown in Fig. 4.10, and the basic equation for the scattered ray counting rate is

$$I_S = \frac{K_s I_0 \sigma}{\frac{\mu_0}{\sin\alpha} + \frac{\mu_s}{\sin\beta}} \cdot \left[1 - e^{-\left(\frac{\mu_0}{\sin\alpha} + \frac{\mu_s}{\sin\beta}\right)d}\right] \tag{4.4}$$

where

I_s the counting rate of scattered rays recorded by the detector.
K_s constant of proportionality.

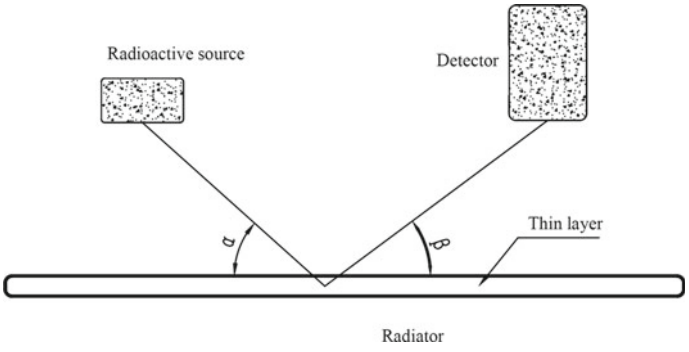


Fig. 4.10 Principle of thickness measurement by backscattering method

σ the total scattering cross-section of the scattered rays generated by the primary rays of the source produce in the sample being measured ($\sigma_{coherent}$ and $\sigma_{incoherent}$).
μ_0 the linear absorption coefficient of the incident radiation by the thin layer.
μ_s the linear attenuation coefficient of the scattered rays.
α the incidence angle of the primary rays of the source.
β the emergence angle of the scattered rays.

The other parameters are the same as Eq. (4.3).

3. **Nuclear scale**

The nuclear scale is a new type of online measuring device for bulk materials. It is a high-tech product combining modern nuclear technology and computer technology. Nucleon scales are widely used, especially suitable for various industrial sites with poor environmental conditions. The biggest feature of weighing materials by the nucleon scale is "non-contact". It is an ideal non-contact continuous weighing and measuring control equipment with high measurement and control accuracy and good long-term stability. It overcomes the measurement errors caused by mechanical variation (such as belt deviation, wear, tension change, material impact, etc.) of other weighing equipment.

Compared with electronic scales, nuclear scales have the following unique advantages:

① It is not affected by the temperature and corrosiveness of materials, nor by conveyor vibration, deviation, tension change, inertia force, impact of large materials, etc.
② It has high dynamic measurement accuracy and long-term stability.
③ It is simple in structure, convenient in operation and maintenance, and can be installed and maintained without dismantling or modifying the original conveying device or stopping production.
④ It has strong environmental adaptability and can work in harsh environments of high temperature, high dust, and strong vibration.
⑤ It has a wide range of applications. In addition to the belt conveyor, it can also be used for online measurement of the screw, link plate, and bucket conveyors.
⑥ It can make up for the shortcomings of electronic scales. Although the accuracy of the electronic scale can reach a very high level, its sensors are relatively delicate, the mechanical structure is complex, and the technical level of the operation and maintenance personnel required is high. In addition, electronic scales are mainly used for belt conveyors, which are difficult to be applied to other conveyors.

The world's leading nuclear scales are the products of Kayray of the United States and Berthold of Germany. Kayraw uses a point radioactive source for emission and a high-pressure gas-filled long ionization chamber for reception, while Berthold uses a linear radioactive source for emission and a scintillation detector for the reception.

(1) Basic principle of nuclear scales

The working principle of the nuclear scale is based on the fact that when the γ-ray passes through the medium being measured, the attenuation of its intensity obeys the exponential law, that is, when the energy of the γ-ray is constant, the attenuation of its intensity is exponentially related to the composition and density of the medium, and the thickness in the direction of the ray. Continuously measure the radiation intensity when the material is loaded, and compare it with that when the belt is empty (or other conveyors). At the same time, measure the running speed of the belt. Then, through the calculation of the computer system, the process parameters such as unit load, instant flow rate, and accumulation can be directly displayed online.

(2) Composition of nuclear scales

A nuclear scale is generally composed of a radioactive source (γ-ray source and protective lead tank), support, ionizing γ-ray detector, preamplifier, speed sensor, nuclear scale host system, etc. Its structure is shown in Fig. 4.11.

① Radioactive source: ^{137}Cs is generally used, which is characterized by a long half-life (30 a) and moderate radioactive energy (0.661 meV). The intensity of the radioactive source is generally around 3.7×10^9 Bq. The source sealed in the lead tank is installed on the support.

② Support: The function of the support is to firmly connect the gamma radioactive source and the scale body to ensure that no relative displacement occurs. The support generally adopts an A-frame, and its specific size depends on the length of the ionization chamber and site conditions.

③ Ionization chamber: The function of the ionization chamber is to convert the intensity of γ-rays into electrical signals proportional to it. The ionization chamber is a cylindrical container filled with inert gas, with two insulated electrodes, and a direct current voltage of about 500 V is applied between the two electrodes. When γ-rays are irradiated on the ionization chamber, high-energy secondary electrons will be released from the wall and the inert gas. The secondary electrons ionize the gas, forming the ionization current proportional to the intensity of the ray. The current, which is very weak, generally in the order of 10^{-9}–10^{-11} A, is converted to a voltage signal by the preamplifier. The ionization chamber is the core component of the nuclear scale, its performance directly affects the measurement accuracy of the whole instrument.

④ Speed sensor: The function of the speed sensor is to convert the speed of the belt into a voltage signal and send it to the host machine. Commonly used speed sensors include magnetoelectric induction pulse speed measuring motors, photoelectric speed sensors, and constant speed devices.

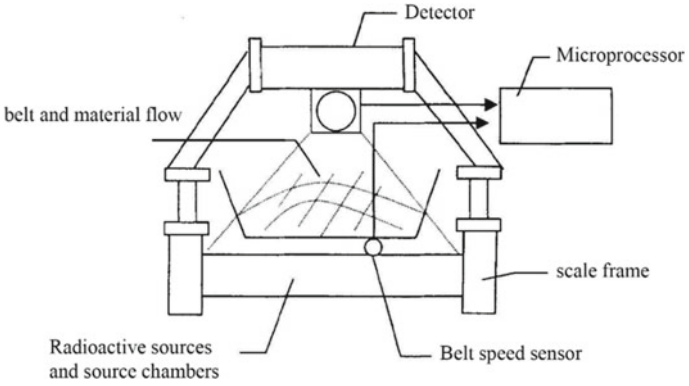


Fig. 4.11 Structural diagram of the nuclear scale. 1—Radioactive source and source chamber, 2—Scale frame, 3—Belt and material flow, 4—Detector, 5—Belt speed sensor, 6—Microprocessor

⑤ Host machine: In the early days, the host machine generally used the data processing and operation control device with the CPU as the core. In recent years, more and more manufacturers have directly adopted advanced industrial computers as the host machine, which are characterized by fast calculation, good anti-interference, convenient networking, and centralized control. Its function includes collecting signals from the ionization chamber and speed sensor for arithmetic processing, displaying and printing instantaneous flow of belt load, upper limit, lower limit, and fixed value alarm, digital display of flow, automatic empty belt identification, automatic calibration of the current source strength I_0 and related parameters, the output of analog and digital signals, with PID fixed value and proportional control, fault self-diagnosis. Besides, for the host machine, both one machine and one scale, and one machine and multiple scales can be realized.

(3) Example of the application of nuclear scales

Since different materials have different absorption coefficients of γ-rays, in theory, nuclear scales are only applicable to the measurement of the same material. But in actual production, nuclear scales have their special applications. For example, nuclear scales can be used to automatically control the proportion of mixed materials. Take the proportion of clinker, slag, and gypsum that needs to be controlled in the cement mill of the cement plant as an example, whose principle is shown in Fig. 4.12. Material A passes through the $1^{\#}$ scale, and the mixture of material A and B passes through the $2^{\#}$ scale. Material A and B are two different materials, and the flow rate

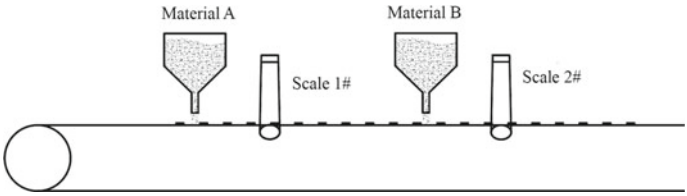


Fig. 4.12 Diagram of a batching equipment

and proportion of the two materials are variable. In this case, the instantaneous loads of the two materials can be measured respectively by the 1# scale and the 2# scale. The calculation is given in Eq. (4.5).

The measurement of F_A (instantaneous load of material A) is completed by the 1# scale:

$$F_A = K_{A1} \ln \frac{U_{A1}}{U_{o1}} \tag{4.5}$$

where

K_{Al} the load constant of material A in the 1# scale.
U_{Al} the signal voltage of the 1# scale after loading material A.
U_{ol} the null load voltage of the 1# scale.

The measurement of F_B (instantaneous load of material B) is jointly completed by 1# scale and 2# scale:

$$F_B = K_{B2} \cdot \left(\ln \frac{U_2}{U_{o2}} - \frac{K_{A1}}{K_{A2}} \ln \frac{U_{A1\Delta t}}{U_{o2}} \right) \tag{4.6}$$

where

K_{B2} the load constant of material B in the 2# scale.
U_2 the signal voltage of the 2# scale after loading materials A and B.
U_{o2} the null load voltage of the 2# scale.
K_{A2} the load constant of material A in the 2# scale.
$U_{A1\Delta t}$ the signal voltage of the 1# scale before Δt.
Δt the time taken for the materials to move from the l# scale to the 2# scale. If the material flow is relatively uniform, U_{A1} can also be used to replace $U_{A1\Delta t}$.

(4) Other applications of nuclear scales

In addition to weighing, nuclear scales have a wide range of applications, such as:

Mining and beneficiation: total ore mining, feeding capacity of crusher, concentrate metering, etc.

Chemical industry: metering of raw materials, dry slag, etc.
Cement: measurement and proportioning control of various raw materials in the kiln.
Papermaking: wood chip metering, continuous and batch digester feeding.
Food: grain conveyor feeding metering.
Coal: mining, coal preparation and feeding, coal handling measurement at wharf and port, coal blending for power generation, raw coal and clean coal measurement.
Steel: coal transportation and blending, beneficiation feeding, coke metering, etc.
Applicable conveyors: belt conveyor, scraper conveyor, chain feeder, vibrating feeder, etc.

4. **Density (concentration) meter**

The density (concentration) meter adopts the principle of gamma-ray transmission to measure and control the density, concentration, and interface changes of the liquid in the sealed tank or the pipeline online without contact. Because of non-contact measurement, density (concentration) meters can be widely used in pharmaceutical, oil extraction and refining, chemical industry, coal, metallurgy, water conservancy, food, and other industrial sectors, especially in high temperature, high pressure, harmful gas, explosive, high dust and other environments, which have obvious advantages over conventional instruments.

The density meter can determine the density of various fluids, semi-fluids, or mixtures, such as cement slurry, mortar, mineral slurry, and paper pulp, as well as the random density in the process of chemical and pharmaceutical products.

The concentration meter can determine the percentage concentration (or proportion) of solutions or mixtures such as pulp, slurry, mortar, beverage flotation agent, etc. When used in conjunction with the flow meter, the instantaneous mass flow and the cumulative amount of dry minerals can be easily calculated.

5. **Single photon bone mineral density meter**

The single photon bone mineral density meter is mainly used to measure the bone mineral content of human and animal living bodies. It can be used for early diagnosis, clinical diagnosis, and curative effect observation of osteoporosis caused by renal insufficiency, metabolic diseases, blood diseases, lack of light, lack of exercise, malnutrition, drug application, etc. It can also be used for the basic theoretical research of bone metabolism.

The linear scanning system of the single photon bone mineral density meter is driven by a lead screw, with small error, low noise, and stable and reliable operation. The ^{241}Am gamma source with a half-life of 432.6 a is adopted, which can be used for a long time without replacement. The scanner is designed with a radioactive source automatic shielding device, which automatically resets after scanning to shield the ray emission window so that users do not have to worry about radiation leakage due to careless operation. The data processing and scanning control of the instrumentation

adopts a microcomputer to display the bone absorption curve in time. The microcomputer automatically determines the average value of soft tissue and bone width delimitation, which eliminates the subjective uncertainty of artificial delimitation.

6. **Crude oil moisture analyzer**

The crude oil moisture analyzer can be widely used in oil extraction, refining, chemical industry, and other fields. Since it is non-contact online measuring instrumentation, it is especially suitable for online measurement of process parameters (such as the mixed density of crude oil, the content of pure oil in crude oil, the content of water in crude oil, the instantaneous mass flow, the wax content in crude oil, etc.) in closed systems with high temperature, high pressure, high viscosity, highly toxic, deep cold, flammable and explosive, which is incomparable to conventional instrumentation.

4.4.2 Digital Image Processing Instrumentation

The radiation imaging technology combines translational scanning and image processing technology to obtain the radiation projection image of the object being detected. It can reflect the object in real-time and intuitively, and can easily judge and identify defects. Therefore, this type of instrumentation has been more and more widely used and promoted in nuclear technology, aviation and aerospace, metallurgy, machinery manufacturing, and other industries, and has become a hotspot of nondestructive detecting worldwide.

The methods of realizing radiation imaging technology include transmission and backscattering. The transmission imaging is to arrange the radioactive source and the detector on both sides of the workpiece to obtain information about the material density on the ray travel route. In backscatter imaging, the radioactive source and the detector are placed on the same side of the workpiece, and the Compton rays scattered from the object are measured to obtain an image of the electron distribution of the substance inside the object.

Transmission and backscattering have their own characteristics under different application conditions. By measuring Compton scattering rays, the electron density information at a point in the three-dimensional space of an object can be obtained, while the transmitted rays provide two-dimensional density information in the direction of projection. Due to the enhancement of Compton scattering by light matter, the backscattering method is more suitable for detecting light matter objects behind heavy matter objects. Additionally, due to the low energy of scattered rays, backscatter imaging can only obtain information about the surface layer of the object, while transmission imaging can obtain information about the deeper layers of the object.

Digital image processing instrumentation is mainly non-destructive inspection (radiographic inspection) devices, such as X-ray detectors, accelerator detectors, neutron radiography, industrial CT, etc.

Industrial CT is the abbreviation of industrial computerized tomography. It is a comprehensive high-technology integrating radiation, optics, electronics, computers, and many other technologies. The basic principles of industrial CT and medical CT are the same. Due to different fields of application, industrial CT constitutes another relatively independent and important branch of CT technology, which is mainly used for non-destructive testing (DNT) and non-destructive evaluation (NDE) of industrial products. The products being evaluated are as small as a few millimeters and as large as a few meters. Nowadays, industrial CT is recognized as the best non-destructive testing technology worldwide. Industrial CT technology was first applied to important sectors such as aerospace, aviation, and national defense because of its importance of the role, progressiveness of technology, and high economic benefits. It has been widely used in the overall testing of rockets, the non-destructive testing of space shuttles, weapons and ammunition, the regular inspection of various pipelines and piles, the online testing of industrial production, etc.

In recent years, with the internationalization of commodity production, container transport has become the main mode of international freight transport. However, while bringing convenience, it has also been used to smuggle goods, sell drugs, smuggle weapons and explosives, as well as for commercial fraud and terrorist activities, which seriously threaten the economic order and social security all over the world. Faced with these problems, the ^{60}Co container inspection system can be effective.

Tsinghua University has developed a ^{60}Co container CT inspection system, which is composed of six parts including a radiation source, detector, image processing system, dragging system, control system, and radiation protection and safety system. When the container passes through, the shutter automatically opens, and the γ-ray emitted by ^{60}Co is constrained into a fan-shaped sheet-like narrow beam by the collimator, passing through the container and reaching the detector. The γ-ray received will be converted into electrical signals by the detector and transmitted to the computer for image processing. In this way, smuggled goods, drugs, weapons, and explosives hidden in the container can be displayed on the screen.

Radiographic testing can be divided into many methods according to different characteristics (such as types of rays used, recording equipment, characteristics of the process and technical, etc.). Among them, radiography is the most basic and widely used radiographic testing method. It refers to the non-destructive testing method that uses X-ray or γ-ray to penetrate the specimen and uses film as the recording equipment.

1. **X-ray flaw detector**

There are many types of rays, among which X-rays, γ-rays, and neutron rays are easy to penetrate substances. These three kinds of rays can be used for non-destructive testing, of which X-rays and γ-rays are widely used for defect detection of boiler pressure vessel welds, other industrial products, and structural materials, while neutron rays are only used for some special conditions. Radiographic instrumentation can be divided into three categories: X-ray flaw detector, high-energy radiographic

testing equipment (including high-energy linear accelerator and electron cyclotron as radioactive sources), and γ-ray flaw detector. The tube voltage of the X-ray flaw detector is below 450 kV, the photon radiation energy of the high-energy accelerator is generally 2–24 meV, and the ray energy of the γ-ray flaw detectors depends on the type of radionuclide.

(1) Principle of radiography

X-rays are generated from the X-ray tube, which is a bipolar electron tube. When the cathode filament is energized to make it incandescent, electrons escape in the vacuum. If a voltage of several tens to hundreds of kilovolts (i.e. tube voltage) is applied between the two poles, the escaped electrons will accelerate from the cathode to the anode gain and obtain great kinetic energy. When these high-speed electrons hit the anode, they interact with the Coulomb field outside the metal nucleus of the anode and emit X-rays. The kinetic energy of the electrons is partly converted into X-ray energy and partly into thermal energy. Electrons move from the cathode to the anode, while the current flows from the anode to the cathode. This current is the tube current. To adjust the tube current, just adjust the filament heating current. The tube voltage can be adjusted by adjusting the primary voltage of the main transformer of the X-ray device.

Radiography is to detect defects by measuring the absorption of rays affected by defects in materials by taking advantage of the characteristics of absorption and scattering of rays when they pass through objects. When interacting with substances, the intensity of X-rays and γ-rays gradually weaken. Another important property of rays is that they can make the film sensitive to light. When X-rays or γ-rays irradiate the film, the silver halide in the emulsion layer of the film can produce a latent image center, which will be blackened after development and fixing. The more rays are received, the higher the degree of blackening, which is called radiographic action. Because the photosensitivity of silver halide led by X-rays or γ-rays is much smaller than that of ordinary light, a special X-ray film that is coated with thick latex on both sides must be used. In addition, it is also necessary to use an intensifying screen to enhance the photosensitivity. The screen is usually made of lead foil. Develop, fix, wash and dry the exposed film in the darkroom, and then place the dry negative on the film viewing lamp for observation. According to the different blackness images of defective and non-defective parts on the negative film, the type, quantity, and size of defects can be determined, which is the principle of radiographic flaw detection.

(2) Composition of X-ray flaw detector

The X-ray flaw detector is mainly composed of four parts: the head, the high-voltage generator, the power supply and control system, and the cooling protection facilities, which can be divided into two types: portable and mobile. The mobile X-ray flaw detector is used for radiographic testing in the transillumination room, which has relatively high tube voltage and tube current. The tube voltage can reach 450 kV, the tube current can reach 20 mA, and the maximum transmission thickness is about

100 mm. The high-voltage generator, cooling device, and head are installed independently. The head of the X-ray flaw detector is connected to the high-voltage generator through a high-voltage cable and can be moved in a small range through a bracket with wheels or can be fixed on the bracket. The portable X-ray flaw detector is mainly used for on-site radiography. Its tube voltage is generally less than 320 kV, and the maximum penetration thickness is about 50 mm. The head is composed of a high-voltage generator and a ray tube and is connected to the control box through low-voltage cables.

The portable ultra-thin X-ray flaw detector uses a constant-current X-ray tube, which can provide X-rays with a variety of energy, such as 80, 100, and 120 keV. Since low-density organic materials such as drugs and explosives are sensitive to low-energy X-rays, and high-density materials such as metals and ceramics are sensitive to high-energy X-rays, the use of multi-energy X-ray imaging technology can effectively distinguish organic substances from metals, which is commonly used in security inspection, explosive disposal, anti-terrorism, drug and smuggling detection.

The portable ultra-thin X-ray flaw detector has the following outstanding performance:

① The detection box is ultra-thin and portable, with a thickness of less than 8 cm.
② A large imaging area of up to 30 cm × 40 cm, only one X-ray fluoroscopy is required to detect every corner of a large bag.
③ High detection efficiency, which can greatly reduce radiation dose.
④ Strong penetration ability, capable of human body perspective.
⑤ The detection box can be adjusted arbitrarily according to the shape and position of the object to be detected.
⑥ Equipped with high-power and high-performance lithium-ion batteries, which can detect more than 100 suspected bags or suspects on a single charge.
⑦ Adopt the high-quality X-ray tube with a long service life, which can provide X-rays with a variety of energies, and is conducive to the detection of organic substances such as drugs and explosives.
⑧ 16-bit image gray level, the image contrast can reach 65,535:1, 200 times higher than that of the ordinary X-ray fluoroscopy image.

2. **Gamma-ray flaw detector**

(1) Principle of gamma-ray flaw detector

Gamma-ray flaw detection is a method that uses the extremely strong penetrability and linearity of gamma rays to detect defects. Its working principle is based on the attenuation effect of rays passing through the material. Although the gamma ray can not be directly observed by the naked eye, it can make the photographic film sensitive to light and can be received by a special receiver. When gamma rays pass through (irradiate) a substance, the greater the density of the substance, the more the intensity of the ray decreases, that is, the less the intensity of the rays that can pass through the substance. At this time, if a photographic negative is used for reception, the photosensitivity of the negative will be small. If a detector is used for reception,

the signal obtained will be weak. Therefore, when gamma rays are used to irradiate the parts to be detected, if defects such as pores and slag inclusions exist inside the part, the density of the material transmitted by the rays through the defective path is much smaller than that through the path without defects, and the intensity of gamma rays is weakened less, that is, the intensity of gamma rays that pass through the material is greater. If a negative is used to receive gamma rays, the photosensitivity will be greater, and the plane projection of defects perpendicular to the ray direction can be reflected from the negative. If other receivers are used, instrumentation can also be used to reflect the corresponding parameters. In general, it is difficult to find cracks by gamma-ray flaw detection, in other words, it is not sensitive to cracks. But gamma ray flaw detection is most sensitive to volumetric defects such as porosity and slag inclusion. That's to say, gamma ray flaw detection is suitable for volumetric flaw detection, but not for area defect detection.

Several methods that can be used to determine defects by measuring the intensity of penetrated rays of the workpiece, including radiography, fluorescence screen observation, television observation, and radiation intensity measurement. Among them, the radiographic method has higher sensitivity but requires darkroom processing and other processes with a relatively long detection cycle. The fluorescence screen observation has a low cost and can be continuously detected, and the results can be obtained quickly. However, the sensitivity of this method is relatively low and the thickness that can be detected is limited. It is generally suitable for detecting light metals less than 50 mm (such as aluminum, magnesium, and their alloys) or steel workpieces less than 20 mm. The television observation method is developed based on the fluorescence screen observation method, which can meet the needs of rapid, direct, and continuous automatic nondestructive testing. In addition, as this method can be operated and observed far away from the radiation field, radiation damage can be completely avoided. The disadvantages and application scope of this method are the same as that of the fluorescence screen observation method. The advantage of the radiation intensity measurement is that it can detect the object rapidly and continuously, which can be used in automatic production lines.

(2) Several types of gamma-ray flaw detectors

① ^{192}Ir gamma ray flaw detector

Both the γX-3M type and the γX-3M-1 type gamma ray flaw detectors use the ^{192}Ir radioactive source (whose half-life is 74.3 d, energy is 0.3–0.6 meV). The ^{137}Cs radioactive source can also be used. Besides, after a little modification, ^{75}Se radioactive sources can also be adopted.

② ^{75}Se gamma ray flaw detector

The γX-3 M-B gamma ray flaw detector is a gamma ray flaw detector using the ^{75}Se radioactive source. This kind of instrument is more compact, smaller, and more reliable. Since the average energy of the ^{75}Se source is 0.206 meV, which is lower than that of ^{192}Ir, higher quality images can be obtained. In addition, the half-life of

the ^{75}Se source is 119.8 d, which is the best choice for flaw detection of in-service pipelines, pressure vessels, and long-distance pipelines. Currently, the ^{75}Se source is usually used to replace the traditional ^{192}Ir source in the radiographic detection of small-diameter pipes.

As can be seen from Table 4.9, the ^{75}Se source has a relatively low energy range and is suitable for transilluminating iron-based materials with a thickness of less than 40 mm. The half-life of the ^{75}Se source is 119.8 d. It takes about 396 days for a ^{75}Se source with an activity of 3.7×10^{12} Bq to decay to a waste source with an activity of 3.7×10^{11} Bq, but that only takes about 245 d for a ^{192}Ir source. In addition, the radiation dose rate coefficient of the ^{75}Se source is 0.20 C kg^{-1} s^{-1} at 1 m in the air, while that of the ^{192}Ir source is 0.47 C kg^{-1}·s^{-1}. Thus, the ^{75}Se source reduces the scattered radiation of the surrounding environment and the radiation absorbed dose of radiation operators.

③ ^{60}Co gamma-ray flaw detector

The TK-100 gamma ray flaw detector applies ^{60}Co as the radioactive source. It is generally equipped with a trolley for transportation, with excellent performance, which is safe and reliable.

3. Neutron radiography

For the introduction to neutron radiography, see Chap. 3 for more details.

4. Container CT inspection system

The world's first mobile industrial CT system was developed by Los Alamos National Laboratory in the United States, which is the most advanced three-dimensional CT system in the world.

Tsinghua University developed the ^{60}Co container CT inspection system in 2002. This system has excellent detection performance and can detect items hidden in the container, such as soap wrapped in butter hidden in containers, gasoline and water hidden in rice bags, and polytetrafluoroethylene mixed in the cigarette stacks. The ^{60}Co container CT inspection system adopts a special structural design, which can make the detection equipment rotate around the container, and scan the contents in the container at any angle, which significantly improves the capacity of detection. The development of the ^{60}Co container CT inspection system provides a practical and

Table 4.9 Comparison of ^{75}Se, ^{192}Ir, and X-ray properties

Type of radioactive source	Average energy/kV	Half-life/d	Radiation dose rate/(C kg^{-1} s^{-1})	Quality of the rays
^{75}Se	206	119.8	0.20	Very hard
^{192}Ir	355	74	0.47	Hard
X-ray	130–280	–	Direction-related	Soft

effective means for the findings of drugs, explosives, flammable dangerous goods, etc.

(1) Introduction of the container CT inspection system

The container CT inspection system is a device that uses the method of tomographic imaging to carry out a non-destructive inspection on large objects such as containers. The ^{60}Co container CT inspection system is mainly composed of a radiation source (^{60}Co industrial flaw detector), array detector, data acquisition system, mechanical system, control system, data transmission system, image reconstruction system, and image display analysis system. The control subsystem is an important part of the ^{60}Co container CT inspection system, which is of great significance to ensure the stable and reliable operation of the entire inspection system.

The CT ring gantry installed with the radioactive source and the array detector can be rotated at any angle within the vertical plane. Therefore, the ^{60}Co container CT inspection system can not only perform CT scanning on the suspicious area of the inspected object but also perform DR projection scanning at any angle on the large inspected object. The inspection system obtains tomographic digital images of the selected part of the container through computer image reconstruction technology, which improves the ability to recognize the shape of the inspected object. In addition, the system also has the function of discriminating the physical properties based on the characteristic that the gray value (CT value) of the CT image is related to the density of the material, which can distinguish sugar from salt, water from oil (or alcohol), etc. according to the difference in density.

(2) Function of the control subsystem

The control subsystem of the ^{60}Co container CT inspection system includes a safety monitoring system, a scanning control system, and the main control system. The main function of the safety monitoring system is safety interlock, which realizes the management of radiation sources and the control of radiation to ensure the equipment and personal safety during the operation of the ^{60}Co container CT inspection system. The main function of the scanning control system is to control the movement of the mechanical system to realize the random rotation, fixed position rotation, and continuous rotation functions of the CT ring gantry and the forward, backward, and positioning of the translation mechanism, so as to ensure the smooth completion of digit radiography (DR) scanning and CT scanning of the container.

The main control system is the control hub of the ^{60}Co container CT inspection system, its main functions include: ① Complete the process control of DR scanning and CT scanning of the container. The scanning modes of the inspection system include frontal projection, overhead projection, dual projection, CT scanning and conventional scanning (dual projection plus CT scanning); ② Communicate with the scanning control system and the safety monitoring system, send process control commands and receive the status information fed back from the inspection system; ③ Communicate with the data transmission system, send the container scanning

mode command and data acquisition control command, receive the original DR image and CT image of the container acquired by the data acquisition system, and display and save the original container image in real time; ④ Communicate with the image reconstruction system, assign the obtained original DR image and CT image of the container to the image reconstruction system, and perform scale correction and image reconstruction respectively; ⑤ Communicate with the image display and analysis system and assign the DR image and CT image of the container processed by the image reconstruction system to the image display and analysis system, so as to inspect the images of the container and determine whether there is suspected contraband in the container.

4.4.3 Energy Spectrum Nuclear Analytical Instrumentation

Physical effects such as excitation, ionization, scattering, and nuclear reaction produced by substances under the action of rays can induce substances to emit secondary rays. According to the energy spectrum intensity of the secondary rays of the substance, the identification of the material elements can be carried out and the analysis of trace material composition can be realized. In recent years, due to the emergence of nuclear electronics instrumentation such as high-resolution radiation detectors and multi-channel pulse amplitude analyzers, the sensitivity and accuracy of analysis and measurement have been greatly improved. The wide application of electronic computers has further improved the speed and scale of data processing, making the structure of the developed energy spectrum analytical instrumentation more compact and portable, especially providing convenience for the field application and field operation of the instrumentation. The energy spectrum nuclear analytical instrumentation can be divided into three categories: fluorescence (such as radionuclide X-ray fluorescence analyzers), activation (mainly refers to neutron activation), and nuclear logging (such as nuclear instrumentation for oil, coal, and metal logging).

The X-ray fluorescence analyzer and neutron activation analyzer have already been introduced in Chap. 3, thus, only the nuclear logging instrumentation will be introduced here.

Nuclear logging is the application of nuclear technology to borehole measurement. It is a nuclear geophysical method that uses various effects of interactions between radiation and substances or radioactivity of rock itself to study the geological profile of the well to explore oil, natural gas, coal, and metal and non-metallic mineral deposits, and study petroleum geology, well engineering, and oil field development. It is also known as radioactive logging.

Nuclear logging technology is one of the cutting-edge logging technologies that developed rapidly with the development of modern nuclear technology and the need for nuclear logging technology in oil, coal, geology, and minerals. With the development of artificial radiation source technology, sensor technology, measurement technology, information processing technology, and computer technology, nuclear

logging is developing rapidly at present. Nowadays, nuclear logging instrumentation is more and more widely used. In the United States, the petroleum nuclear logging industry has become the second largest isotope application field after nuclear medicine.

(1) Radiation source-based nuclear logging instrumentation

Most methods of nuclear logging technology rely on the performance of the radiation source, and a few methods use the natural radioactivity of the downhole formation for measurements. The existing ray sources for logging are mainly gamma-ray sources and neutron sources. Restricted by the borehole size (small, curved, irregular, etc.) and the downhole environment (high temperature, high pressure, etc.), it is difficult to apply technologies such as accelerator gamma sources for surface experiments to the logging field. Most of the gamma sources commonly used in logging are radionuclide sources, which are mainly used for tracer logging. The development of nuclear technology, the continuous construction of nuclear reactors and accelerators, and the establishment of the nuclear fuel cycle system have provided an increasingly rich material basis for the application of radionuclides. The wide application and research of radionuclides have opened up new ways to make better use of the existing equipment and resources. The fluid density meters, fluid identification devices, gamma ray flaw detectors, and thickness detectors adopted in logging all make use of radionuclide information source technology.

(2) Sensor-based nuclear logging instrumentation

The sensor is a device that can sense a specified measured signal and convert it into a usable signal according to certain rules, which can meet the requirements of information transmission, storage, display, recording, and control. It usually consists of a sensitive element and a conversion element. Sensors belonging to the bottleneck industry of high-tech, which plays an important role in the development of science and technology.

The core component of logging sensors is the detector. Different nuclear radiation needs to be measured with different detectors. All nuclear detectors are designed based on the principle of interaction of rays and matter, that is, radiation has different spatial distribution, energy distribution, time distribution, and characteristics in matter.

Nuclear logging detectors require high efficiency, high counting pass rate, high energy resolution, high temperature and pressure resistance, high vibration resistance, small volume, moderate price, etc. The commonly used gamma and X-ray detectors for logging are scintillation detectors, which are mainly composed of scintillators, photomultipliers, and electronic instrumentation.

4.5 Trend of Development

At present, nuclear instrumentation is constantly updating the structure, improving the functions, increasing the accuracy, and improving stability and reliability. It has gradually realized the standardization, serialization, universality, miniaturization, automation, and intelligence to meet the requirements of continuity, high speed, and precision of modern industry. With the progress and development of computers and other science and technology, the stability and reliability of nuclear instrumentation have been greatly improved, and the automatic data collection, processing, and closed-loop control of the production process have been realized. Currently, the development of nuclear instrumentation has reached a new height, which will continue to expand its applications in industry, agriculture, national defense, resource development, medicine, environmental protection, scientific research, and many other fields, and will achieve significant economic and social benefits to comprehensively promote the development of social productivity.

Nuclear instrumentation is applied technology. Although it is difficult to make a breakthrough in the theory, nuclear instrumentation will continue to develop with the development of radioactive sources, nuclear electronics, and detectors in the future. It is expected that:

(1) The yield, life, and stability of portable neutron generators will be improved, and the applications of neutron logging and neutron activation online elemental analysis will develop more rapidly. The activated stable isotope tracer technology will also be further applied in scientific research, well logging, medicine, agriculture, and water conservancy. In particular, the neutron generator with automatic yield control, good stability, and long service life will be more conducive to promotion than the isotope neutron source.
(2) X-ray machines (X-ray generators) will replace isotope gamma (X) ray sources in many respects and will be superior to isotope radiation sources in microanalysis.
(3) The development of small-scale room-temperature semiconductor γ-ray detectors with high detection efficiency will overcome the shortcomings of gas detectors and semiconductor detectors operating at low temperatures in the past. A high-sensitivity imaging system can be formed by using this type of detector. And the use of a small probe composed of the point source and the point detector can solve the problem of measuring two-phase flow parameters in a small range under boundary conditions.
(4) With the further improvement of production requirements, the composition analysis instrumentation will develop towards digitalization and automation, especially the nuclear instrumentation with artificial intelligence as the core, which process and reproduce the detected radiation signals with algorithms as the core, with better image quality and can be applied in more fields.
(5) Industrial CT will further improve its technical performance and expand its applications.

In the future, industrial nuclear instrumentation is likely to develop in the following directions:

(1) In terms of the overall structure, the whole instrumentation will develop from unit combination to functional assembly.
(2) In terms of measurement methods, the means will transition from simple detection to complex measurement devices with high efficiency and high resolution.
(3) In terms of intelligence, the whole instrumentation will develop towards networking of data processing and management, information sharing, and remote diagnosis faults. It will be of great significance for a nuclear emergency to combine UAVs with remote-controlled unmanned intelligent nuclear instrumentation.
(4) In terms of function, nuclear instrumentation is developing from single-point and single-parameter detection to multi-point and multi-parameter automatic direction, such as the dual-parameter mass flow meter composed of the radionuclide density meter, the flow meter, and a microcomputer. An example of application is the ^{252}Cf neutron moisture meter, which can simultaneously measure the moisture and density of the materials. Another example is the use of an X-ray thickness gauge, which can simultaneously detect the total thickness of steel wire and rubber, the thickness of the steel wire layer, and the thickness of the upper and lower rubber layers in rubber products in the steel wire interlayer. In addition, the integrated application of industrial nuclear instrumentation with other non-nuclear technologies will help expand the application range and improve the application functions of nuclear instrumentation.
(5) In terms of universality and safety, industrial nuclear instrumentation will further realize serialization and standardization. In the United States, the safety standard *ANSI-N538* for radionuclide instrumentation has been formulated, and it is expected that similar international standards for nuclear instrumentation will be put on the agenda in the near future.

With the development of various supporting technologies, especially the widespread use of electronic computer technology, the technical level of nuclear instrumentation has reached a new height. After the adoption of electronic computers, the structure of nuclear instrumentation is more compact and the volume is reduced. Measurement develops from analog to digital, realizing automatic compensation of input information. The system starts, adjusts, and operates programmatically and calculates, judges, analyzes, and processes the collected data, which expands the information function of the instrumentation and improves the detection accuracy, laying the foundation for multi-parameter measurement and closed-loop control of the production process. The instrumentation is composed of hardware and software, reflecting the rationality of design and simplicity of operation. The fault self-diagnosis function of the instrumentation greatly reduces the workload of equipment maintenance, thus improving reliability. Through the color display of image and video, better man–machine integration is achieved, the requirements of modern

industrial production of continuity, automation, and high speed are met, and non-contact detection, non-destructive detection, and out-of-tolerance sensing are realized to ensure 100% inspection of products and to correct over-difference before it occurs. Through digital and image information display, better human–machine integration can also be achieved to meet the requirements of modern nuclear logging production for continuity, automation, intelligence, high speed, and integration.

Exercise

1. Describe the key indicators that measure the performance of radiation detectors in detail.
2. Describe the operating principle of energy spectrum nuclear instrumentation.
3. What is the operating principle of the intensity nuclear instrumentation?
4. What is meant by nuclear logging?

Bibliography

An, J., Xiang, X., Wu, Z., Zhou, L., Wang, L., & Wu, H. (2003). Progress on developing ^{60}Co container inspection systems. *Applied Radiation and Isotopes, 58*(3), 315–320.

Anand, R. S., & Kumar, P. (2006). Flaw detection in radiographic weld images using morphological approach. *NDT & E International, 39*(1), 29–33.

Anand, R. S., & Kumar, P. (2009). Flaw detection in radiographic weldment images using morphological watershed segmentation technique. *NDT & E International, 42*(1), 2–8.

Arkhinov, G., Romashov, V., & Vazhdaev, M. (1975). Back-scattering gamma-ray flaw detector and thickness gauge. *Soviet Journal of Nondestructive Testing (English Translation) (United States), 11*(6).

Belcher, D., Sack, H., & Cuykendall, T. (1952). *Nuclear meters for measuring soil density and moisture in thin surface layers* (Vol. 161). Civil Aeronautics Administration Technical Development and Evaluation Center.

Boerner, H., & Strecker, H. (1988). Automated X-ray inspection of aluminum castings. *IEEE Transactions on Pattern Analysis and Machine Intelligence, 10*(1), 79–91.

Bukowski, R., & Mulholland, G. W. (1978). *Smoke detector design and smoke properties* (Vol. 973). Department of Commerce, National Bureau of Standards, National Engineering.

Cai, S., & Zhou, Z. (1999). Sealed techniques of 85 Kr gas sources. *Journal of Isotopes, 12*(2), 85–89.

Caldwell, R. L. (1969). Nuclear logging methods. *Isotopes & Radiation Technology.*

De Chiffre, L., Carmignato, S., Kruth, J.-P., Schmitt, R., & Weckenmann, A. (2014). Industrial applications of computed tomography. *CIRP Annals, 63*(2), 655–677.

Ferrucci, M., Leach, R. K., Giusca, C., Carmignato, S., & Dewulf, W. (2015). Towards geometrical calibration of X-ray computed tomography systems—A review. *Measurement Science and Technology, 26*(9), 092003.

Hearst, J. R., & Nelson, P. H. (1985). *Well logging for physical properties.*

Huang, Y., Cong, P., & Yuan, Y. (2005). The design and realization of the main control station of ^{60}Co container CT inspection system. *Nuclear Electronics and Detection Technology, 25*(6), 620–622.

Korzhik, M., & Gektin, A. (2017). *Engineering of scintillation materials and radiation technologies.* Springer.

Lane, D., Torchinsky, B., & Spinks, J. (1953). *Determining soil moisture and density by nuclear radiations*. Paper presented at the Symposium on the Use of Radioisotopes in Soil Mechanics.

Lehmke, J., Bogner, U., Felsenberg, D., Peters, H., & Schleusener, H. (1992). Determination of bone mineral density by quantitative computed tomography and single photon absorptiometry in subclinical hyperthyroidism: A risk of early osteopaenia in post-menopausal women. *Clinical Endocrinology, 36*(5), 511–517.

Li, Z., Zhou, F., Yao, H., Ci, Z., Yang, Z., & Jin, Z. (2021). Halide perovskites for high-performance X-ray detector. *Materials Today, 48*, 155–175.

Liao, T. W., & Li, Y. (1998). An automated radiographic NDT system for weld inspection: Part II—Flaw detection. *NDT & E International, 31*(3), 183–192.

Liu, H. (2017). *Principles and applications of well logging*. Springer.

Manchun, L., Hongchang, Y., & Zhikang, Z. (2006). A new method of weighing materials online. *Nuclear Electronics and Detection Technology*, 26.

Martz, H., Azevedo, S., Brase, J., Waltjen, K., & Schneberk, D. (1990). Computed tomography systems and their industrial applications. *International Journal of Radiation Applications and Instrumentation. Part A. Applied Radiation and Isotopes, 41*(10–11), 943–961.

Melcher, C., Schweitzer, J., Manente, R., & Peterson, C. (1991). Applicability of GSO scintillators for well logging. *IEEE Transactions on Nuclear Science, 38*(2), 506–509.

Mery, D. (2011). *Automated detection in complex objects using a tracking algorithm in multiple X-ray views*. Paper presented at the CVPR 2011 Workshops.

Mills, W., Stromswold, D., & Allen, L. (1991). Advances in nuclear oil well logging. *Nuclear Geophysics, 5*(3), 209–227.

Nikitin, A., Fedorov, A., & Korjik, M. (2013). Novel glass ceramic scintillator for detection of slow neutrons in well logging applications. *IEEE Transactions on Nuclear Science, 60*(2), 1044–1048.

Ran, H., Zunnian, L., & Aige, R. (2011). *Experimental study of spectrum analytical method by natural gamma ray energy spectrum*. Paper presented at the 2011 4th International Congress on Image and Signal Processing.

Sharma, A., Weindorf, D. C., Man, T., Aldabaa, A. A. A., & Chakraborty, S. (2014). Characterizing soils via portable X-ray fluorescence spectrometer: 3. Soil reaction (pH). *Geoderma, 232*, 141–147.

Stepanov, V., Ivanov, O., Potapov, V., Sudarkin, A., & Urutskoev, L. (1999). Application of gamma-ray imager for non-destructive testing. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 422*(1–3), 724–728.

Tomasek, M., Stukheil, K., & Wilhelmova, L. (1986). Use of ^{241}Am as reference source of CaF_2 (Eu) scintillation detector in counting radioactive gaseous samples. *Radioisotopy, 27*(2–3), 87–92.

Wallingford, R. M., Siwek, E., & Gray, J. (1992). Application of two-dimensional matched filters to X-ray radiographic flaw detection and enhancement. In *Review of progress in quantitative nondestructive evaluation* (pp. 879–886). Springer.

Wang, M. (2015). *Industrial tomography: Systems and applications*. Elsevier.

Xiqi, Q. (1989). Advantages of using sup ^{192}Ir gamma-ray flaw detector for some products. *Journal of Isotopes (China), 2*(3).

Yongkang, W. (2001). Scintillation detectors used in industry nuclear instrument. *Nuclear Electronics and Detection Technology*, 21.

Chapter 5
Radiation Processing



Radiation processing is a technology that changes the structure (ionization effect) or state (excitation) of substances by using the ionization and excitation effects inside substances caused by the interaction between rays and substances. When ionization occurs after the interaction, the formed ion pairs, free radicals, electrons, or long-chain molecules in the excited state, and other active groups or particles will undergo a series of reactions to form new chemical bonds, which causes crosslinking between polymer molecular chains and transform the two-dimensional structure into a three-dimensional network structure, which can improve the mechanical and electrical properties of materials. The molecular chains of some polymers will break and degrade into small molecules under the high-energy radiation of particle beams, that is, radiation degradation. Some broken small molecules react with the main chain to form grafts. The whole process is a mixed reaction, that is, polymer chains are crosslinked, degraded, and grafted in the process of radiation. Which reaction is dominant, the characteristics of which reactor will be shown on the macro level.

Irradiation can realize material modification, it can also be used to polymerize small organic molecules into macromolecules, which is much milder than the traditional high-temperature and high-pressure polymerization conditions. It can realize polymerization under normal temperature and pressure, or even at a low temperature below minus 100 °C. The polymerization process does not need initiators and catalysts, which is of great significance for the synthesis of biological functional materials. The initiators, catalysts, and their residues used in conventional chemical polymerization often cause anaphylaxis in human cells. Therefore, radiation technology provides a better method for the synthesis of new biological functional materials. In addition, it can also carry out research and industrialization of radiation breeding, irradiation preservation (preservation), disinfection and sterilization, and has a wide range of applications. Radiation processing is known as the "green" technology as it hardly emits toxic and harmful gases to the environment and human beings during the irradiation process. The processing parameters can be strictly controlled to achieve "accurate" processing. It has gradually replaced the traditional processing methods in

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6_5

many fields to achieve the purpose of energy conservation, environmental protection, high efficiency, and cost-effectiveness.

The basis of radiation processing is the interaction between rays and substances. The result of the action is the ionization, excitation, and other changes in the interior of the material, that is the radiation effect. The science of studying this effect is called radiation chemistry. When a substance is irradiated by the particle beam, its structure (ionization effect) and state (excitation) will change. The amount of this change is represented by the technical term G value of radiation chemistry. G is defined as changes in the number of molecules, ions, free radicals, or electrons in a 1 g substance after absorbing 100 eV energy.

This chapter focuses on the basic theory, method, process, and evaluation of radiation technology in material preparation and product development, especially the radiation polymerization and radiation curing of organic molecules (or oligomers), the radiation crosslinking of polymers or their compounds, the radiation degradation of organic molecules and polymers, and the use of related radiation processed products. The research and industrialization of radiation disinfection and sterilization of medical supplies shall comply with the standards such as *ISO 11137-1:2006—Sterilization of health care products.* Studying the irradiation technology and dose according to the specific products to meet the requirements of the standards does not involve complex science and technology, which will not be introduced in detail. Radiation breeding and irradiation preservation will be introduced in detail in Chap. 8.

This chapter seeks to achieve an accurate and standardized description of the development and processes of radiation processing.

5.1 Basic Knowledge of Radiation Processing

5.1.1 Definition of Radiation Processing

Generalized radiation processing includes all technologies that use particles, light waves, and rays to engage in the research, development, and production of radiation chemistry and technology. Some applications of radiation processing are as follows:

- Applications of α-particle etching, (α, n) reaction, (α, β) reaction, (α, γ) reaction, etc.
- The use of neutrons of various energies produced by isotope neutron source, accelerator neutron source or reactors to realize nuclide production, thermal neutron irradiation transmutation doping of monocrystalline silicon, etc.
- Heavy particle injection processing.
- Use electron beam and gamma rays for modification of polymer materials, radiation sterilization of medical devices, disinfection of sanitary materials and drugs, food preservation, environmental protection, especially desulfurization and denitrification of waste gas discharged from coal-fired power plants, and irradiation treatment of sludge sewage.

- Radiation curing of ultraviolet light curing coating, printing inks and surface coating of packaging materials, etc.
- Use electron pulse radiation for basic mechanism research, such as exploring the radiation damage mechanism of DNA.
- Use positron source (e^+ or β^+) and X-ray or muon (μ^+, μ^-) radiation as research tools and means in other fields of applications, etc.

All the above radioactive sources can be used for radiation effects, mechanism studies, and radiation processing of specific materials and substances. But for the professional researchers engaged in the research and application of nuclear technology, the accepted scope of radiation processing is industrial processing with the electron beam, cobalt source, and ultraviolet light as radioactive sources. This chapter will mainly introduce the research on formulation and performance of materials, as well as irradiation effect, based on radioactive sources such as electron beam and gamma sources, to improve the performance and applicability of materials, so as to explore and develop new materials, new products, and new processes.

5.1.2 Irradiation Facility

Radiation chemistry research and industrial radiation processing depend on irradiation facilities (radioactive sources). Irradiation facilities generally include gamma radiation facilities (with γ-ray wavelength 1.0×10^{-3} nm, energy ~ keV to ~ MeV), electron beam accelerators (electron beam is abbreviated as EB, with beam current ~ μA to ~ mA level, energy ~ keV to ~ MeV), X-ray installations (with wavelength 4.1×10^{-3} nm, energy ~ 300 keV), ion beam devices, heavy ion beam accelerators (devices), etc.

Within the categories of radiation processing listed above, radiation facilities generally refer to γ-radiation facilities, electron beam accelerators, and the related auxiliary systems. This section mainly introduces γ-ray devices and compares these devices with electron beam radiation processing.

The radioactive source used in the gamma irradiation facilities shall have the characteristics of high power, stable radiation, a long half-life, and suitable for industrial production. ^{60}Co and ^{137}Cs meet the above characteristics and are the main radioactive sources for the research and application of radiation technology. Compared with the electron accelerators, ^{60}Co sources have higher costs in production, processing, transportation, use, source decay correction, operation supervision regulations, and decommissioning. As for electron beam radiation processing, when the electron beam energy is low, the penetration will be insufficient, which is not suitable for radiation processing of large volume (or thicker) materials and articles. When the energy of the electron beam is higher than 10 meV, the penetration will be strong, but it will also easily lead to the activation of the irradiated material to produce radioactivity. In recent years, converting high-energy electron beams into X-rays for radiation processing has become a trend in the research and development of industrial

radiation processing because it not only retains the advantages of both γ-rays and electron beams but also overcomes their disadvantages. In 2011, the International Atomic Energy Agency published the report *Industrial Radiation Processing with Electron Beams and X-rays*, which listed the advantages of using X-rays, such as deeper penetration thickness (which can be used for disinfection, sterilization, and fresh-keeping of medical products and food in large packages), adjustable dose rate, no thermal processing, etc. Whether to convert the electron beam into X-rays depends on the energy of the electron beam and the atomic number (Z) of the target material. For example, the efficiency of converting 5 and 7 meV electron beams into X-rays is only 8 and 12%. Such energy utilization efficiency is too low, which has become a bottleneck problem in the development of X-ray industrial radiation processing. At present, the focus of X-ray industrial radiation processing research and development is to improve energy conversion efficiency. Therefore, electron beam processing and ^{60}Co radiation processing still occupy the main position for a certain period.

Irradiate ^{59}Co sources in the reactor for 18–24 months and the ^{60}Co source with a specific activity $\leq$ 120 Ci/g (4×10^{12} Bq/g) can be obtained through the ^{59}Co(n, γ) ^{60}Co reaction. ^{60}Co emits 0.313 meV β^--particles and decays into ^{60m}Ni, which then decays into stable ^{60}Ni through γ-decay. The decay chain of ^{60}Co is:

$$^{60}\mathrm{Co} \xrightarrow{\beta^-} {}^{60\,\mathrm{m}}\mathrm{Ni} \xrightarrow{\gamma} {}^{60}\mathrm{Ni}.$$

^{137}Cs can also be used for radiation processing. However, ^{137}Cs is a fission product of ^{235}U, which has complex separation and extraction processes, thus, the amount used in practical industrial applications is very small. Table 5.1 lists the basic characteristics of ^{60}Co and ^{137}Cs radioactive sources.

It can be seen that although ^{1}Cs has a long service life, it is a product extracted from the spent fuel reprocessing after decommissioning of nuclear power plants, with low production, low γ-ray energy emitted, complex source preparation method, low specific power activity, non-reusable, complex and costly source decommissioning. Therefore, it is mainly used for radiation sterilization and disinfection of medical supplies, nuclear instrumentation, and scientific research. Most gamma irradiation

Table 5.1 Basic characteristics of ^{60}Co and ^{137}Cs radioactive sources

Radionuclide	^{60}Co	^{137}Cs
Element symbol	$^{60}_{27}$Co	$^{137}_{55}$Cs
γ-ray energy	1.17 meV, 1.33 meV; average 1.25 meV	$\overline{E}_\gamma = 0.661$ MeV
Existing form	Metal Co	CsCl
Preparation method	Irradiate ^{59}Co in the reactor	Obtained by post-processing of reactor element
Half-life	5.27 years	29.99 years
The activity of power per watt	2.5×10^{12} Bq	1.11×10^{13} Bq

facilities use ^{60}Co sources for production. This is because the preparation technology of the ^{60}Co source is relatively simple, and it can be produced on a large scale. In addition, the ^{60}Co source beyond the service life can be reactivated and put into use.

The ^{60}Co γ source irradiation facility is mainly composed of the following parts:

① **Radioactive source chamber**: A room built with concrete, which is the place where the radioactive source irradiates products. The concrete wall and roof are thick enough to shield γ-rays and ensure the safety of people outside the chamber. A source well is built in the chamber to store the radioactive sources that are not in use.

② **Radioactive source**: Including single-plate source, dual-plate source, column source, etc. The single-plate source is flexible with high energy utilization, while the dual-plate source has good uniformity with low energy utilization.

③ **Well and water**: The well is used to store radioactive sources, with a general depth of about 7 m. The water in the well is preferably deionized water whose conductivity should reach 10^{-10} μS-cm^{-1}, and with a pH of 5.5–8.5, to protect the stainless steel shell of the source from water corrosion, and a self-circulation filtration system is generally used to treat polluted water.

④ **Source elevator**: The principle of an advanced source elevator is that the hydraulic cylinder drives the pulley block to drag the source frame through the wire rope. Compared with the winch source elevating system, it has the advantages of stable lifting, high position repetition accuracy, automatic source lowering after power failure, etc.

⑤ **Safety interlock system**: Gamma irradiation facilities must be equipped with a safety interlock system with complete functions and reliable performance, especially to effectively monitor and interlock the entrance and exit, source operating system, transmission system, etc.

⑥ **Transmission system**: It is the equipment for automatic transmission of irradiated products. It is generally realized by an overhead conveyor, which is driven by a motor chain or an air cylinder, and some are transmitted by an air cylinder and a ground roller. Multiple passes are arranged on both sides of the source plate in the irradiation chamber to increase the utilization rate of energy. This requires side changing and inversion devices to reduce the unevenness of the absorbed dose.

⑦ **Ventilation system**: Composed of air inlet and exhaust equipment. The volume of exhaust air is slightly larger than that of inlet air, and it is ensured that the system changes air at least 20 times per hour.

⑧ **Control system**: Mainly used to control the production process under various working conditions and to ensure the safety of personnel. Most advanced control systems are automatically controlled by the programmable logic controller (PLC).

⑨ **Control Room**: In order to realize automatic remote control of the source elevator and product transmission. A console is arranged in the control room, and various operations are carried out on the console. Most devices have consoles on the spot.

⑩ **Dose monitoring system**: The dose monitoring system is used for dose monitoring of radiation workplaces and personnel to ensure safety. The multi-channel γ-ray monitor places probes in the irradiation chamber, outlet, etc. to monitor the status of the γ-source. The wearable accumulative dosimeter is used for regular monitoring of the personal dose of operators. The portable dosimeter is used for real-time dose monitoring in the irradiation chamber. In addition, it is very important to monitor the absorbed dose of irradiated products. Thus, the operation of the irradiation facility must have at least one set of routine dose monitoring systems, including dosimeters and testing equipment.

⑪ **Operating room**: This is the place for loading irradiated products into the irradiation box and taking irradiated products out of the irradiation box. In some cases, the process of inversing the irradiated product is also done in the operating room.

⑫ **Raw material storage and final product storage**: According to the regulations, the two storages must be separated, and raw materials and final products must be stacked separately according to their locations.

The energy required for ionization of organic molecules or polymer molecules during irradiation is in the order of ~ 10 eV (1 eV = 1.602×10^{-19} J). The dose rate of the high-energy electron accelerator is 100 kGy s^{-1}, which is about 5 orders of magnitude higher than that of the Co source (2.8×10^{-3} kGy s^{-1}). Obviously, the efficiency of electron beam radiation processing is higher. See Table 5.2 for the comparison between ^{60}Co γ-radiation sources and electron beam sources. See Table 5.3 for the energy range and the penetration thickness of the electron beam required for radiation processing of main products. When the energy of the electron beam exceeds 10 meV, nuclear reactions will occur, and the irradiated objects will be activated to produce radioactivity. Therefore, the energy of the electron beam used for radiation processing generally does not exceed 10 meV.

Table 5.2 Comparison of the performance of the two radiation sources

Features	γ-radiation source	Electron beam
Energy	1.17–1.33 meV	0.2–10 meV
Power	1.48 kW/3.7 × 10^{15} Bq	1.5–400 kW/unit
Dose rate	Low (~ 10 kGy/h)	High (10 kGy/s)
Penetrability	High 43 cm in the water)	Low (0.35 cm/MeV)
Energy utilization rate	Low (40%)	10–90%
Productivity	Low	High
Maintenance	Replacement (cobalt source decays 12.3% annually)	Management of technicians

Table 5.3 Range of electron beam energies required for radiation processing of different products and their penetration thickness

Irradiated product	Electron beam energy	Maximum thickness of penetration (mm)
Surface curing	80–300 keV	0.4
Heat shrinkable film	80–300 keV	2
Wires, cables, and heat shrinkable products	0.4–3 meV	10
Sterilization of medical products, food, etc.	3–10 meV	40

5.1.3 Advantages of Radiation Processing Technology

Radiation processing is highly specialized and involves a wide range of knowledge. Understanding its terms and concepts requires certain knowledge of nuclear physics and radiochemistry. In addition, it also involves knowledge of radiation protection, radiation chemistry, polymer chemistry and materials, biochemistry, bacteriology, mechanics of materials, polymer composites and formulation, polymer molding processes, machining, mold design, and product performance testing.

As an advanced process technology, radiation processing supported by radiation technology has unique advantages in new material research, new product development, and new process exploration. First, the process parameters are stable and adjustable. Once the radioactive source is determined, the type and energy of the radiation are determined accordingly. Second, the process of radiation processing is simple, fast, safe, and energy-saving. Third, compared with the chemical method, radiation processing does not need high temperature and high pressure, which basically belongs to “cold processing”, and the quality and performance of products are stable and reliable. Fourth, the labor intensity is low, operators only need to press the control keys on the console according to the regulations. Fifth, the working environment is excellent, with almost no harmful substances emission except for the small molecules emitted by the irradiated objects and the ozone emitted during the operation of the electron accelerator (usually discharged by the ventilation system of the irradiation field), which is called “green processing”.

5.2 Radiation Crosslinking

To understand and study the radiation crosslinking technology of polymer materials, the basic knowledge of the disciplines of polymer chemistry and polymer physics is necessary to be known. Polymer chemistry and materials are one of the great discoveries of the twentieth century. The petroleum industry and synthetic chemical industry provide the material basis for the emergence of new polymer materials.

Through catalytic hydrocracking of crude petroleum products, a series of polymer products such as alkanes, olefins, and aromatic compounds can be obtained. A series of polymer materials with different functions and uses can be prepared by synthesis, which promotes the development of polymer materials science. The molecular structure, composition, properties, and processing of polymer materials are described in detail in professional books of polymer chemistry and polymer materials science. This section focuses on the basic knowledge of polymers, which will help students and relevant researchers better carry out the research and product development of radiation processing technology.

5.2.1 Mechanisms of Polymer Radiation Crosslinking

1. **Basic knowledge of polymer**

The molecular structure of a polymer determines its physical properties, and its physical state is determined by the aggregation form of the polymer chain. The polymer chain is composed of specific basic units. The generalized structure of polymers is multi-layered and can be divided into three levels. The primary structure refers to the chemical structure, spatial structure, unit sequence, branching (or crosslinking), and distribution of one polymer chain unit, and includes polymer stereochemistry, which is the most basic polymer structure. The secondary structure refers to various conformations of a polymer chain due to the internal rotation of the valence bond of the main chain and the thermal movement of the chain segment. The conformation of amorphous polymers is long-range disordered, while that of crystalline polymers is long-range ordered, showing certain spatial regularity and repeatability. The tertiary structure is the aggregation structure. When many polymer chains gather, the relative spatial positions between their segments can be divided into tight or loose, regular or messy, and the interaction forces between the segments can also be different. According to the compactness and regularity of the aggregation state, polymers can be divided into amorphous, mesocrystalline (including liquid crystal), and crystalline phases.

All levels of polymer structure comprehensively determine its various physical states and properties. The primary structure is mainly determined by the chemical process of synthesizing polymers through the polymerization of monomers. In order to change the primary structure of a polymer, chemical reactions (i.e., the change of valence bonds) are necessary. The secondary and tertiary structures are mainly affected by external physical factors and change with the change in external temperature, pressure, and processing conditions. At the same time, the secondary and tertiary structures also affect the primary structure, they restrict each other to determine the properties of the polymer. In addition, the polymer has a quaternary structure. In polymers, different aggregation states or crystal states exist, and there are often interfaces or quasi-interfaces between them. The aggregated (single or multiple) structures observed by electron microscopy is called the texture structure,

and the configuration observed by light microscopy is classified as the macrostructure. In terms of size, the quaternary structure can be regarded as a transitional region between the microstructure and the macrostructure. The properties of polymers are closely related to their structures, thus, both solid and liquid properties can be seen. Among the solid-state properties, thermomechanical properties are the most important. As a synthetic material, polymers must have certain mechanical strength and heat resistance when applied. During the molding process of the product, the effects of temperature, hydrodynamics (rheology), and other factors are also important. The most important contribution to the properties of materials comes from the types of atoms in the molecules of monomer units, molecular structure, stereoisomerism, and degree of polymerization. Therefore, it is necessary to introduce the chain structure of polymers.

2. **Chain structure of polymer**

The chain unit composition and properties of polymers, and the properties of materials depend on the structure and composition of material molecules. Therefore, understanding the chemical structure of polymers is conducive to radiation research and optimization of material selection and process parameters in the radiation process.

Typical polymers include polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), etc., which are the most used polymers. The structure of the polymer is composed of several repeating units, the structure of some typical polymer molecules is shown in Fig. 5.1.

In the figure, the ethylene molecule, propylene group, and styrene group are referred to as repeat units, n is the degree of polymerization, and the molecular weight increases with the increase of n. They take vinyl molecules as the basic framework, continuously expand the chain and form polymers. There are many unsaturated groups in the molecular chain, thus, it has very active reactivity. Under the action of peroxide free radicals, particle beam, or light, a large number of free radicals are generated and initiate chain reactions, the molecular chains are crosslinked or rearranged or degraded, resulting in significant changes in the overall properties of materials.

Under the action of catalyst and initiator, ethylene and other monomers produce a large number of free radicals to initiate the chain reaction of monomers. The polymerization reaction is carried out randomly and gradually. In the process of chain extension, it is easy to generate branches. In general, 1000 monomer molecular

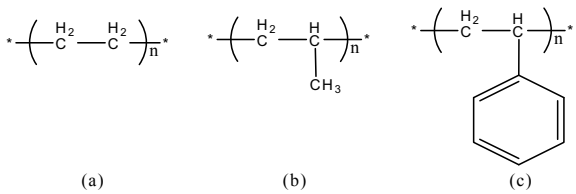


Fig. 5.1 Structural diagram of general linear polymers **a** polyethylene; **b** polypropylene; **c** polystyrene

chains will have one or several branches. The existence of branched chains improves the reactivity of materials. For materials to be modified, the existence of branched chains is conducive to improving the mechanical strength, electrical properties, and processability of polymer materials through physical and chemical effects. But for engineering materials, the existence of branched chains reduces the crystallinity and regularity of materials, thus reducing the mechanical strength of basic materials. According to different needs, different synthesis processes are designed to control the number of branch chains and the molecular chain of the polymer, so that the desired polymer with appropriate molecular weight can be synthesized.

Some monomers have chirality and stereoisomerism, and their polymerized molecular chains also have the same structure depending on the configuration of chain units. Isomerism can be divided into regular isomerism, geometric isomerism, and optical isomerism. Typical isomers include propylene, vinyl chloride, styrene, and formaldehyde.

Typical isomers, such as polypropylene, have two chain unit configurations: d- and l- (Fig. 5.2).

When the polymer chains of polypropylene are all connected by d-units (or all by l-units), it is called isotactic polypropylene, and its melting point is 175 °C. If the d-unit and the l-unit are alternately connected, it is called syndiotactic polypropylene, and its melting point is 134 °C. If the d-unit and the l-unit are connected irregularly, it is called random polypropylene. At room temperature, the random polypropylene with low molecular weight is liquid, and that of relatively high molecular weight is solid wax. From the perspective of the effect of the stereochemistry of polypropylene on the properties of polymer products, if the stereostructure of polymers is different, the melting point, mechanical properties, and processing parameters of their products will also be different, which shows that stereoisomerism is very important for polymer products. Therefore, the stereoisomerism of polymers must be considered when studying the molecular structure.

Polystyrene, polyvinyl chloride, polyformaldehyde, polymethyl ether, polymethyl methacrylate, and other macromolecular polymers have similar stereoregularity and stereoisomerism structures. Based on the d-unit and l-unit, the following figure shows their isomerism:

The changes in the three-dimensional structure of the isomeric polymers in Fig. 5.3 determine the physical properties of the final product. In general, the more regular the polymer is, the higher its glass transition temperature and melting point are, and the higher its density is. This is because isotactic isomers have better crystal

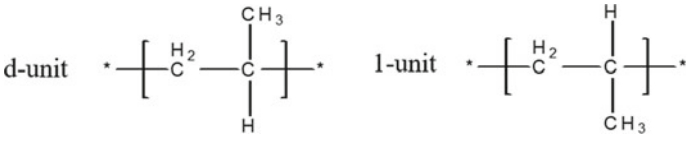


Fig. 5.2 Stereotactic structure of polypropylene

Isotactic polypropylene	...ddddddd ...(or ...lllllll ...)
Syndiotactic polypropylene	...dldldldldldldldld ...
Random polypropylene	...dllddddlldlllllddddldlldddddllld ...

Fig. 5.3 Schematic diagram of chain unit configuration of polymers

accumulation, and molecular chains are densely stacked according to certain rules when they are accumulated.

In addition to the stereoisomerization of polymers, the copolymerization of two types of monomers is often used to synthesize polymers with excellent comprehensive properties in polymer synthesis. Some polymers synthesized by self-polymerization of monomers have good flexibility, but their rigidity is not enough, and their melting point is low, which cannot meet the actual needs. Some polymers synthesized by self-polymerization of monomers have high rigidity, but with poor low-temperature brittleness resistance and poor flexibility, which will be difficult in processing and molding. Therefore, the two monomers can block copolymerized, and the synthesized polymer will have both appropriate rigidity and flexibility, which can meet the application requirements. For example, acrylonitrile butadiene styrene (ABS) and butadiene styrene (BS) are two kinds of block copolymers, which make use of the rigidity of styrene and the flexibility of butadiene and are good engineering plastics.

The main chain structure, the crosslinking of substituents, and other factors are the internal factors that determine the flexibility of macromolecular chains. Many physical–mechanical properties such as heat resistance, high elasticity, and mechanical strength, are the result of the comprehensive influence of molecular flexibility and intermolecular force. The conformation number of the carbon chain is expressed as $3n - 1$. If n (number of carbon atoms) is infinite, 1 is omitted to be approximately 3n conformation numbers, then:

① The longer the molecular chain is, the more the conformation number is. If the chain grows according to the 3n dynamic geometric series, the more likely the chain is to be curly, the more flexible the chain will be.

② In all conformations of polymers, fully extended chains (ttttt…) and fully curled chains (ggggg…) may occur once theoretically. The vast majority of chains lie between two conformations, which are neither fully extended nor fully curled, but the general natural tendency is to form curly coils. If an external force is applied to straighten it, and then the external force is removed, it will shrink to a natural curl state with less potential energy. This property of elongation and retraction is the reason why polymers have a certain elasticity.

③ The end distance of a molecular chain is closely related to its conformation. The distance between the ends of the fully extended chain is the longest, while the distance between the ends of the curly conformation chain is shorter. For the same polymer with the same molecular weight, the shorter the chain end distance is, the greater the molecular curl is. Therefore, the flexibility of the polymer chain can be quantitatively described by the end distance of the chain.

However, the same polymer chain has different end distances with different conformations. According to the statistical principle, it should be represented by the most probable average end distance of the chain.

Copolymers include alternative copolymers, random copolymers, graft copolymers, and block copolymers. According to actual needs, copolymers with different properties can be synthesized by selecting different monomers and different proportions of monomers.

3. Crystalline structure of polymer

The crystalline structure of the polymer is the same as that of low molecular weight organic compounds, metals, and inorganic salts. Under appropriate conditions, crystals are formed according to certain rules. The biggest difference between substances with high molecular chains and low molecular chains is that polymers have large molecular weights and long molecular chains. In the process of forming crystals, it is necessary to overcome various covalent repulsion forces. Therefore, the crystallinity of polymers is much lower than that of small molecular substances. With the increase in the number of atoms in each link of the polymer backbone, the steric hindrance of polymer crystallization increases, and the crystallization rate decreases. The factors affecting polymer crystallization are as follows:

(1) **Structure and composition**: The structure determines properties. Therefore, the elements, components, molecular polarity, atomic radius, degree of polymerization, etc. that make up the polymer determine the crystallization temperature, crystallization rate, and degree of crystallinity. That is, the simpler the chemical structure of the polymer chain is, the greater the regularity and symmetry of the stereo configuration of the main chain, and the smaller the steric hindrance of the side groups of the main chain. The polar group of the main chain can increase the force between molecular chains. For example, the existence of amide groups, carbonyl groups, halogen atoms, hydroxyl groups, and carboxyl groups can induce the formation of hydrogen bonds between molecular chains. Strong hydrogen bonds are conducive to the crystallization of the polymer chains. In the process of polymer synthesis, in order to improve the heat resistance of polymers, polymer materials with high crystallinity are often prepared through the selection of monomers and the setting of process parameters. On the contrary, it is to increase the flexibility and elasticity of polymers, reduce the crystallinity of materials as much as possible, and control the formation of crystals.

(2) **Temperature**: Due to the large geometric size of polymer chains, the movement of molecular chains is restricted. In the process of crystal formation, the moving space and range of molecular chains is the key to ensure crystal formation. According to the law of thermodynamics, the thermal motion of molecules increases with the increase of temperature. If the temperature is too low, the polymer chain cannot be folded in time to form a regular structure—crystal, the molecular chain will be frozen and become an irregular structure and cannot be crystallized. If the temperature is too high, the thermal movement of the

molecular chain is accelerated, and the molecular chain cannot be folded regularly to form crystals neither. Therefore, temperature control is one of the basic conditions for the crystallization of polymer chains. The optimal crystallization temperature of polymer is generally between glass temperature (T_g) and melting point (T_m). Defined the optimal crystallization temperature as T_k, then

$$T_k = 0.5(T_g + T_m) \tag{5.1}$$

(3) **Stretching force**: Under the action of the external tensile force, the molecular chains will be oriented and arranged more closely, the force between the chains will be greater, and the ability to form crystals will be stronger. The polymer chain generally forms folded lamellar crystals, spherulites, etc. The material structure consists of crystalline, transition, and amorphous regions. When being stretched by an external force, the molecular chains in the amorphous region will be converted into shish-kebab under the guidance of gravity to form polymer fibers, which greatly improves the mechanical strength of the material. For example, the tensile strength of polyethylene can be increased several times or even more than ten times after being stretched. Another example is that the fiber after stretching of linear high-density polyethylene can be the core material of bulletproof clothing, whose strength is higher than that of steel.

(4) **Nucleating agent**: The crystallization process of polymer chains is the same as that of inorganic compounds, it also needs appropriate nucleating agent materials to start the process. The nucleating agent plays the role of seed crystals. With the induction of seed crystals, the crystallization rate will be greatly accelerated. Some optical materials need polymer chains to form good crystals to improve optical transmittance, such as artificial polymer crystals, glasses, and camera lenses. For materials with strict requirements on transmittance, nucleating agents should be added to form uniform microcrystals so that the size of microcrystals can be smaller than the wavelength of light, which not only improves the transparency of materials but also enhances the mechanical strength of materials.

The typical crystalline structures of polymers include single crystal, spherulite, microcrystal, as well as the semi-crystalline structure connected by fiber chain bundle and amorphous region, the crystalline structure of extended chains connected by extended chain bundles and crystalline regions, single molecular crystal, and double helix crystalline structure. The first few types are the crystalline structures of organic polymers, and the last few types are crystalline structures of biological macromolecules such as proteins.

4. Radiation crosslinking mechanism of polymer

Crosslinking refers to the generation of free radicals by linear polymers under the action of initiators or rays, which initiate chemical reactions between molecular chains and form a three-dimensional network structure. After crosslinking, the material changes from fusible and soluble to infusible and insoluble, and swelling can

occur in the solvent. When the temperature rises, the material will soften and cannot form polymer melt, which is unable to carry out normal injection molding, blow molding, extrusion, and lamination.

In Fig. 5.4, (a) is a flexible linear structure and (b) is a rigid three-dimensional structure formed after radiation, also known as a T-shaped structure. The change of structure brings significant changes in the properties of materials, such as the improvement of mechanical properties, electrical properties, and temperature alternating resistance, which meet the application requirements of materials under severe conditions.

From the molecular level, after the incidence of high-energy electron beams or γ-rays, polymer chains are excited, and active atoms such as hydrogen are very easy to fall off from the main chain to form free radicals or ionize to form positive and negative ion pairs. Taking the typical radiation crosslinkable polymer-polyethylene as an example, the polymer chain generates free radicals after being irradiated, which have high activity. Chemical processes such as chain transfer of free radicals, annihilation of free radicals, breaking and arrangement of polymer chains, and grafting small molecules on long chain molecules will occur in molecular chains.

Figure 5.5(1) shows the average bond energy of each chemical bond of the polyethylene molecular chain, in kilojoules per mole (kJ/mol), where the C_2–C_3, C_5–C_6, and C_6–C_7 bonds have the smallest bond energy, which is easy to break or fall off atoms when exposed to radiation, forming free radicals or excited macromolecules. When excited macromolecules are ionized, groups with high reactivity will also be to participate in crosslinking, grafting, and degradation reactions, dehydrogenate and generate double bonds, resulting in higher reactivity of polymer chains, thus accelerating crosslinking and other reactions, and improving the macroscopic properties of materials.

From the above reaction steps, Step (2) is the key step to determine the efficiency of the crosslinking reaction, that is, the generation of free radicals determines the rate and yield of reaction. The mechanism of cross-linking is similar to that of the synthetization of free radicals by polymer, which goes through the following steps: The first step is chain initiation, that is, the generation of free radicals by the molecular chains under the action of high-energy rays. The second step is chain growth, which gives rise to the rearrangement reactions among molecular chains, free radicals and free radicals, and in free radicals themselves, leading to the growth of molecular chains to form larger molecules or supermolecules. The third step is

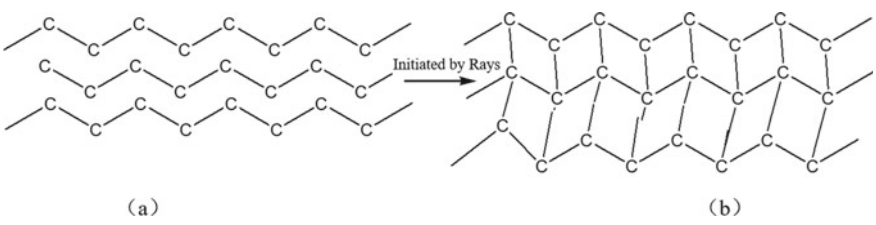


Fig. 5.4 Schematic diagram of radiation crosslinking of polymer chain

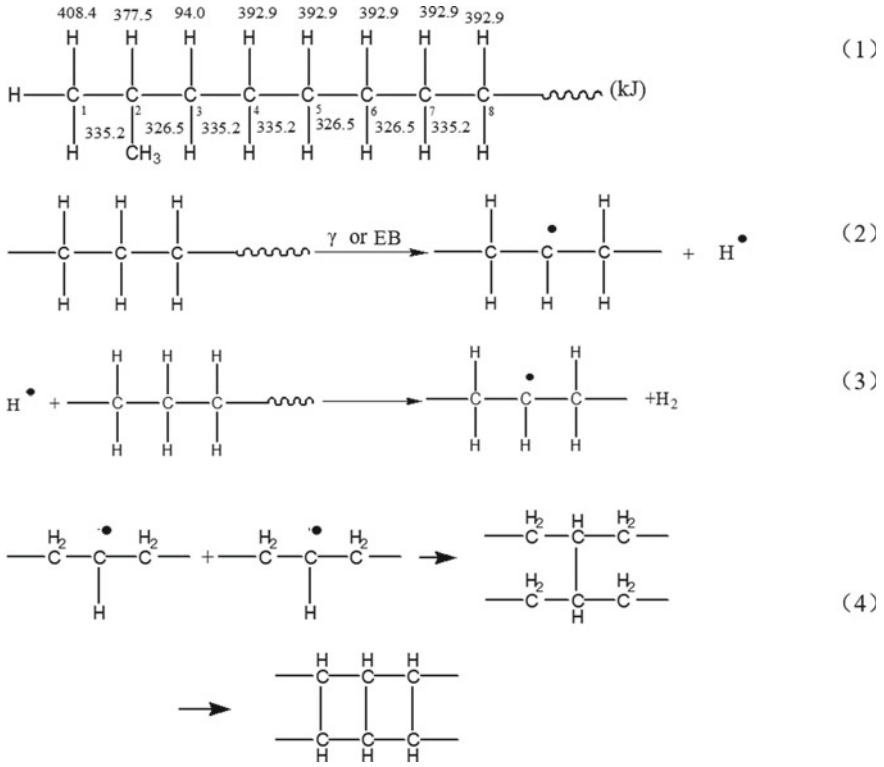


Fig. 5.5 Three-dimensional network structure formed by radiation crosslinking of polymer

chain transfer, which moves to macromolecules, causing branching or crosslinking of macromolecules. And the final step is chain termination.

Step (4) in Fig. 5.5 is the process of annihilation of two free radicals to form a crosslinking bond, which can also be the reaction shown in Fig. 5.6, that is, the free radical macromolecule is very active. Free electrons transfer on the chain, sometimes annihilation, disproportionation, rearrangement, and grafting occur. Sometimes when encountering a hydrocarbon bond at a weak position, the hydrogen is removed and a double bond will be formed on the main chain. The addition reaction between the double bond and saturated carbon chain polymer can take place under the action of many factors, and cross-linking products can also be produced.

According to the basic theory of radiation chemistry, factors such as free radicals, secondary electrons, positive and negative ion pairs, etc. that are conducive to radiation crosslinking increase with the increase of irradiation dose. However, the excessive dosage is harmful to crosslinking. The result is that large polymer chains degrade and form small molecules under the action of excessive irradiation dose, which cannot achieve the purpose of improving the comprehensive properties of materials by irradiation. Charsby-Pinner put forward the famous classical equation in the early days, which requires several basic assumptions for the establishment.

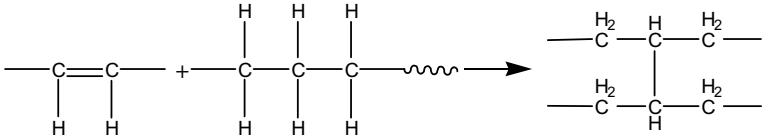


Fig. 5.6 Crosslinking between unsaturated double bond molecules and saturated molecules under radiation

Firstly, in polymer chains, the crosslinking between two molecular chains and the degradation of macromolecular single chains led by radiation occur randomly, and the chain length between two crosslinkable adjacent points obeys the most probable distribution. Secondly, the radiation-induced crosslinking and degradation occur independently. Thirdly, when the crosslinking density and degradation density are low, they are only related to and proportional to the absorbed dose.

When the polymer materials absorbed the irradiation dose, the probability of crosslinking of each unit on the polymer main chain is defined as the crosslinking density, which is expressed by q. If a polymer chain has A_1 repeating units, the number of units involved in crosslinking is qA_1. But crosslinking occurs between two units, so the number of crosslinking bonds is $\frac{1}{2}qA_1$. With the increase in irradiation dose, the crosslinking density of polymer chains increases gradually. In an ideal state, the polymer chain is highly crosslinked, and the crosslinking bond is infinite with respect to the end of the polymer chain, so the end of the molecular chain can be ignored, and the whole system can be regarded as a network structure and become a closed system. That is, the chain end of the molecule can also be crosslinked. When the crosslinking group is divided into many crosslinking units, it is considered that each unit is a crosslinking unit, so that the crosslinking density is easy to calculate. That's to say, if a polymer chain has A_1 units, the units that have been crosslinked are qA_1, and the average crosslinking segment is $\frac{A_1}{A_1 q} = \frac{1}{q}$ units. For polymers, the molecular weight of each unit is generally the molecular weight of the monomer, assume it to be w. Thus, the weight of the crosslinking unit can be obtained, which is expressed in M_c:

$$M_c = \frac{w}{q} \tag{5.2}$$

M_c is very important for radiation chemistry. The smaller the M_c, the higher the degree of crosslinking, and the higher the solvent resistance of the irradiated polymer material. The polymer material with a three-dimensional network structure has low swelling in the solvent, the elasticity of the material decreases, the tensile strength and shear strength increase, and the elongation at break decreases.

The radiation crosslinking experiment confirms that the crosslinking density q is proportional to the crosslinking dose D absorbed by the polymer material, and has little relationship with the irradiation dose rate, thus:

$$q = q_0 D \tag{5.3}$$

In the above equation, q_0 is the constant of the radiation sensitivity of polymer materials, which is determined by the properties, structure, molecular weight, composition, and other parameters of polymer materials, and is proportional to the crosslinking value G. The crosslinking dose D was expressed in the unit Rad in the early days, but now the international unit is Gy or kGy.

$$1\,\text{Rad} = 10^{-2}\,\text{Gy} = 0.624 \times 10^{20}\,\text{eV/g} \tag{5.4}$$

After absorbing 0.624×10^{20} eV/g of energy, the energy absorbed by each mole of repeating unit energy converted into a polymer unit is

$$\frac{0.624 \times 10^{20} w}{6.023 \times 10^{23}} = 1.04 \times 10^{-4} w\,\text{eV} \tag{5.5}$$

The absorbed energy can generate q_0 crosslinking units, so every 1 eV of energy absorbed by the polymer material will generate $\frac{q_0}{1.04 \times 10^{-4}} w$ crosslinking units. According to the number of crosslinking units, the number of crosslinking bonds can be deduced:

$$G(crosslinking\,unit) = \frac{q_0}{1.04 \times 10^{-4} w} \times 100 = \frac{0.96 \times 10^4 q_0}{w} \times 100 \tag{5.6}$$

Thus,

$$G(crosslinking\,unit) = \frac{0.96 \times 10^6 q_0}{w} \tag{5.7}$$

$$\begin{aligned} G(crosslinking\,bond) &= \frac{q}{2} = \frac{G(crosslinking\,unit)}{2} = \frac{0.96 \times 10^6 q_0}{2w} \\ &= \frac{0.48 \times 10^6 q_0}{w} \end{aligned} \tag{5.8}$$

From this, it can be deduced that the calculation formula of MC is

$$M_c = \frac{w}{q} = \frac{w}{q_0 D} = \frac{0.48 \times 10^6}{GD} \tag{5.9}$$

Equation (5.9) gives the calculation formula of crosslinking density, where the values of q_0 and G are determined by the chemical structure and composition of the polymer. When these two parameters are determined, M_c is only related to irradiation dose. Sometimes, temperature also have certain impact, but does not play a decisive role.

In addition to crosslinking, irradiated polymers also undergo cleavage. Generally speaking, p is defined as the probability of radiation cleavage of each unit, also known as degradation density. For purposes of improving the properties of materials through

radiation crosslinking, radiation cleavage needs to be avoided. As with crosslinking, radiation cleavage is also proportional to irradiation dose.

$$p = p_0 D \tag{5.10}$$

$$G(cleavage) = \frac{0.96 \times 10^6 p_0}{w} \tag{5.11}$$

In the theory of radiation crosslinking, another parameter is very important, namely the gel point. Before reaching the gel point, the thermoplastic polymer is completely soluble, and the effect of radiation is only to increase the average molecular weight of the system and the degree of branching of the molecular chain. However, with the increase in irradiation dose, the polymer chain will be crosslinked continuously. Every time a crosslinking bond is formed, two independent molecules will be reduced, so that the molecular weight distribution of the system changes continuously with the increase of radiation crosslinking. Changes in molecular weight lead to changes in various properties of polymers. The relationship between gel content, molecular weight change in the system, and irradiation dose is shown in Eq. (5.12).

$$\frac{1}{M_w} = \frac{1}{(M_w)_0} + \frac{\left(\frac{1}{2} p_0 - q_0\right) D}{W} \tag{5.12}$$

where

M_w weight-average molecular weight at any time of irradiation.
$(M_w)_0$ weight-average molecular weight at the beginning of the system.
p_0, q_0 radiation cleavage density and radiation crosslinking density.

The gel content is expressed by δ. When $\delta = 1$, gel began to appear in the system. When $\delta > 1$, the system consists of two parts. One part is linear polymers soluble in the solvent or slightly crosslinked gel, which is called sol. The other part is macromolecules that are completely insoluble in solvents and can swell under the action of solvents and heat, that is, the solvent of small molecules penetrates into the crosslinked network structure and expands in the system, this part is called gel.

Charlesby-Pinner obtained the famous formula based on the assumption of random cross-linking:

$$s + s^{1/2} = \frac{p_0}{q_0} + \frac{1}{(q_0 u_1 D)} \tag{5.13}$$

where

s solute fraction;
u number-average or weight-average molecular weight, or the number of molecules.

To calculate the sol fraction of the irradiated system by Eq. (5.13), the following assumptions must be met.

① Random crosslinking and random molecular weight distribution.
② The intermolecular crosslinking of polymer is negligible.
③ Random radiation cleavage.
④ Radiation crosslinking and cleavage reactions are carried out independently.
⑤ Relatively small degree of cleavage and crosslinking.
⑥ Both the degree of cleavage and crosslinking are proportional to the absorbed dose.

The above six assumptions provide good boundary conditions for the application of Eq. (5.13), which plays a qualitative role in the practical study of radiation crosslinking which played a positive role in the early research of radiation chemistry. However, with the deepening of radiation chemistry research, a significant difference can be seen between the calculated results and experimental measurements in practical research and work, which cannot solve practical problems. In view of the gap between the theoretical calculation results and the experimental measurement results, many people have proposed amendments to the equation. For example, A. Keller argued that polymers are often not random and they have certain degree of crystallinity. In the crystal, the free radicals generated by radiation are more or less randomly distributed in the crystal, and the lattice energy restricts the movement of the free radicals and reduces the probability of crosslinking. Therefore, the influence of polymer crystals on radiation effect cannot be ignored. Although it is still unclear how to quantify this effect, many people have modified it on the basis of the Charlesby-Pinner formula and in combination with the properties and characteristics of polymers themselves, in order to guide the specific practice of radiochemistry research.

After the polymer is irradiated by electron beams or γ-rays, free radicals are formed to initiate crosslinking reactions and cleavage reactions between polymer chains. There are similarities and differences between the study of reaction kinetics and the mechanism of polymer synthesis. The parameters that affect the properties of the final material such as degree of crosslinking, gel content, degradation rate, etc. cannot be obtained simply according to a certain factor or condition. For more detailed theories, see relevant articles and books for deeper understanding, this book will not discuss them in depth.

In the formulation design and application of materials, various influencing factors should be comprehensively considered to fully utilize the advantages of radiation, and the radiation dose should be reduced to reduce unnecessary material damage (such as the cleavage, grafting, rearrangement, and other reactions of polymer chains) caused by high-dose radiation, and realize the crosslinking necessary for material modification. In fact, in the formulation of radiation crosslinked polymer materials, there are other auxiliaries besides polymers. In order to meet different application purposes, it is often necessary to add many auxiliaries such as antioxidants, mold-proof agents, antistatic agents, UV stabilizers, etc. Besides, various inorganic fillers

are also needed to improve the mechanical strength. The addition of these auxiliaries will seriously influence the radiation effect and prevent the generation of free radicals. They either absorb free radicals or decompose polymer chains with free radicals, greatly reducing the efficiency of radiation crosslinking. At the same time, the catalyst that could not be washed during the synthesis of polymer also affect the radiation crosslinking efficiency. Therefore, in practical application, the derivation of the relevant formula needs to test the relationship curve between the radiation dose and the gel content, mechanical strength, electrical strength, elongation at break, and other parameters of the composite for each formula. Determining the appropriate irradiation dose is the key to developing new materials. Only through experiments can high-performance and applicable products be prepared.

5.2.2 Radiation Crosslinking of Thermoplastic Polymers

Thermoplastic polymers generally have an obvious melting range and melting point. Typical thermoplastic polymers include polyethylene (PE), polypropylene (PP), ethylene–vinyl acetate (EVA) copolymers, etc. They have good mouldability, extrudability spinnability, and stretchability. Thermoplastic polymers can be extruded, layered, blown, molded, and injection molded by utilizing their different properties and melting point ranges. According to the end use and shape of the product, different molding methods can be used.

For certain purposes, pure polymer resins cannot satisfy the required performances for various applications, which must be considered in the material formulation. The processed products can be mainly divided into structural members, insulation protectors, and thermal insulation materials according to the end use. Structural members are generally shells, supports, containers, etc. of machinery and equipment. Insulation protectors include the insulation layer and protective layer of wires and cables, as well as joint protectors of wires and cables. Thermal insulation materials such as polyurethane are widely used in air conditioners, refrigerators, gas and oil pipelines, and urban heating pipelines.

Therefore, for different applications, the following factors need to be considered in formulation design.

1. **Polymer matrix**

The polymer matrix is the decisive material in the entire radiation crosslinking system. Its properties determine the performance and service life of the final products, which requires that the main substrate has a suitable molecular weight. The molecular weight can be characterized by viscosity-average molecular weight, weight-average molecular weight ($\overline{M_W}$), and number-average molecular weight. Viscosity-average molecular weight usually refers to the average molecular weight measured by the viscosity method. Weight-average molecular weight refers to the statistical average molecular weight according to the molecular weight distribution function,

which can be measured by the light scattering method. Number-average molecular weight is the statistical average molecular weight according to the molecular number distribution function, which can be measured by osmotic pressure method, ebullioscopy, cryoscopy, or end group analysis process. The relationship among the three molecular weights is: weight-average molecular weight > viscosity-average molecular weight > number-average molecular weight. But polymer manufacturers generally only give the value of the weight-average molecular weight, and the other two molecular weights are only for reference in practical application.

The classical Flory empirical formula gives the relationship between the viscosity-average molecular weight and the weight-average molecular weight of the polymer as follows:

$$\log \eta = A + B\overline{M}_w^{1/2} \tag{5.14}$$

where A and B are constants and depend on the properties of the polymer and the temperature. Therefore, the viscosity-average molecular weight of the polymer is closely related to that of the weight-average molecular weight. Once the polymer is selected, the weight-average molecular weight can be determined. By introducing the Arrhenius equation, the relationship between the viscosity of polymers and temperature can be obtained. With this relationship, the calculated viscosity can be provided to the molding process as a decisive parameter.

In order to achieve good processability and mechanical properties, the polymer selected must have the best molecular weight distribution. Generally speaking, the presence of high molecular weight polymers will increase the toughness of materials, but also greatly improve the melt viscosity, which makes processing difficult, that is, high molecular weight polymers have a high melting temperature. Therefore, it is necessary to increase the processing temperature to facilitate molding, which will inevitably increase the probability of polymer degradation and significantly increase the decomposition rate of the polymer. On the other hand, high molecular weight polymers will also increase the processing time. In the presence of high temperature and high molding pressure, the polymer undergoes greater oxidation and mechanochemical reactions, and the degradation of the polymer chain is accelerated, resulting in a significant decline in mechanical properties, electrical properties, and stress cracking resistance, which affects the service life of the product. Therefore, an appropriate molecular weight distribution of polymer should be selected to meet the requirements of both the product performance and the processing technology.

The melting index (MI) of the polymer matrix is the main parameter to measure the processability of a polymer, and an index to reflect the melt fluidity characteristics and molecular weight of the polymer. The MI is defined as the mass of polymer, flowing in ten minutes through a capillary of a specific diameter (generally 0.2 cm) and length by a pressure (2160 g) applied via prescribed alternative gravimetric weights for alternative prescribed temperatures (generally 196 °C). For different processing methods, product shapes, and uses, the appropriate melt index should be selected. Based on the experience of polymer molding processing, the relationship between the melt index and the molding processing method can be obtained in Table 5.4.

Table 5.4 Empirical values of polymer melt index corresponding to different molding methods

Processing method	Product	MI of resin	Processing method	Product	MI of resin
Extruding	Pipe	< 0.1	Injection	Bottle (glassy substance)	1–2
	Sheet and bottle	0.1–0.5		Film (salivating film)	9–15
	Thin-walled tube			Molded parts	1–2
	Wire and cable	0.1–1		Thin-walled products	3–6
	Thin slice	0.5–1	Coating	Coated paper	9–15
	Monofilament (rope)		Blowing	Part	0.2–0.5
	Multi-strand wire or fiber	≈ 1			

For polymers, the melting point of the polymer matrix is generally called the melting range. Two main parameters are used to characterize the melting range of polymers, one is the ring and ball softening point, and the other is the Vicat softening point. The ring and ball softening point is generally used for adhesives and coating monomers with better fluidity, while the Vicat softening point is generally used for polymer materials with relatively high viscosity. The melting range has a decisive influence on the temperature of the final use of the product. Therefore, in the radiation polymerization system, the melting point or melting range of the polymer must be seriously considered, and sometimes the crystallization temperature of the polymer.

The crystallinity of the polymer matrix also needs to be considered. According to the general theory of radiation chemistry, radiation crosslinking occurs in the amorphous region of polymer materials, where the rays destroy the crystalline region and constantly form new amorphous regions to participate in the crosslinking reaction.

The length of the molecular chain and degree of branching of the polymer matrix also affect the radiation crosslinking. If the molecular chain is long, the free radical activity generated by radiation is low, and the efficiency of participating in crosslinking is also low. The degree of branching of the molecular chains is favorable to the radiation crosslinking reaction. However, the increase of the branching degree of the molecular chain will increase the intermolecular distance and reduce the intermolecular force, thus reducing the tensile strength of the polymer materials, but increasing the impact strength. In the actual formulation of radiation crosslinked materials, the selection of materials with appropriate parameters is the basis for achieving ideal results.

2. **Secondary polymer**

In the formulation system, a single kind of polymer cannot fully meet the performance requirements. Therefore, the addition of a secondary polymer is an effectively supplement to the performance of the polymer matrix and the entire material system. The purpose is to enhance the processability of the compound and to improve the electrical properties, compatibility, irradiation sensitivity, etc. For example, in systems based on polyethylene, ethylene–vinyl acetate (EVA), ethylene ethyl acrylic (EEA) copolymer, ethylene acrylic acid (EAA) copolymer, etc. are often added. Modified polymers such as ethylene grafted acrylic acid, ethylene grafted acrylate, etc. are also added. They have good compatibility with both the polymer matrix and various auxiliaries. After compounding and blending, macrohomogeneous phase will be formed, and during the service life, material delamination, migration of component out of the surface of the part, or crazing will not occur.

In terms of modifiers, the DuPont has launched a variety of products, such as Surlun®, Fusabond®, etc., which are all excellent modifiers. Surlun® is used for toughening nylon materials and improving the compatibility between nylon and various inorganic fillers. Its chemical composition is ion-bonded trimer. Fusabond® is the anhydride modified polyethylene, typically maleic anhydride grafted polyethylene, and maleic anhydride grafted ethylene–vinyl acetate, which has the characteristics of polymers and strong polarity of inorganic materials, and plays a key role in the composite formulation system to improve material properties. Therefore, improving material properties is essential for material formulation.

When selecting the secondary polymer, the matching between the second polymer and the polymer matrix must be considered. The melting ranges of the two materials should be similar. After blending, they can form macrohomogeneous phases to improve the properties of the materials. Generally speaking, if the polymer matrix is 100 phr, the secondary polymer is better to be added no more than 20 phr. If too much secondary polymer is added, it will play a dominant role in the material formula, which will reduce the role of the polymer matrix and cannot meet the performance requirements of the final product.

3. **Sensitizer**

In the composite system, the molecular chains of the polymer matrix and the secondary polymer are very easy to break under the action of high-energy rays, which cannot achieve the purpose of enhancing the performance of materials but will be counterproductive. Therefore, it is necessary to reduce the damage of high-energy rays such as electron beams, γ-rays, etc. to polymer chains. Adding sensitizer is an effective way to solve this problem. Under the action of rays, the unsaturated bonds of sensitizers are broken to form a large number of free radicals, which enhances the efficiency of radiation crosslinking. Since the rate of the radiation crosslinking

reaction depends on the concentration of initial free radicals, a large number of free radicals generated by sensitizers during irradiation can greatly accelerate the radiation crosslinking reaction, thereby reducing the irradiation dose.

Sensitizers are generally unsaturated compounds containing multi-functional groups. In the actual formula, as triallyl isocyanurate (TAIC), triallyl methyl-acrylate (TAMA), triallyl cyanurate, diallyl aconitate, tetraallyl pyromellitate, N,N[11]-ethylene-bismaleimide, etc. are often used.

The compatibility of the sensitizer and the composite system is an issue that must be paid attention to. The sensitizer should be selected according to the structure and properties of the polymer matrix and the secondary polymer. Only when the structure is similar can the above two have certain compatibility. The molecular weight of the sensitizer is only several hundred or thousands, which is insignificant compared with the polymer. Therefore, the sensitizer is generally liquid at room temperature. At low temperatures, some sensitizers will condense into solid, depending on their molecular weight and structure. The melting point and boiling point of the sensitizer are other parameters that should be paid attention to. During blending and molding, the polymer needs to be melted by heating. If the boiling point of the sensitizer is far lower than the processing temperature of the formulation system, it is easy to vaporize and evaporate during heating, migrate from the formulation system and diffuse into the air, reducing the effective amount of the sensitizer in the formulation system and cannot promote radiation crosslinking. Therefore, ensuring that the boiling point of the sensitizer is higher than the processing temperature of the material is an important guarantee for the sensitizer to be effective in the formulation system.

The amount of sensitizer added in the formulation system depends on the specific formulation, and is generally several thousandths to several percent.

4. **Plasticizer**

In the formulation system, the existence of polymers and auxiliaries leads to an increase in melt viscosity. Excessive viscosity will bring potential safety hazards to processing equipment and adversely affect product molding. Adding the plasticizer to polymers can reduce the viscosity and glass transition temperature of the polymer system. With the increase in plasticizer content, properties of polymers such as elasticity modulus, yield pressure, tensile strength, and brittleness temperature generally decrease, while the elongation at break and impact strength will increase. Plasticizers can not only lower the glass transition temperature of polymers but also increase the width of the transition zone, which is the main means to solve the problem of high melt viscosity at processing temperature.

The role of plasticizers is to reduce the interaction between polymer chains. When the non-polar plasticizer is dissolved in the non-polar polymer, the distance between the polymer chains increases, the force between polymer chains decreases, the friction of relative movement between chain segments is reduced, and the chain segments are easier to move, thus reducing the glass transition temperature and elastic modulus of the polymer and improving the impact resistance. The mixed system made of non-polar plasticizers and non-polar polymers is equivalent to a concentrated polymer

solution. The polymer molecular chains are separated by plasticizer molecules at a certain distance, which weakens the secondary crosslinking between polymer molecules. The more plasticizer is used, the greater the isolation effect between molecular chains. Moreover, the contact opportunities between the long-chain plasticizer and the polymer molecular chain are more than those of the cyclic plasticizers, and the isolation effect is more significant. The plasticizer itself has a glass transition temperature. According to the free volume theory, assuming that the free volume of the two components of polymer and non-polar plasticizer have additivity, then when the plasticizer is added, the free volume of the mixture is equal to the sum of the free volume of the polymer and the free volume of the plasticizer. Thus, the glass transition temperature of the polymer that is reduced after plasticizing is directly proportional to the volume of the plasticizer, that is

$$\Delta T = kV \tag{5.15}$$

The free volume of the polymer is

$$V_{fp} = \left[0.025 + a_p(T - T_{GP})\right]_P \tag{5.16}$$

The free volume of the plasticizer is

$$V_{fd} = 0.025 + a_d(T - T_{gds})]V_d \tag{5.17}$$

$$V_{fp} + V_{fd} = V_f = 0.025\left(V_p + V_d\right) + a_p\left(T - T_{gp}\right)V_p + a_d\left(T - T_{gd}\right)V_d \tag{5.18}$$

When $T = T_g, f = 0.025$.

$$a_p\left(T_g - T_{gp}\right)V_p + a_d\left(T_g - T_{gd}\right)V_d = 0 \tag{5.19}$$

$$T_g = \frac{a_p\, T_{gp}\, V_p + a_d\, T_{gp}\left(1 - V_p\right)}{a_p\, V_{\,p} + a_d\left(1 - V_p\right)} \tag{5.20}$$

The larger the volume of plasticizer molecules, the better the plasticizing effect, and long-chain molecules have better plasticizing effective than cyclic molecules. The influence of non-polar plasticizers on the glass transition temperature of non-polar polymers can be expressed as

$$\Delta T = a\Phi \tag{5.21}$$

where

Φ volume fraction of plasticizer.
a constant of proportionality.
ΔT the value of glass transition temperature reduction of the polymer.

The plasticizing effect of polar plasticizers on polymers is not an isolation effect between molecular chains, but the interaction between the polar group of plasticizers and the polar group of polymer molecular chains. It weakens the interaction of polymer molecular chains and reduces the number of secondary crosslinking points formed by the interaction of polymer molecular chains. Therefore, the reduction of the glass transition temperature of polar polymers caused by polar plasticizers is proportional to the number of moles of the plasticizer.

$$\Delta T_g = \beta n \tag{5.22}$$

where

β constant of proportionality.
n number of moles of the plasticizer.

The glass transition temperature of the polymer is the temperature at which the chain segment begins to move. Therefore, the application of external force is conducive to the movement of the chain segment, which lowers the glass transition temperature of the polymer. The greater the force, the more reduction of the glass transition temperature.

Commonly used plasticizers such as paraffin wax and paraffin oil, polyethylene wax, and diethyl phthalate are all excellent plasticizers. The amount of plasticizer added should be determined by the composition, processing methods, and process parameters in the formulation system.

5. **Antioxidant, heat stabilizer, and flame retardant**

Antioxidants and heat stabilizers can eliminate or reduce the degradation of polymers during processing, and can also prevent the aging and oxidation of materials during the use of products. The main causes of polymer degradation are the peroxide generated during processing, the catalyst residue of polymer synthesis, the metal particles brought in during processing, and the residual free radicals in the crosslinking process. Below the softening point, the branched chains, and the amorphous region are oxidized first, while above the melting point, the crystalline region, the amorphous region, and the branched chains are oxidized simultaneously. An antioxidant is a small molecule substance, which is dispersed in PE, PP, and PO that does not volatilize during storage or use. However, the most ideal antioxidants are those combined with PE, PP, and PO molecules to achieve good free radical transfer.

Therefore, the general basic principles for selecting antioxidants and stabilizers are:

(1) The effect of the thermal history experienced by the formulation system on the photooxidation performance of the stabilizer system after processing and other processes. The chemical changes of additives during processing must be carefully considered, which may affect the photostability of the stable system of polymers.
(2) Light stability of the stabilizer or its conversion products.

(3) The nature of the environment over the lifetime of the polymer. This environment may be simple photooxidation or a combination of photooxidation and thermal aging.
(4) The influence of the environment of the polymer on its physical behavior. For example, the stabilizer should not be lost due to volatilization or leaching from the polymer product system in use.

Some physical processes will also affect the stability of the polymer. The crystallization of polymers has an effect on their oxidation kinetics, and the influence of orientation on oxidation kinetics is not only determined by the stretch ratio. Rapoport once reported that the oxidation rate of oriented polypropylene samples increased after annealing, while the stretching rate remained unchanged. It was also found that the activity of the amorphous phase chain segment increased with annealing, which makes the difference between samples with different stretching rates smaller. According to Yasuda and Peterlin, this can be attributed to the non-equilibrium state of the amorphous phase chain segment after uniaxial plastic deformation induced by low-temperature stretching. Annealing above this stretching temperature will produce more relaxed amorphous components. In addition to the stretching rate, the stretching conditions and the post-treatment conditions of the oriented samples also affect the oxidation kinetics, because these variables also determine the morphology of the polymer. The γ-initiation and photooxidation of polypropylene monofilaments are independent of the degree of orientation but significantly depend on the extrusion and stretching conditions. It was also found that high-speed stretching at low temperatures will reduce light stability. Oxidation during stretching plays an important role because stretching to monofilament in vacuum is more stable than that in air. Oxidation is caused by the free radicals generated by the chain breakage when the polymer is stretched. After stretching the neck, the aging rate will be slowed down by stress.

The stabilizing mechanism of stabilizers is the chain-breaking donor (CB-D) mechanism. Hindered phenolics such as butylated hydroxytoluene (BHT) (I) and Irganox 1076 (II) are suitable melt stabilizers for polyethylene. For many applications, relatively low concentration ($< 10^{-2}$/100 g) can achieve the purpose.

For polymer molecular chains of heteroatoms such as polyamides, there are two types of thermal-oxidative aging stabilizers. One is the inorganic stabilizer, which includes copper and its inorganic and organic acid salts, alkali metal salts of bromine and iodine, and phosphoric acid and its aryl esters. These stabilizers are often mixed. For example, when polyamide slices are used for spinning, $CuCl_2$, RI, or phthalimide methyl salt are mixed to improve the heat resistance. Generally speaking, most copper salts have the effect of accelerating aging in other polymers, but they have a stabilizing effect on the polyamide (Fig. 5.7).

Another type of organic antioxidant stabilizer is used to improve the thermal stability of polyamides. The common kinds used are as follows.

(1) Aromatic amine (Figs. 5.8, 5.9, 5.10 and 5.11)

(2) Phenolic compound (Figs. 5.12 and 5.13)

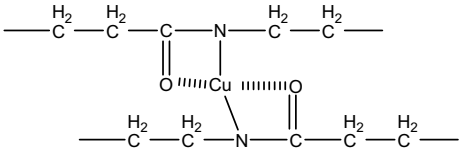


Fig. 5.7 Stable complex formed by copper stabilizer and polyamide

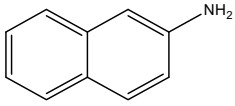


Fig. 5.8 β-Naphthylamine

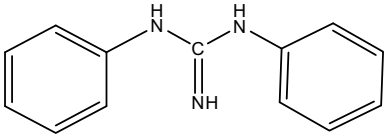


Fig. 5.9 Diphenylguanidine

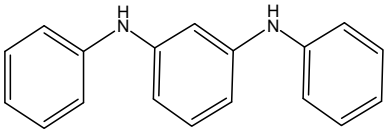
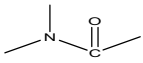


Fig. 5.10 N,N-diphenyl-p-phenylenediamine

(3) Polyhydroxy aliphatic compound

The mixture of stearic acid, ethylene glycol, and ω-hydroxyl hexanoic acid is prone to yellowing and embrittlement under the action of ultraviolet light for polyamide fiber and film, especially for nylon film that is most vulnerable to light damage. Different varieties of polyamides have different stability to light. For example, the light stability of nylon-66 is better than that of nylon-6. Polyamide is sensitive to light with a wavelength of 350 μmm, the  will fracture

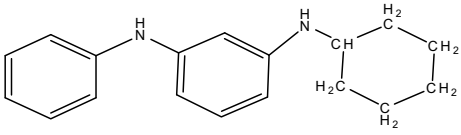


Fig. 5.11 N,N-phenylcyclohexyl-p-phenylenediamine

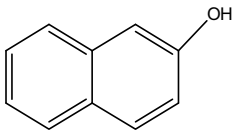


Fig. 5.12 β-Naphthol

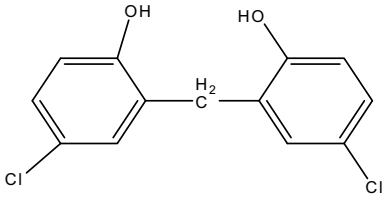
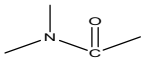


Fig. 5.13 Bis-(2-hydroxy-5-chlorophenylmethane)

because the fracture energy of the  is 222 kJ/mol, while the fracture energy of the C–C bond is 335 kJ/mol.

Some products made of polymers need flame retardation, so the addition of flame retardants is conducive to maintaining the performance of products under extreme conditions. For example, wires and cables need to maintain a certain amount of power in case of fire to increase the probability of escape of trapped people. Adding flame retardants to the sheath layer of wires and cables can ensure that they can maintain power supply for a period of time when the fire occurs.

The types of flame retardants include inorganic materials and polyhalogenated organic molecules. Common inorganic flame retardants include MgOH, $Al(OH)_3$, boron-zinc compounds, perlite, bentonite, etc., but they require extremely fine particles or materials with nanostructures. On the one hand, it can increase the flame-retarded efficiency of inorganic flame retardants, on the other hand, it can improve the mechanical strength of composites. Nano-sized MgOH and $Al(OH)_3$ are more evenly distributed in the polymer and have less impact on the material properties. According to polymer theory, adding inorganic fillers will significantly reduce the flexibility, elongation at break, and the temperature required for low-temperature embrittlement. If the amount of inorganic flame retardant is reduced, the negative effect of filler on material properties will be reduced. In addition to the requirement that the particle size should be small enough, the inorganic flame retardant should also undergo coupling treatment. The basic theory of chemistry tells that only similar substances are compatible. Since the properties of inorganic molecules and organic polymers are far from each other, when inorganic flame retardants are added to polymer materials, they are incompatible, resulting in a serious decline in the mechanical and other performance indexes of the materials. In severe cases, inorganic molecules may even migrate out of polymers. In order to solve the compatibility problem between inorganic flame retardants and organic polymers, coupling agents must be added. Commonly used are silane coupling agents and titanate coupling agents. Different coupling agents are selected for different purposes. Titanate coupling agents are used for products with strict electrical performance requirements, and silane coupling agents are used for products with strong polarity. The amount of coupling agent added is generally 1–5‰ of the weight of the whole system.

Several methods can be used to prevent the aging of polymers.

① Add various stabilizers, such as antioxidants, light stabilizers, etc.

② Implement physical protection, such as surface coatings and surface protection films. But this method is not applicable to some products, which need to be determined according to the specific use.

③ Improve the polymerization conditions and methods, such as adopting high-purity monomers, conducting directional polymerization, improving the polymerization process, reducing the branched chain and unsaturated structure of macromolecules, improving the post-treatment process, and reducing the residual catalyst in the polymer. However, the end-users of polymer raw materials can only select the available resins based on the brands and performance parameters of the raw materials of the synthetic resin manufacturers and cannot participate in upstream processes such as polymerization.

④ Improve the processing and molding process, such as reducing the processing temperature and heating time, controlling the mold temperature and the cooling rate of the molded parts (using gradient cooling), using inert gas protection when melting and tapping, and improving the formula of the coagulation bath during wet tapping. These methods are the main anti-aging measures for polymer material processing. When the structure and properties of the polymer cannot be controlled by the source of resin synthesis, measures can only be taken from the processing methods and processes to prevent aging.

⑤ Improve the use of polymers to avoid unnecessary sun exposure and baking, improve the washing method, and correctly use the detergents.

⑥ Modify the polymers, such as improving the macromolecular structure by copolymerization, blending, crosslinking, and other methods.

The following six points are the requirements for stabilizers.

① It should have good compatibility with the polymer in the formulation system. However, stabilizers include organic molecules and inorganic compounds. Therefore, the necessary treatment of stabilizers is an effective way to solve the problem of poor compatibility between inorganic substances and polymers.

Coupling treatment generally uses silane coupling agents, titanate coupling agents, and aluminum–lithium coupling agents. The structure of the silane coupling agent is X_3SiRY, in which Y is an organic functional group and X is a hydrolytic group. According to the theory of chemical bonds, coupling agents contain functional groups that can react with inorganic molecules and are compatible with polymers. The coupling agent has the infiltration effect and the surface effect. The selection of the organic functional group (Y) of the silane coupling agent requires that it should be reactive or compatible with the polymer, while the hydrolytic group (X) is only an intermediate in the process of generating the silanol group to form an adhesive bond on the inorganic surface.

The structure of the silane determines the performance of the silane coupling agent. For example, aromatic silanes usually have better thermal stability than aliphatic silanes, but as coupling agents of high temperature resistant resins, amino phenyl silanes have no great advantage over chlorophenyl silanes. Amino-functional silanes can be used as coupling agents for almost all condensation

thermosetting polymers, such as epoxy, phenolic, melamine, furan, isocyanate, and other resins, but it is not suitable for unsaturated polyester resins.

Epoxy silanes can be prepared by the addition reaction of silanes with unsaturated epoxy compounds or by the epoxidation reaction of silanes with saturated silanes containing double bonds to prepare organic functional group silicon compounds containing epoxy groups. Vinyl silanes are oxidized with peroxyacetic acid to produce vinyl oxides, but the reaction of this method is slow, and the yields are also low. The reaction product of siloxanes containing epoxy functional groups and polyethylene glycol is a surface active compound, which can be used as a foaming agent for polyurethanes.

Silanes containing epoxy groups are mainly used as coupling agents for reinforced condensation thermosetting polymers, such as epoxy resins, phenolic resins, melamine resins, and polyurethanes.

When silanes containing epoxy functional groups are coated in the form of an aqueous solution, the pH value of the solution must be kept above 4 to prevent the epoxy compound from hydrolyzing into oil ether. The sulfhydryl functional group silane is a convenient chain growth regulator in vinyl polymers and can introduce trimethoxy silane functional groups into each polymer molecule through the chain transfer reaction. Other silane functional groups can also be introduced by means of copolymerization of unsaturated silanes with other monomers. In order to achieve the adhesion of thermoplastic to glass, about ten functional groups of trimethoxy silane are required in each polymer molecule. When the silane coupling agent used glass fibers has three hydrolyzable groups, the wet strength retention rate of the composite will be the best.

In order to make the addition reaction of sulfhydryl functional group silane with inactive double bonds in styrene-butadiene rubbers and other sulfhydrizable organic elastomers, radical initiators can be used. The sulfhydryl functional group silane can be used as the coupling agent in the treatment of granular inorganic fillers, so as to upgrade such fillers to the reinforcing fillers of the sulfhydryl rubber.

Organic silicone materials containing carboxylic acid functional groups are usually coated in the form of the aqueous solution, so the free acid is not necessary to be removed. Organic silicates containing carboxylic acid functional groups are excellent coupling agents for epoxy resins but have not yet been applied in the industry. Organic carboxyphenyl silicates have excellent thermal stability and can be used in polybenzimidazole composites, but not polyimides. The hydroxyethyl in silane is easy to detach from the silicon atom, and hydroxymethyl silane will crack in strong bases, but the hydroxypropyl group on silicon atoms has the normal stability and reactivity of aliphatic alcohols. Silanes containing hydroxyl functional groups can be prepared by various combinations of sulfhydryl functional groups and unsaturated alcohols, epoxy functional group silanes with glycols or water, etc.

The coupling agent forms a monomolecular film on the inorganic substrate, in which each coupling agent molecule is chemically adsorbed on the surface of the substrate through the silanol reaction, while another functional group of the coupling agent molecule can still react with the matrix resin.

Typical molecular structures of coupling agents and the functional groups carried are shown in Fig. 5.14.

② It should have long-term volatility, so that the amount of migration or solvent extraction in the process can be as little as possible. The stabilizer in the product cannot migrate to the product surface rapidly with the increase of time, and some products will inevitably contact with water, oil, chemical solvent, acid, alkali, salt, and other solutions during use. The stabilizer existing in the product cannot be extracted by these solvents or solutions, which will affect the life of the product. If the amount of stabilizer extracted is small during the service life of the product.

③ It should be as colorless as possible. The color of the stabilizer affects the appearance of the product, and some colors are sensitive to light, which is easy to cause the photodegradation of the polymer.

④ It should be non-toxic and odorless. The final products of polymer processing are widely used, if the stabilizer is toxic and odorous, it will cause adverse effects on human body and the environment.

⑤ It should be stable to chemicals and heat. The purpose of stabilizers is to resist the damage of various chemicals to polymers, so they must be stable. In addition to the chemical reactions and degradation expected by the target, it is better to be resistant to other chemicals.

⑥ It should have multiple effects, especially with light, heat, and other stabilizing effects. The more "impurities" are added to the polymer system, the more adverse to the stability of the material. Reducing the type and amount of stabilizer can not only reduce or eliminate the factors that cause instability to the composite but also improve the mechanical and electrical properties of the material. More importantly, it can reduce the irradiation dose and improve the efficiency of radiation crosslinking. The stabilizer is generally composed of inorganic substances and a small amount of organic substances. The presence of inorganic substances will reduce the flexibility, breaking strength, shear strength, elongation at break, etc. of materials. Increasing the glass transition temperature will lead to embrittlement when subject to impact at a higher temperature, and cause the deterioration of material properties such as the appearance of craze. Stabilizers include free radical catchers and free radical decomposers. High-energy radiation leads to the generation of free radicals in polymers, triggering the crosslinking between molecular chains. However, the free radical capture and decomposition function of the stabilizer results in a significant reduction of the initial free radical concentration, reducing the efficiency of radiation crosslinking. In order to achieve a proper degree of crosslinking, it is necessary to increase the irradiation dose to accelerate the degradation of polymers. Therefore, controlling the

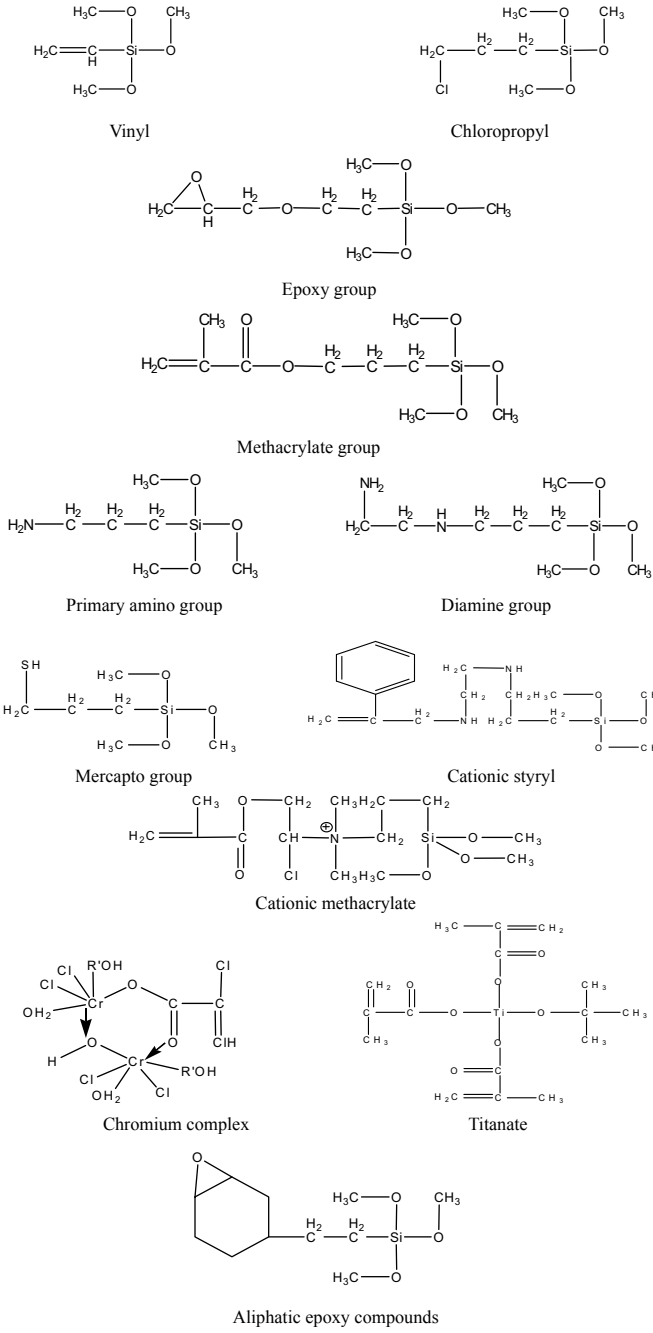


Fig. 5.14 Coupling agents containing different functional groups

amount of stabilizer added is beneficial to the improvement of the comprehensive performance of radiation crosslinked polymer composites.

Flame retardants are generally divided into organic halogenated aromatic compounds and inorganic compounds. The typical organic polyhalogenated compound is the decabromodiphenyl ether, which is the first choice of flame retardants in the early days. It has the advantages of less addition and good flame retardancy. However, products with decabromodiphenyl ether will produce a large amount of toxic smoke when flame retardant, resulting in suffocation and death of personnel trapped in the fire scene or poisoning. At the same time, the polyhalogenated diphenyl ether will cause serious environmental pollution, which is harmful to people, animals, and plants in the environment. Therefore, polyhalogenated diphenyl ethers are gradually prohibited. Currently, inorganic compounds are popular due to their non-toxic and good flame-retardant effect. Inorganic flame retardant compounds generally include $Al(OH)_3$, polyhydrates of Al_2O_3, $Mg(OH)_2$, Sb_2O_3, and boron compounds. $Al(OH)_3$ is generally selected for low-temperature flame retardant, while $Mg(OH)_2$ is used for flame retardant of higher temperature grade. When selecting inorganic flame retardants, the particle size of filler should be considered first. With the development of preparation technology, the particle size of the filler has reached the nanometer level. Nanometer $Al(OH)_3$ and $Mg(OH)_2$ have significant advantages as halogen-free flame retardants:

① The amount of flame retardant added is small. In the early days, it was necessary to add 30–70 phr of the $Al(OH)_3$ flame retardants to 100 phr of polymer to make the limiting oxygen index more than 30. After using the nano $Al(OH)_3$ and $Mg(OH)_2$, the amount added will be less than 30 phr, or even less.
② No toxic and harmful gases are produced. The principle of the flame retardant machine is that $Al(OH)_3$ or $Mg(OH)_2$ decomposes at high temperatures to release a large amount of water vapor, which blocks the acceleration of the combustion reaction and reduces the temperature of the ignition area. Meanwhile, the decomposed inorganic substances such as Al_2O_3 and MgO cover the surface of the polymer, forming a dense barrier layer, thus delaying the combustion.
③ With little or no effect on the radiation crosslinking efficiency. The benzene ring of polybrominated biphenyls is a strong free radical catcher, while $Al(OH)_3$ and $Mg(OH)_2$ will not capture the free radicals that initiate crosslinking.

$Al(OH)_3$ liberates the water at 200 °C, which absorbs 1.97 kJ of heat per gram of $Al(OH)_3$, and thus playing a cooling role. Equation (5.23) shows the formula of the reaction.

$$2Al(OH)_3 \xrightarrow{200\,^{\circ}C} Al_2O_3 + 3H_2O - 300\,kJ \tag{5.23}$$

Al_2O_3 forms a dense protective film with the carbonized layer, which inhibits the contact of oxygen with the polymer.

With the promotion of nanotechnology, the particle size of inorganic flame retardants such as $Al(OH)_3$ is getting smaller and smaller, even reaching several nanometers. In addition, the coupling treatment solves the problem of compatibility between inorganic particles and organic polymers, improves flame retardancy, reduces the amount of filler, and affects the mechanical properties of the composites. Therefore, inorganic flame retardants are widely used in the production and processing of radiation crosslinked halogen-free flame retardant wire and cable insulation and sheath materials, and gradually replace polybrominated diphenyl ether flame retardants.

Other smokeless or less smoky flame retardants include ferrocene, melamine, MoO_3, $CaCO_3$, etc. HCl is the main factor causing asphyxia and poisoning death in the fire, reducing the amount of HCl released can reduce the injury to personnel. $CaCO_3$ can absorb HCl released from polymer decomposition. Some inorganic compounds are conducive to reducing the amount of smoke generated, such as $MgCO_3$, $Na_2B_4O_7$, silicates of Na-Ca-Al, molybdenum compounds, Fe_2O_3, $Fe(OH)_3$, CuO, $Cu_2(CN)_2$, Cu(SCN), Cu_2S, CuS, FeS, SnS_2, MoB_2, TiB_2, V_2O_5, MoO_4Zn, etc. They can effectively transfer the heat and reduce the central flame temperature, promote the carbonization of polymers and combustibles, block the contact between oxygen and combustibles, and achieve the purpose of flame retardant.

Several important flame-retardant test methods and standards are listed below.

- ASTM D3363-77: Method for measuring oxygen index
- ASTM D2843-77: Method for measuring the smoke density of plastics during combustion
- ASTM D4100-80: Test method for the smoke weight of plastic materials
- ASTEM E662-79: Test method for optical density of smoke of solid materials
- UL910: Test method for fire and smoke of space cables
- UL224: Standard for testing performance parameters such as thermal aging and flame retardancy of extruded insulating heat-shrinkable tubing.

6. **Other additives**

Pigments and some structural stabilizers are often added to the formula system to achieve the optimization of materials and meet actual needs. Many kinds of wires and cables are used in large instruments, thus different colors are needed to distinguish wires and cables for different purposes. The amount of color added can be determined based on the actual needs. At present, many manufacturers produce mature master batches for customers to choose from, which avoids adding pigments directly to the system. Due to the dispersion of pigments, it is unnecessary to directly add pigments into the system. When different colors are required, it is only needed to select the master batch with the appropriate color according to the brand and use of resins.

For products with special purpose, antistatic treatment is required. Adding antistatic agents is an effective way to solve this problem.

Structural stabilizers such as glass fiber, clay, $CaCO_3$, $CaSO_4$, TiO_2, etc. can be used as fillers to improve the impact strength and compression strength of the products. According to different purposes and uses, different structural stabilizers

and fillers are selected to make the performance of materials meet the application of final products.

Other additives should be added appropriately based on specific needs, such as additives to prevent plant roots from being invaded, or being bitten by rodents and aquatic organisms. From the viewpoint of radiation chemistry, the more additives are added, the greater the effect on the efficiency of radiation crosslinking. Except for the sensitizer, the addition of other additives will reduce the concentration of free radicals, thus reducing the rate and yield of crosslinking, which is not conducive to achieving the desired.

5.2.3 Typical Radiation Crosslinking Formula of Thermoplastic Polymers

When designing a formula for radiation crosslinking olefin polymer, many factors should be considered. First of all, the purpose of the product should be clarified, and the environment that the product needs to withstand should be understood according to the purpose, such as temperature, indoor and outdoor, acid, alkali, salt, steam, organic solvent, and other factors. In addition, whether the product bears external forces, friction, and voltage should also be considered. The clearer the requirements for use can be understood, the more a material formula with superior comprehensive performance can be designed to achieve better cost performance.

1. **Basic formula of crosslinked polyethylene (PE)**

It's the radiation crosslinking formula for olefin polymers. The main substrate is polyethylene. Products used in indoor general environment such as radiation crosslinked low-voltage wires and cables, signal control wires, and cable connectors, are formulated as follows.

Table 5.5 shows the radiation crosslinking formula of the most common polyethylene-based polymers. In practical application, the materials in the formula will also change with the use of the final product in addition to the main substrate. For example, products such as heat shrink tubes, tapes, and sheets used for the protection of rubber plastic cable joints are required to have good electrical insulation performance. Therefore, when designing the formula, materials that affect the electrical properties should be avoided as far as possible. When the joint is placed outdoors, carbon black should be added to eliminate the damage of ultraviolet light in sunlight to the polymer. When the joint is placed underground, components that can prevent plant roots from being damaged are required, and at the same time, the auxiliary should be able to prevent the acid, alkali, salt, organic solvent, etc. in the sewage from damaging the joint. When used for the protection of high-voltage cable joints, the additives added should focus on whether they can improve the resistance to high-voltage breakdown. Therefore, the formula design needs to be determined according to the specific application and use of environmental conditions.

Table 5.5 Basic formula of radiation crosslinked polyethylene

Index	Material name	PHR	Function
1	LDPE (MI1.5)	100	Main material for cable shielding and insulation protection
2	EVA (VA% = 18, MI1)	5–20	Reinforcing agent, compatibility, and toughening component
3	TMPTMA or TAIC	0–1	Sensitizer, radiation can produce a large number of free radicals, which is helpful for crosslinking
4	Antioxidant 1010	0.5–2	Resistance to oxygen damage to polymers during processing and use
5	Plasticizer (dibutyl phthalate)	0–10	Product molding includes extrusion, blow molding, molding, etc. Different molding methods have different requirements for melt viscosity and different dosage
6	Pigment	0–2	Generally added in the form of master batch, or not
7	Filler	0–30	Add according to specific conditions
8	Others such as antistatic agents, etc.	0–0.5	Add appropriate amount of mildew inhibitor and plant root infestation inhibitor depending on the application environment

When designing the formula, in addition to the use environment of the product and the performance parameters of various materials, the material processing technology is also a key factor to be considered. Materials with different components and properties can be granulated by mixing, blending, or extruding to prepare macroscopic homogeneous granules for processing and molding. In the formula, the properties of various components are different. They include solid polymers, liquid polymers or small organic molecules, inorganic particles or powders that are easy to agglomerate, elastomers (such as rubber toughening agents), etc. Therefore, to achieve uniform mixing between components, proper blending methods must be adopted. The best blending method is to realize macroscopic homogeneous granular materials through mixing granulation. However, the mixing granulation system usually requires an investment of hundreds of thousands to millions of dollars, which brings huge financial pressure to small and medium-sized investors. Therefore, it is generally selected to use a high-speed mixer to initially mix the formula materials, and then use a twin-screw extruder or a four-screw extruder to extrude and granulate to prepare raw materials for molding and processing products. If the mixing effect is not satisfactory, a second extrusion granulation can be carried out. In the extrusion granulation process, the processing time should be shortened as much as possible to avoid the degradation of polymers (Fig. 5.15).

The granulated materials are processed into the final product shape by such processing methods as blow molding, molding, injection molding, lamination, and

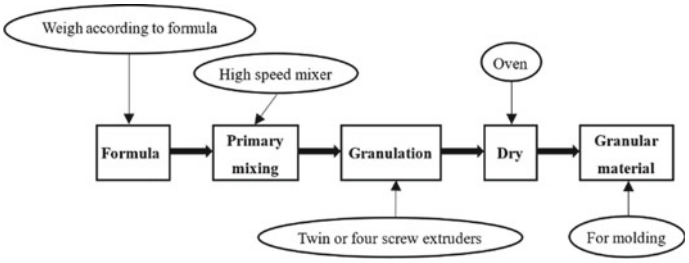


Fig. 5.15 Schematic diagram of the material treatment process of radiation crosslinking products

extrusion. The heat-shrinkable film is generally processed and shaped by the blow molding method. The multilayer radiation crosslinking enhancement product is processed by laminating or the continuous composite method, and then the finished product will be obtained by irradiation. Products in the shapes of tubes, wires and cables, sheets, and tapes are processed by extrusion, while structural parts are produced by injection molding. The molding method of crosslinked polyethylene is basically the same as that of ordinary plastic products, with only one more irradiation process. Some products are directly sold or used after irradiation, such as radiation crosslinked wires and cables. Some products need further processing after irradiation, such as heat shrinkage products. After an appropriate dose of irradiation, the product is processed for the second time, that is, heat the irradiated tube, strip, sheet, etc. to the softening temperature, and then place them in the mold to expand them to a size larger than the original size (some are double or several times of the original size). After rapid cooling and shaping, the product will be heated by using the memory effect of radiation crosslinked polymer material to restore the shape and size to that of extrusion molding (Fig. 5.16).

For the processed products, a certain quantity should be selected based on the statistical principle, and the quality inspection should be carried out according to the relevant requirements to determine whether the products are released. Generally, the parameters to be inspected include mechanical strength, electrical strength, chemical media resistance, aging resistance, degree of crosslinking (also known as gel content), etc., which are the key specifications to determine the performance of products.

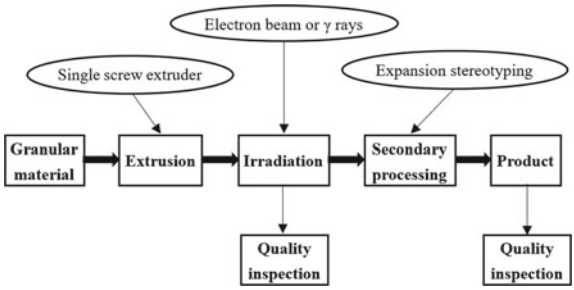


Fig. 5.16 Schematic diagram of the radiation crosslinking product forming and process

2. **Selection of the optimal irradiation dose**

Radiation is the key step in radiation crosslinking. Whether the γ-ray irradiation such as ^{60}Co sources or the electron beam irradiation using electron accelerators, appropriate irradiation dose and irradiation time should be selected. Many related references have theoretical formulas for the gel content of radiation crosslinking. However, in practical work, theoretical formulas are generally not used to directly calculate the degree of crosslinking (also known as gel content) of polymer composite systems to obtain accurate irradiation dose and irradiation time. Generally speaking, the mechanical strength, electrical strength, chemical media resistance, aging resistance, degree of crosslinking, etc. of the polymer composite can be directly determined according to the specific formula to select the best irradiation dose and irradiation time. Table 5.6 shows the comparison of ^{60}Co radiation sources and electron accelerators in the field of radiation processing. Whether to use the ^{60}Co radiation source or the electron accelerator depends on the specific situation. At present, a considerable number of ^{60}Co radiation fields have been built in many areas, processing companies can directly use them without purchasing or installing them. Once the radiation source is fixed, many process parameters can be determined, which provides good conditions for the development and production of the product.

Table 5.7 describes the different uses of accelerators with different energies.

There are many components in the polymer composite system of radiation crosslinking. In the theoretical calculation of gel content, too many parameters, complex formulas, and many steps are required, resulting in the calculated conclusions deviating from the actual needs. Therefore, determining the performance change and gel content of each sample of a formula after irradiation it the more direct and practical method.

Several specific examples will be introduced in the following paragraphs to illustrate the relationship between radiation crosslinking and gel content. The testing principles include the solvent method, thermal deformation method, and mechanical method. The solvent method is to cut the irradiated sample into small particles, place it in the Soxhlet extractor, and wash it with the appropriate solvent for a long time. The extraction solvent used for polyethylene radiation crosslinking samples is generally toluene or xylene. Continuously reflow and extract until the sample is constant weight, accurately weigh and calculate the content of gel after drying. In the calculation, it is necessary to consider the influence of inorganic fillers in the formula, otherwise, the data of gel content will be inaccurate, which will adversely affect the formula screening.

The thermal deformation method is to make dumbbell-shaped strips of samples irradiated with different radiation doses based on the specified specifications, place the strips in the oven, hang weights of different weights under the strips, raise the temperature from room temperature section by section, and observe the relationship between the test sample deformation and radiation dose. With the increase of temperature in the oven, the samples with a low degree of crosslinking will be stretched first. When the temperature rises to a certain level, these strips will be broken. But strips with an appropriate degree of crosslinking will not change after being stretched to

Table 5.6 Accelerator energy and application areas

Content	^{60}Co radiation source	Electron accelerator
Energy level	10^{15}–10^{10} J	Dozens of keV ~ 10 meV (When the electron beam energy is higher than 10 meV, the irradiated object will undergo nuclear reaction, and the product will be activated with radioactivity)
Wavelength	10^{10}–10^{14} m	10^{-8}–10^{-13} m
Absorbed dose rate	10–10^3 Gy/min	10^3–10^5 Gy/min
Penetrating power to irradiant	Strong penetrability	The higher the electron energy, the stronger the penetration ability. Converts electrons to X-rays for greater penetration
Production efficiency	Relatively low	High
Purpose	Suitable for disinfection, sterilization, pest control and fresh-keeping	Disinfection and sterilization, insecticidal and fresh-keeping, polymer radiation cross-linking, grafting, and degradation, more suitable for disinfection of medical equipment, small oxidation, no discoloration, small change in brittleness
Operation mode	Continuous production can be controlled automatically by computer	Same as ^{60}Co radiation source
Radiation protection	Radiation sources need to be stored in wells	No radiation after power failure, simple and safe protection
Environmental protection	Eliminated ^{60}Co sources need to be treated according to strict environmental protection regulations, which is expensive	It has no pollution to the environment and is called green processing but pay attention to the ventilation of the irradiation field to eliminate the harm of ozone to human body
Construction investment	Relatively large	Large
Comprehensive cost	Relatively high	Cheap

Table 5.7 Application fields corresponding to different accelerator energies

Accelerator energy	Application fields
Low energy (15–450 keV)	Wood modification and surface curing, surface curing treatment of plastic floor leather and other building materials, paper modification, surface treatment of color printing and textiles, surface curing of magnetic recording materials, cross-linking of plastic films, etc.
Medium energy (500 keV–3 meV)	Radiation cross-linked wires and cables, heat shrinkable materials, plastic foam, high-speed car tire vulcanization, sanitary drinking water pipes, molds, polymer degradation, gem coloring, and semiconductor device modification
High energy (5–10 meV)	Food preservation, medical supplies disinfection, cosmetics and sanitary supplies disinfection

a certain length. This method is particularly useful for products that need secondary processing after radiation, such as the expansion of heat-shrinkable products. The radiation dose measured by the thermal deformation method can be directly used to select the optimal radiation dose, which is intuitive and effective and is more practical than the solvent method. The selected temperature in the oven is the processing temperature of the product, and the weight is set as the tension of expansion.

The mechanical method is to make the irradiated samples into dumbbell-shaped strips specified in the standard, stretch them with a universal tensile machine, measure the relationship between the tensile strength and elongation at break of the sample and the radiation dose to select the best radiation dose. In general, the tensile strength increases with the increase of radiation dose. When the radiation dose increases, which leads to the degradation of polyethylene, the tensile strength and elongation at break of the material, especially the elongation at break will decrease. Therefore, the mechanical method is one of the better methods to select the radiation dose, which has a more intuitive guiding significance. Mechanical strength is an important index after material modification. The main purpose of radiation crosslinking is to improve the mechanical strength of the polymer materials so that they can be used in harsh environments. If the mechanical strength decreases, it indicates that the radiation dose is excessive.

Whether the γ-ray radiation processing by ^{60}Co radiation sources or the electron beam radiation by accelerators, the hysteresis radiation effect will exist. That is, there are still some free radicals, small molecule fragments, peroxides, and residual electrons in the sample after irradiation. Under the action of these residues, residual crosslinking and other reactions will occur. During secondary processing of irradiated products, the residues will have adverse impacts on the processing, which often leads to cracking of the product during expansion, uneven thickness of the expanded product, reduced product performance, etc. Production technicians with practical experience often leave the irradiated samples for a period of time or consider the effects of these factors when setting the baking temperature. For samples that do not require secondary processing, such as radiation crosslinked wires and cables, if used directly, discharge or breakdown will occur. When the heat-shrinkable rubber-plastic joint of radiation crosslinked power cable is subjected to high voltage, the static electricity existing in the product is easy to discharge on the track, forming a three-dimensional dendritic “electric tree”, which seriously reduces the performance of the product, or even making it unusable.

3. **Performance index of radiation crosslinked polyethylene**

Radiation crosslinking products with polyolefin as the polymer matrix are widely used in power, communication, anti-corrosion, positive temperature coefficient composite polymer devices, and many other fields. With the development of technology, its application has become more and more extensive. It is the main direction of the polymer radiation crosslinking industry, it is also an industrial field with simple methods, low investment, and quick effect, which is known as the

"green processing industry". Table 5.8 shows the changes in material properties after radiation crosslinking with a typical polyethylene formula.

The data reflects that the mechanical strength, stress cracking resistance, chemical medium resistance, thermal aging resistance, and other parameters of polyethylene after irradiation have been significantly improved. Meanwhile, the memory effect plays a good role in the anti-corrosion of wire and cable joints, weld junctions and joints of metal pipes, and metal pipe surfaces, ensuring the normal work of joints and pipes, and greatly improving the service life of wires, cables, and metal pipes. The use of heat-shrinkable polymer products has the advantages of high efficiency, environmental protection, reliability, and convenient construction, etc., and gradually replaces other technologies.

To coordinate with the use of heat-shrinkable products, a layer of hot-melt adhesive is often applied on the inner surface of the products, that is, the side directly contacting with the surface of wires and cables, metal, or plastic pipes. Corresponding to the radiation crosslinked polyethylene, the hot-melt adhesive selected includes EVA-based hot-melt adhesive, polyamide-based hot-melt adhesive, and acrylate-based hot-melt adhesive. Hot melt adhesive plays an important role in the application of heat-shrinkable products. Firstly, it acts as the binder between the heat-shrinkable products and the protected object. Bind heat-shrinkable products with cables, pipes,

Table 5.8 Comparison of parameters of radiation crosslinked polyethylene and uncrosslinked polyethylene

Project	Parameter (uncrosslinked)	Parameter (crosslinked)
Tensile strength (MPa)	15–18	≥ 25
Elongation at break (23°C) (%)	100–650	100–600
Vicat softening point (°C)	77	≥ 90
Low temperature embrittlement temperature (°C)	− 68	− 65
Breakdown strength (MV/m)	18	30
Volume resistivity (23 °C) (Ω/m)	10^{16}	10^{16}
Environmental stress cracking resistance (F50) (h)	–	≥ 1000
Shore hardness	50	≥ 60
Impact strength (J/mm)	–	≥ 10
Water absorption (%)	< 0.01	< 0.01
Resistance to chemical medium corrosion (7d) (%)		
10% HCl	≥ 85	≥ 85
10% NaOH	≥ 85	≥ 85
10% NaCl	≥ 85	≥ 85
Heat-proof aging (150 °C, 168 h)		
Tensile strength (MPa)	< 10	≥ 14
Elongation at break (%)	< 300	≥ 300

etc. to prevent them from falling off, protect joints from corrosion of acids, alkalis, salts, sewage, organic solvents, etc. to ensure smooth communication, normal power supply, accurate equipment control signals, and metal pipes from corrosion. Some thermal-shrinkable products need to be applied to a certain atmospheric pressure environment, such as rubber-plastic communication cables with large pairs. In order to maintain normal operation, the cable joint must be filled with inert gas of certain atmospheric pressure, such as nitrogen. After wrapping the connected cable joints with thermal-shrinkable products, inject the required atmospheric pressure through the valve core on the heat-shrinkable products, generally 70 kPa ± 2 kPa. If there is no adhesive, the pressure of nitrogen will strip the heat-shrinkable products from the cable or pipe. Secondly, it acts as a sealant. During the heating construction of heat-shrinkable products, the hot-melt adhesive melts. Under the effect of shrinkage stress, the adhesive fully flows and soaks on the surface of cables or pipes, fills the gap, and expels corrosive gases such as oxygen, so as to ensure the normal operation of the cable and pipe. Thirdly, it acts as a stress absorber. Heat-shrinkable products generate a lot of stress in the process of shrinkage. Due to the existence of these stresses, when the anti-corrosion layer of the joint or metal pipeline is subjected to high temperature, external impact, low-temperature impact, scratches, etc. However, when the hot-melt adhesive exists, the heat-shrinkable layer can inhibit the expansion of the crack and absorb most of the stress (Table 5.9).

Tables 5.10 and 5.11 show typical formulas and performance parameters of the two hot-melt adhesives.

The softening point of this formula is 75–90 °C, the normal temperature peel strength of radiation crosslinked polyethylene is more than 100 N, the shear strength is more than 1500 N, and the adhesive performance of radiation crosslinked polyethylene materials is good.

The hot-melt adhesive of this formula is especially suitable for radiation crosslinked polyolefin heat-shrinkable products. The peel strength at normal temperature can reach more than 200 N, or even more than 300 N. The shear strength is

Table 5.9 Formula of EVA hot-melt adhesive

Name	Technical indicators	PHR
EVA (main substrate)	MI: 1–20, VA%: 18–20	100
EVA (auxiliary substrate)	MI: 1, VA%: 5–8	5–15
EVA (auxiliary substrate)	MI: 150–300, VA%: 25–33	5–15
Diluent (paraffin)	Can also be powdered polyethylene	2–8
Tackifier (rosin)	Modified rosin, etc.	5–10
Filler (calcium carbonate)	Titanium dioxide, calcium sulfate, etc.	Add as appropriate
Pigment (carbon black, red)	Can be added or not, generally add master batch	1–2
Antioxidant (1010)	Ciba Gagy products	0.5–1
Others	Such as plant root inhibitor, mildew inhibitor and anti-static agent	/

Table 5.10 Formula of dimer fatty acid polyamide based hot-melt adhesives

Name	Technical indicators	PHR
Polyamide (main substrate)	Molecular weight: 6000–10,000	100
Polyamide (auxiliary substrate 1)	Molecular weight: 3000–5000	10–20
Polyamide (auxiliary substrate 2)	Molecular weight: 1000–1500	5–10
Low molecular weight polyolefin	Powdered polyethylene or paraffin	5–10
Ethylene acrylate copolymer	EEA or EAA	15–25
Elastomer toughener	Olefin copolymer rubber, unsaturated	1–5
Tackifier	Rosin	5–15
Antioxidant	Antioxidant 1010	0.5–2
Filler	Add as appropriate	Appropriate amount, or not
Pigment	Add as appropriate, generally masterbatch	1‰–1%
Others	Depends on specific usage	/

more than 2500 N. It has a strong ability to withstand the alternating temperature (−70–50 °C) and is mainly used for joint protection of air pressure maintenance cables.

The formula of acrylate hot-melt adhesive is similar to that of the EVA hot-melt adhesive and will not be introduced in detail. The formula can be obtained by replacing EVA with EEA and EAA macromolecular thermoplastic polymer. This type of hot-melt adhesive has a better bonding performance than the EVA hot-melt adhesive, but its price is much higher. Therefore, in the actual production and processing of products, each material should be selected according to the best proportion of product performance and cost, as long as the products meet the practical requirements.

5.2.4 Main Applications of Thermoplastic Polymer Radiation Crosslinking Products

Radiation crosslinking polymers have been widely used in electric power, electronics, communications, transportation, construction, chemical industry, automobile, shipbuilding, national defense, military industry, aerospace, and other fields. But the application in the field of wire and cable and heat-shrinkable products is the earliest, the most mature technology, and the largest market share.

Table 5.11 Comparison between electron beam radiation crosslinking and chemical crosslinking of polymers

Advantages and disadvantages	Chemical crosslinking	Radiation crosslinking
Advantages	1. This technology has been well mastered by managers and operators and does not require a high technical level like electron beam technology	1. High energy utilization rate and low operation cost after initial operation
	2. When the specifications of wires and cables produced are the same as those of electron beam crosslinking equipment, the purchase and installation costs of steam crosslinking equipment are low. The cost of second-hand steam crosslinking equipment and installation, including boiler, is 250,000 US dollars	2. Extrusion can be separated from the production line and can be completed with a general extruder
	3. The chemical crosslinking equipment is applicable to the mass production of conventional wires and cables	3. Compared with the chemical crosslinking equipment, the electron beam crosslinking equipment has a compact structure and small floor area
		4. The electron beam crosslinking equipment is usually controlled by a computer, and only one technician is needed after the program is set
		5. The equipment operates stably and reliably with less maintenance. 90% of the users are satisfied with the electron beam irradiation crosslinking
		6. It can efficiently produce conventional wire and cable products. Its production speed is 10 times that of chemical crosslinking equipment, and the wire speed of small size wires can reach 1000 m per min

(continued)

Table 5.11 (continued)

Advantages and disadvantages	Chemical crosslinking	Radiation crosslinking
Disadvantages	1. It can only be used to crosslink those materials that are suitable for peroxide or vulcanizing crosslinking agent	1. At the beginning, the one-time investment of electron beam crosslinking equipment was high, and the price of new equipment was between 1 million and 2.5 million dollars
	2. The residue of the crosslinking agent will remain in the cable, which will cause the aging of the sheath or insulation layer after a certain period of time	2. Due to the good performance of the equipment and user satisfaction, there are almost no second-hand equipment in the market
	3. The high pressure required for chemical crosslinking will affect the inherent structure of the cable	3. A large number of concrete protective screens are required to absorb the X-rays generated in the cross-linking process
	4. The high temperature required for chemical crosslinking will melt the internal components of the cable	4. Complex under beam conveying system is required
	5. Changing the cable model and specification requires replacing a large number of tooling parts (it takes more than 3 h)	5. The misunderstanding of electron beam radiation energy will cause people's fear and public communication problems
	6. In order to determine the appropriate extrusion and curing conditions, a large number of cables will be wasted at the initial start-up of the chemical crosslinking production line	6. The customization and installation time of new equipment is about 18 months, and the installation and commissioning time is long
	7. The chemical crosslinking equipment covers a large area, usually more than 150 m long and more than 15 m wide	7. Limited by the conditions of the under beam conveying system, the electron beam crosslinking equipment cannot produce cables with a diameter greater than 5 cm
	8. Large energy consumption and maintenance and operation costs of equipment	
	9. Do not produce wires of small size	

1. Radiation crosslinked wire and cable

In the early days, the insulating materials of wires and cables, especially civil low-voltage wires and cables, were made of polyvinyl chloride (PVC), which was cheap and easy to get with simple processes, and quickly spread to the low-voltage wire and cable field. However, many fatal problems have appeared in the application of polyvinyl chloride wires and cables. Firstly, it is easy to age. With the increase in service time, low molecular organic compounds such as plasticizers added to polyvinyl chloride will slowly migrate out, and the insulation layer becomes hard and brittle. Once subjected to external force, the insulation layer will break and lose the protection of the metal conductor in the core wire. Secondly, when various fire accidents occur, a large amount of toxic and harmful smoke generated by the burning of polyvinyl chloride will cause asphyxiation and death of the personnel at the fire scene. Therefore, developing low-smoke halogen-free flame retardant wires and cables to replace polyvinyl chloride wire and cable is an important direction.

Radiation crosslinked polyethylene can just overcome the above shortcomings and improve the life of wires and cables. In many countries, it is mandatory to use radiation crosslinked polyethylene low-voltage wires and cables for indoor wiring of civil buildings, and it is not allowed to use polyvinyl chloride low-voltage (< 1000 V) wires and cables. In addition, with the development of nanotechnology, inorganic flame retardants such as aluminum hydroxide can prepare particles with a particle size below 100 nm, some even below 40 nm. On the other hand, the treatment technology of coupling agents on aluminum hydroxide and other nanoparticles is also improving, which greatly improves the compatibility between inorganic particles and organic polymers, reduces the amount of filler added, enhances the flame retardancy, improves the mechanical strength, and realizes low-smoke halogen-free flame retardant or smoke-free halogen-free flame retardant. Besides, in case of fire, the burning of wires and cables will not emit toxic and harmful smoke that suffocates people.

Radiation crosslinked wires and cables can be used for indoor wiring in civil buildings, 10 kV overhead cables, signal control cables, flame retardant wires, and many other products. They are also widely used in equipment and instruments in aviation, aerospace, power stations, electronics, weapons, shipbuilding, locomotives, and other industries because of their good flame retardancy, cold resistance, heat resistance, sunlight radiation resistance, harsh environment resistance, and other special characteristics. They have also become the preferred wire and cable in communication, power transmission and substation, automobile, and other industries, which plays a vital role in the stability of product quality and performance upgrading.

2. Heat-shrinkable materials and products

Heat-shrinkable products are the first radiation crosslinking products put into practice. In the 1950s and 1960s, when the aerospace and weapon industries in the United States urgently needed the traction of high-performance materials, the memory effect of radiation crosslinked polyethylene was used to successfully develop

heat-shrinkable materials, which were prepared into heat-shrinkable tubes, heat-shrinkable sheets, heat-shrinkable tapes, and other products, or made into structural parts and special-shaped pipe fittings that were used for surface protection and anti-corrosion of metal special-shaped components after expansion.

Radiation crosslinked polymers can also be used in aerospace, missiles, ocean-going vessels, and other cables that require high or low temperature resistance, oil circuit seals, structural parts and sealing materials, and various high-performance packaging materials.

5.2.5 Comparison Between Radiation Crosslinking Technology and Chemical Crosslinking Technology

The radiation crosslinking technology of polymers has become a mature industrial application technology, and the products represented by wires and cables and heat-shrinkable products have been continuously applied. However, the radiation crosslinking, especially the electron beam radiation crosslinking technology, is affected by the thickness of the product, and its ability to penetrate the thickness is limited. This limits the crosslinking of ultra-thick products or leads to low crosslinking efficiency. Therefore, for the crosslinking of large and thick products, peroxide and silane crosslinking technologies have been developed.

For the peroxide and silane crosslinking technology and the electron beam crosslinking technology, A. M. Zamore compares their advantages and disadvantages. The electron beam equipment uses high-energy electrons to realize the crosslinking between flexible molecular chains. The crosslinking is carried out under normal temperature and pressure, and the maximum production speed of wires and cables can reach nearly 103 m per min. The chemical crosslinking equipment is a continuous vulcanization device based on heating. The typical equipment is a long pipe, with allowable temperature up to 200 °C, allowable pressure up to 1.7 MPa, and production linear velocity of 60 m/min. The heat source used by most chemical crosslinking equipment is water vapor, hot nitrogen, or molten salt. All chemical crosslinking requires the use of peroxide, silane, or the vulcanizing agent as a crosslinking agent.

The crosslinking of polymers can improve the physical properties of materials. For wires and cables, the outstanding progress after improvement are:

① The melting point and dropping point of the polymer are improved, and the high-temperature fluidity is reduced.
② The oil resistance and organic solvent resistance are improved.
③ The dielectric strength and tensile strength are improved, and the wear resistance is enhanced.

Table 5.11 shows that both crosslinking technologies have their limitations. The relationship curve between wire diameter and insulation thickness shown in

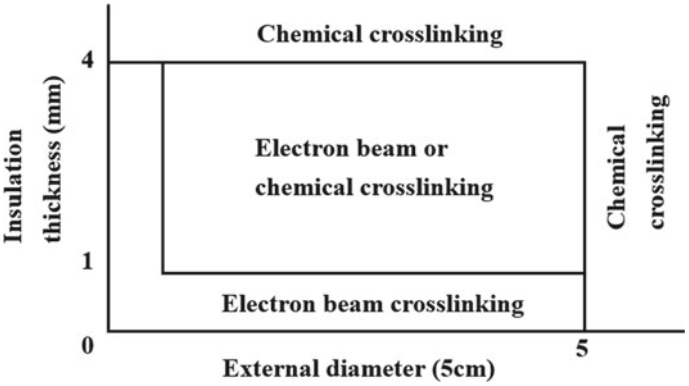


Fig. 5.17 Optimal working range of electron beam and chemical crosslinking

Fig. 5.17 shows that different application combinations of electron beam and chemical crosslinking technology can be used optimally. When the thickness of the insulation layer or sheath layer is greater than 38.1 mm, the chemical crosslinking method is preferred, while when it is less than 7.62 mm, the electron beam crosslinking method will be preferred. Wire and cable with small diameters can only be crosslinked by the electron beam. When the thickness of the cable insulation layer is between 7.62 and 38.1 mm, both the two crosslinking modes can be used. When the diameter is greater than 50 mm, only chemical crosslinking technology can achieve good crosslinking of cables. These scopes truly reflect the experience of users rather than theoretical derivation.

The efficiency of electron beam radiation crosslinking is far greater than that of chemical crosslinking. One accelerator can meet the production requirements of multiple wire and cable factories. But considering the overall production cost, there is almost no difference between the two. The main reasons for selecting the electron beam radiation crosslinking technology are as follows. Firstly, special wires and cables need to be produced by electron beam radiation crosslinking instead of chemical crosslinking. Second, its equipment production process is flexible, with a low scrap rate, and the requirements for material are loose. Thirdly, there is no need to purchase equipment exclusively, the joint purchase of several manufacturers can reduce the initial investment. If the existing electron beam irradiation processing center can be used, crosslinked wires and cables can be produced without investment in crosslinking equipment. Fourth, it is conducive to the development and production of new products, flexible production, and development of crosslinked wires and cables that can meet the urgent needs of users, and using the electron beam radiation crosslinking method is convenient, fast, and high quality. As the production of radiation method does not require peroxide, water, steam, heat, and high pressure, it is most suitable to produce new, single, and high-value-added wires and cables.

5.2.6 Summary

After decades of development, radiation crosslinking technology has gradually matured in the development of formula, process, and technology, and has been widely used in industry. However, the detailed mechanism of radiation crosslinking is not completely clear so far. For a system, there are many components, which are both chemical components conducive to crosslinking and components that inhibit crosslinking. For example, sensitizers produce a large number of active free radicals in the irradiation process to accelerate and promote the crosslinking of olefin molecules, while flame retardants and processing stabilizers will absorb a large number of free radicals. This process is complex and hard to be quantified, which is affected by many factors such as temperature, humidity, local chemical concentration, etc. Inorganic fillers and additives will dilute the concentration of free radicals and reduce the probability of crosslinking. In addition, when the whole formula system is irradiated, olefin molecules will break and produce smaller molecules, which attack macromolecular chains and cause degradation. The annihilation of some free radicals in the system reduces the efficiency of crosslinking, while the small molecules generated after degradation are grafted onto other molecular chains, increasing the degree of branching and increasing the steric hindrance of crosslinking. The above series of thermodynamic and kinetic processes cannot be quantified, thus, it is difficult to predict and solve the problem of the whole crosslinking process through theory. In the scientific research and production of radiation crosslinking, sometimes there is no need for detailed derivation. According to the existing empirical formulas and experiments, the required parameters can be accurately obtained. The specific process formula, material selection, processing technology, radiation dose, etc. should be determined through tests based on the specific technical force, test equipment, production equipment, end-use of products, accelerator energy, etc.

Radiation crosslinking of thermoplastic polymers is developing towards heteroatom polymers with high-temperature resistance. It is very difficult to realize radiation crosslinking of polymers containing nitrogen, sulfur, or polymers replaced by halogen atoms such as fluorine, chlorine, and bromine because the carbon–fluorine bond is much stronger than the carbon–carbon bond. Under the action of high-energy rays (electron beam or γ-rays), the carbon–carbon bond breaks first, leading to the degradation of the polymer main chain rather than the desired crosslinking reaction. The carbon-chlorine bond, carbon-bromine bond, and carbon-iodine bond are weaker than the carbon–carbon bond. Under the action of rays, halogen elements fall off and form halides, leading to the fracture of the carbon main chain, which is not easy to cross link. At present, radiation crosslinking of polyamide (nylon) has become the next focus of research. Its material formula system is gradually improved, and the entire technology and process are gradually matured, which is an excellent engineering material and structural part that can be used in aerospace, petroleum, and engineering. With the progress of technology, new crosslinking sensitizers are constantly synthesized, especially the emergence of sensitizers with high boiling

point sensitizers, which makes the radiation crosslinking of high melting point polymers containing heteroatoms much easier. More radiation crosslinking materials with high-temperature resistance will be continuously developed in the future for space development, ships, weapons, and aircraft.

5.3 Radiation Polymerization

Radiation polymerization of polymers has unique advantages over traditional polymerization. Traditional polymerization often requires high temperature and high pressure, with complex processes and large equipment, and the residual catalyst in the product will affect the performance and applications. The parameters of radiation polymerization are adjustable and controllable, and it can be polymerized at normal temperature, high temperature, low temperature, or ultra-low temperature without catalysts and initiators. These advantages make the radiation synthesized polymers become excellent biological and medical materials. The polymerization system can be liquid, solid, or gaseous, and the composition of the polymerization system can be one monomer or a variety of monomers irradiated for polymerization. The main directions of polymerization include synthesis of polymers with ethylene as the main monomer, synthesis of trioxymethylene by the radiation of formaldehyde, preparation of special polymers by radiation polymerization of fluorine-containing monomers, radiation polymerization of acrylic acid derivatives or acrylamide, and synthesis of other functional polymers, some of which have been industrialized.

Radiation polymerization has the same mechanism as thermochemical polymerization of polymers, which includes free radical polymerization and ionic polymerization. The factors that determine the mechanism include temperature, kinetics, solvents, additives, components, etc. When the temperature of the system is reduced, if the polymerization speed is not affected by the reduction of temperature, the mechanism is ionic polymerization. If the polymerization speed is affected by the temperature, it is free radical polymerization. The polymerization speed V is proportional to the square root of the dose rate I, that is, when $V \propto \sqrt{I}$, it is the free radical polymerization, and when $V \propto I$, it will be the ionic polymerization.

5.3.1 Liquid Phase Polymerization and Homogeneous Polymerization

When the monomer is in the liquid state, the properties of the solvent determined by the molecular structure have a great impact on the radiation and polymerization mechanism of the monomer, resulting in a complex reaction process. The solvent molecules are decomposed under the action of radiation to produce a series of intermediate

active particles and final products. For comprehensive reactions such as active particles and intermediates generated by the radiation of monomer molecules, the direct polymerization of particles generated by the radiation of monomer molecules should not be considered the only factor, but the solvent effect should be considered. The particles or products produced by some solvents under the action of radiation can promote polymerization, while some solvents can inhibit polymerization. Experiments have shown that the reaction that is beneficial to the radiation-initiated free radical polymerization can also promote anionic polymerization.

The vast majority of bulk polymerization requires the use of sodium and potassium alloys for drying and polymerization in the form of free radicals. For example, the reaction rate of dried α-methylstyrene is 1000 times higher than that of aqueous systems. Thus, water has a strong inhibitory effect on bulk polymerization. The mechanism is that the water molecule absorbs the positive carbon ions generated by α-methylstyrene during radiation, and then neutralizes the negative ions (containing excess electrons) generated in the system, reducing the effective concentration of ions and slowing down the polymerization rate. In this way, water becomes a proton scavenger. For example, the radiation polymerization rate of styrene after drying is 100 times faster than that of hydrous styrene radical.

Whether it is ionic polymerization or free radical polymerization, with the increase in radiation dose, the production of products increases, and the monomer conversion will also increase. However, when the conversion increases to a certain amount, the gel will appear. Due to the long polymer chain, the activity of the growth chain becomes small, which leads to the reduction of the bimolecular termination and the acceleration of the polymerization speed, becoming the gel effect of radiation polymerization. On the other hand, when the conversion rate exceeds 90%, the viscosity of the reaction system continues to increase, the monomer concentration continues to decrease, the probability of collision between the monomer molecules and the free radicals (or ions) on the growth chain will decrease, and the polymerization speed starts to decline.

A few examples of liquid-phase polymerization are given below, along with the illustration of solvent effects.

Styrene can undergo cationic polymerization in dichloroethane at a low temperature (− 78 °C). The radiation polymerization rate of styrene is largely dependent on the dose rate. When the dose rate is low (< 50 kGy/h), the polymerization rate is proportional to the first power of the dose rate. When the dose rate is greater than 50 kGy/h, the polymerization rate is proportional to the square root of the dose rate. If there is silica gel in this polymerization system, this relationship will be just the opposite, this is because silica gel has strong adsorption on anions, resulting in this opposite result.

When ethylene is polymerized by radiation in chloroethane solution, the polyethylene formed will precipitate immediately and the polymerization system will become heterogeneous. The polymerization rate appears to be proportional to the quadratic of the monomer concentration. The general index is between 1 and 2, depending on the coating of the growing active chain caused by polymer precipitation. In the case of chloropropane, the index is 1.41. In 1-chloropropane or tert-butylchlorosane, the

activation energy of ethylene radiation polymerization is 23.41 kJ/mol and 30.93 kJ/mol respectively, which is slightly higher than that of other bulk (liquefication) polymerization (18.39 kJ/mol), indicating that the radiation polymerization of ethylene proceeds according to the free radical mechanism.

For homogeneous polymerization of methyl methacrylate, after irradiation of about 10 kGy, the polymerization system is moved out of the radiation field, and polymerized at 20–50 °C to prepare large area and thick polymethyl methacrylate plastics, whose optical properties are far superior to those of products synthesized by thermochemical methods.

The difluoro chloromethane ($CHClF_2$) solution of tetrafluoroethylene is polymerized by radiation initiation at – 78–0 °C, and then the polymerization system is placed outside the irradiation field for polymerization. Its G value can reach 3.3×10^5, conversion up to 100%, and molecular weight up to 1.2×10^6, which is of great significance for the preparation of high-quality polytetrafluoroethylene.

5.3.2 Solid Phase Polymerization

The so-called solid phase polymerization refers to the radiation polymerization in which the polymerization system does not use liquid solvent and the monomer is, which has significant advantages. High-energy radiation can uniformly penetrate the solid monomer, resulting in the polymerization reaction of the whole system. One of the difficulties of solid-phase is that the catalyst is difficult to disperse uniformly in the system and initiate the homogeneous reaction. Moreover, the catalyst cannot penetrate the monomer lattice, which greatly affects the catalytic efficiency and reaction rate. Even if the catalyst penetrates the lattice, it will destroy the lattice structure. So far, hundreds of monomers can be polymerized by solid-phase polymerization, among which trioxymethylene, acrylamide, and methyl methacrylate can already be applied to industrial-grade products.

The main factor affecting the solid phase polymerization is the structure of the solid monomer, such as crystal size, crystalline or glassy state, polymerization temperature, etc. If the crystal structure of the monomer is not consistent with that of the product, the polymerization will be greatly affected. If the monomer is in the glassy state, the polymerization rate of the system will be very high during radiation polymerization, and there will be a slow acceleration. With the increase in the viscosity of the monomer system, the speed of chain termination decreases, leading to an increase in the polymerization rate.

The crystal structure of acrylamide determines that it is not conducive to radiation solid phase polymerization. However, if a small amount of ammonia or sodium hydroxide aqueous solution is added to the system to form an incomplete solid phase, followed by radiation polymerization, the effect will be very significant. For example, in the absence of oxygen, irradiate the acrylamide with a concentration of 95% at room temperature, with a dose rate of 0.07 Gy/s and time of 30 min, the conversion rate can reach 100%, and the molecular weight of the polymer can be 6 ×

10^6. If 1.2% or 0.45% NaOH aqueous solution is added to the system, the molecular weight will increase to 1×10^7. The efficiency of this method is 3–10 times higher than that of the chemical synthesis.

The crystal shape of the trioxymethylene monomer controls the shape of the polyoxymethylene, that is, the crystal structure of the polyoxymethylene is similar to that of the trioxymethylene. The fibrous polymer can be obtained by solid phase polymerization of trioxymethylene under direct radiation at a dose rate of 5×10^2 Gy/h at 55 °C, and the conversion rate is about 40%. However, the molecular weight of the polymer is too low, and its intrinsic viscosity is only 0.5. Irradiate the crystalline trioxymethylene at 25 °C, then placed it for polymerization at 55 °C, a highly crystalline fibrous polymer with a high molecular weight and an intrinsic viscosity of 2.5 can be generated. It was found that there was a regular relationship between the molecular weight of polyoxymethylene and the size of the crystal grains of the trioxymethylene monomer. In addition, the molecular weight is controlled by the temperature (35–65 °C) at the time of placement, while the conversion rate is related to the placement time.

Like trioxymethylene, many cyclic compound monomers can undergo the curing polymerization reaction. However, high molecular weight products can not be obtained by polymerization under liquid conditions. In contrast, under solid-phase conditions, the products obtained have good crystal structures, high molecular weights, and high melting points, such as hexamethylcyclotrisiloxane, 3,3-dichloromethyl epoxypropane, β-propiolactone, diketene, hexacyclic phosphorus nitrogen chloride, etc., among which the molecular weight of the polymer obtained by solid phase polymerization of β-propiolactone is higher than that of the products obtained by any other methods.

5.3.3 *Emulsion Polymerization*

Emulsion polymerization is the radiation polymerization reaction of a polymerization system using water as continuous phase (oil-in-water) in the presence of an emulsifier. Emulsion polymerization generates free radicals by the action of high-energy rays and components in the system. The mechanism is as follows:

$$H_2O \xrightarrow{\gamma\text{-ray or electron beam}} H, OH^-, e_{aq}^-, H_2O^+, H_2O^* \tag{5.24}$$

(Free radicals, ions, active molecules, etc. produced by radiation decomposition of water)

$$M \xrightarrow{\gamma\text{-ray or electron beam}} R_1^{\cdot} \tag{5.25}$$

(Monomer molecule M generates free radicals under the action of rays)

$$E \xrightarrow{\gamma\text{-ray or electron beam}} 2\mathrm{R}_2^{\cdot} \tag{5.26}$$

(Emulsifier E generates free radicals under the action of rays).

These free radicals or active groups initiate the chain reaction of monomer polymerization between micelles and emulsion particles, which is the key kinetic step determining emulsion polymerization. Compared with chemical polymerization, emulsion polymerization has the following advantages:

① Peroxide or other initiators are not required in the emulsion system. Thus, the product does not contain initiator fragments and has high purity, which is critical for medical products because the initiator fragments in the products are often the main chemical substances causing the human allergy.

② The free radical yield of radiation decomposition of water is relatively large ($G_{\mathrm{H}} + G_{\mathrm{OH}} + Ge_{aq}^{-} = 5.9$). The concentration of free radicals can be controlled by controlling the radiation dose rate or controlling the concentration of free radicals as required to reach a constant value of 5.9, or by reducing the free radical concentration to stop the reaction.

③ Due to the large production of radiation decomposing free radicals, the sufficient spatial structure between emulsion particles in the emulsion, and the existence of energy-rich active particles, the reaction speed of emulsion polymerization is fast and the molecular weight of the product is high.

④ The temperature has little effect on emulsion polymerization, which can realize the polymerization under normal temperature, prevent chain transfer and rearrangement reaction, and generate fewer by-products, with regular polymer structure, narrow molecular weight distribution, and superior polymer performance.

⑤ The free radicals formed by water radiation decomposition are light in weight, fast in migration, and high in reaction efficiency. During the emulsion polymerization, no electrolyte will be generated, no buffer is required, ionic strength is low, and pH value approaches 7.

⑥ During emulsion polymerization, the formation rate of the active center is not affected by a few variable ion impurities, so the polymerization process and product quality are stable.

The probability of application of radiation emulsion copolymerization is higher than that of radiation emulsion polymerization. Take the emulsion copolymerization of tetrafluoroethylene-propylene as an example. Pump out the air out of the reactor, add a 2% aqueous solution of ammonium zinc fluoride into the reactor and stir it, then press the given tetrafluoroethylene (75–90% mol) and propylene (25–10% mol) monomers into the reactor to the specified pressure, after that, send the reactor into the irradiation chamber for irradiation, and continuously pump the monomers into the reactor at the same time to maintain the monomer pressure. When the concentration of emulsion reaches 30%, the irradiation is stopped, and the diameter of emulsion particles can be obtained as 100 nm. Coagulate the emulsion by freezing or adding salt, and then dehydrate and dry it, its molecular weight is 2.2×10^5. Systems such as vinyl chloride-vinyl acetate and vinyl acetate-butyl acrylate can be carried out in radiation emulsion copolymerization.

5.4 Radiation Grafting and New Material Preparation

Radiation grafting adopts proper polymers with moderate mechanical strength and non-toxic and are harmless to the human body such as polyethylene, ethylene-vinylacetate copolymer, and styrene to graft to acrylic acid, acrylate ester, acrylamide, N-isopropyl-acrylamide, and other monomers, giving them polymer biocompatibility. Branched chains containing active groups are friendly to biological molecules and will not undergo rejection reactions. These active groups can also be grafted to proteins, polypeptides, antibiotics, anti-cancer drugs, nutrients, etc. according to people's needs to make slow-release capsules, which can be implanted into the human body to maintain the stability of drug and nutrient concentrations in vivo for a certain period of time to achieve better therapeutic effects. In addition, radiation grafting products can also be made into catheters, trauma coating materials, artificial organs, and other products, which have important applications in the medical field. Radiation grafting can also be used to improve the wettability and wrinkle resistance of the materials, improve the performance of polymer materials, and expand their applications.

5.4.1 Basic Principle of Radiation Grafting

Pre-radiation grafting is usually used for radiation grafting of biocompatible materials. The main technical route is to select non-toxic and harmless polymer materials such as ethylene–vinyl acetate, polystyrene, polyethylene, etc. The shape is selected according to medical use. It can be sheets, rods, tubes, wires, films, etc., which are placed in a container. After the gas in the container is pumped to a certain vacuum, inert gas is introduced for protection, and the appropriate dose is irradiated for standby. Dissolve the monomer to be grafted with solvent and add stabilizers, graft accelerators, etc., after air extraction, inert gas is introduced for protection, and the irradiated substrate is immersed in the monomer solution under inert gas protection. After reacting for a certain time under appropriate temperature and pressure, take out the grafted substrate, wash, dry, weigh, and the grafting rate can be calculated.

The grafting mechanism is as follows:

$$\mathrm{I} \rightsquigarrow 2\mathrm{R}^{*} \tag{5.27}$$

where

I substrate;
R^{*} free radicals formed after irradiation of the substrate.

$$2\mathrm{R}^{*} \rightarrow \mathrm{R}-\mathrm{R} \tag{5.28}$$

Free radical annihilation reaction:

$$R^* + M \rightarrow Q \tag{5.29}$$

where

M monomer;
Q graft products.

Equation (5.28) is the free radical reaction formed by irradiating the substrate. Equation (5.29) is a reaction that two free radicals meet to form the original substrate molecule or a product with a longer molecular chain than the original substrate, which reduces the concentration of free radicals and the grafting probability. This is a reaction that should be avoided in the grafting process. Equation (5.30) is the desired reaction. According to the kinetic formula, it is deduced as follows:

$$\frac{d[R^*]}{ndt} = k_1[R^*]^n \tag{5.30}$$

$$\frac{d[Q]}{dt} = k_2[R^*][M] \tag{5.31}$$

where

k_1, k_2 apparent reaction rates of Eq. (5.31) and Eq. (5.32) respectively;
n order of apparent reaction of Eq. (5.32).

Based on the actual situation of the grafting reaction, [M] (monomer concentration) $\gg$ [R^*] (free radical concentration), thus, it is considered that the monomer concentration in the reaction process is constant. The equation for the apparent rate of monomer formation is simplified as

$$\frac{d[Q]}{dt} = k_2'[R^*], \quad \text{where } k_2' = k_2[M] \tag{5.32}$$

If n = 1, it can be deduced that

$$[Q] = [R^*]_0 \frac{k_2'}{k_1}(1 - e^{-k_1 t}) \tag{5.33}$$

If n = 2, then

$$[Q] = \frac{k_2'}{2k_1} \ln(1 + 2[R^*]_0 k_1 t) \tag{5.34}$$

where

$[R^*]_0$ initial concentration of free radicals.

The concentration units used for [Q], $[R^*]_0$, k_1, k_2, etc. are the number of molecules or moles per unit volume, which need to be converted to weight.

The following equation is obtained through conversion:

$$Gr = \frac{Mr}{2W_0} \cdot \frac{k_2'}{k_1} \ln\left(1 + \frac{2DG}{V} k_1 t\right) \tag{5.35}$$

where

W_0 initial weight of the substrate;
Mr molecular weight of monomer;
D irradiation dose received by the substrate;
G number of free radicals formed per unit irradiation dose;
V volume of the reaction system.

According to Eq. (5.35), the theoretical yield of the graft polymer can be calculated.

According to the need, appropriate substrates and monomers can be selected to prepare controlled drug delivery materials, drug coating materials, selective filtration membranes, human-friendly blood transfusion bags, in vivo indwelling catheters, etc. More importantly, they can be made into materials whose function varies with changes in acid, base, salt, charge, protein, temperature, sugar, etc. in the medium, which have important applications in the medical and biological fields.

For mutual radiation grafting, since the products formed by grafting monomers are mainly formed by self-polymerization of monomers, few graft products can be obtained, and the practical application is limited.

The monomer of the radiation polymerization product is water-soluble, and its mechanical strength cannot meet practical requirements. Therefore, the support materials need to be coated and processed into medical products to be used in actual treatment. For example, water-sensitive and temperature-sensitive acrylamide-based polymers are used as burn dressings, which can quickly absorb various exudates secreted by cells, keep the burn site dry, inhibit the growth of bacteria, and speed up the recovery of the burn site.

5.4.2 Principle of the Preparation of New Materials by Radiation

The radiation method provides a new effective method for the preparation of nanomaterials and other materials. The synthesized nanomaterials include polymer nano microgels, nanoparticles, nanoalloys, etc. The typical products are nano poly (N-isopropylacrylamide) micro gel, silver, zinc sulfide, silver-copper nanoalloy, etc.

Radiation sources used for preparing of nanomaterials by radiation are generally high-energy electron beams or the ^{60}Co source, among which the ^{60}Co source is mainly used. The basic principle is that under the action of γ-rays, water is excited

by high-energy radiation, and the excited water is ionized. The formula of the reaction is as follows.

$$H_2O \xrightarrow{\gamma-ray} H_2, H_2O_2, H^*, {}^*OH, e_{aq}^-, H_2O^+, H_2O' \tag{5.36}$$

Free radicals produced by radiation, highly reactive monatomic H^*, hydrated electrons e_{aq}^-, etc. are reducible. The standard reduction potential of e_{aq}^- is -2.77 V, and the reduction potential of some H^* is -2.13 V. They have a strong reduction ability and can reduce some metal ions in the aqueous solution. When the isopropyl alcohol or tert butyl alcohol is added to remove the oxidizing radical ${}^*OH$, H^* and e_{aq}^- in the aqueous solution can gradually reduce metal ions to metal atoms or low-valent metal ions.

$$M^{n+} + e_{aq}^- \dashrightarrow M^{(n-1)+} + e_{aq}^- \dashrightarrow M^{(n-2)+} \tag{5.37}$$

Metal ions are continuously reduced to metal atoms by hydrated electrons or monatomic hydrogen.

$$M^+ + e_{aq}^- \dashrightarrow M \tag{5.38}$$

$$M^{n+} + H^* \dashrightarrow M^{(n-1)+} + H_2O \tag{5.39}$$

$$H^* + M^{(n-1)+} \dashrightarrow M^{(n-2)+} + H_2O \tag{5.40}$$

$$M^+ + H^* \dashrightarrow M + H_2O \tag{5.41}$$

These newly formed metal atoms aggregate into crystal nuclei, grow into nanoparticles according to thermodynamic principle and precipitate out of aqueous solution.

The principle of preparing silicon carbide fiber is different from that of inorganic metal nanomaterials. It is generally believed that under the action of radiation, the polycarbosilane fiber will first undergo crosslinking of the carbon–carbon bond or the carbon-silicon bond, and then undergo the rearrangement reaction. Under the protection of inert gas or specific gas, carry out high-temperature sintering, and regular carbon-silicon bonds will be transformed into, and small alkyl molecules with dehydrogenation or loss of substituents will obtain silicon carbide fibers. Influenced by the preparation technology of polycarbosilane fibers, it is difficult to achieve nano-scale fibers, but ordinary silicon carbide fibers with superior performance can be prepared. During the sintering process, the presence of oxygen significantly lowers the melting point of silicon carbide fibers and reduces the ability to withstand temperature, thus, oxygen removal is a key technology. Figure 5.18 shows the possible mechanism for the formation of silicon carbide fibers by the gradual cracking and rearrangement of irradiated polycarbosilane at high temperatures.

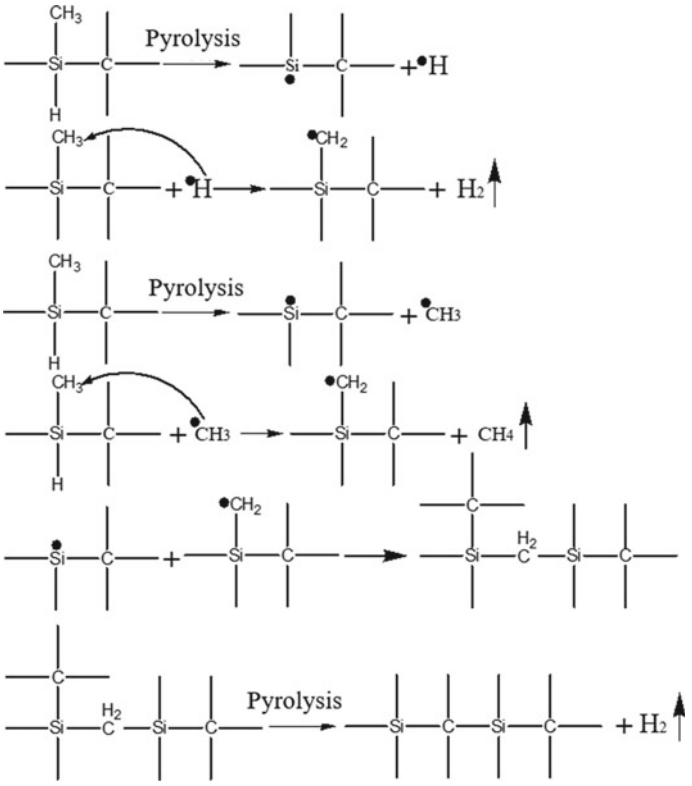


Fig. 5.18 Mechanism of SiC fiber prepared by polycarbosilane radiation

Polymer nanogels such as N-isopropylacrylamide as a monomer are polymerized into nanogels by forming the free radical chain reaction under the action of high energy rays.

5.4.3 Main Methods of Preparing Materials by Radiation

The preparation of nano metal powder can be divided into three steps. First, solution preparation and treatment. Dissolve the metal salt in pure water, add the matching amount of isopropyl alcohol and surfactant, fill in nitrogen until it is saturated, and then seal it. Second, the irradiation of the metal salt solution system. Irradiate the nitrogen saturated solution system, select the appropriate dose, generally 103–104 Gy, and the appropriate irradiation time. Third, the preparation of nanoparticles. The irradiated solution is generally colloidal, which requires hydrothermal treatment. Nanoparticles are precipitated, and the precipitates are washed and dried after separation to obtain products.

Since most systems for preparing materials by radiation are aqueous solutions, it is easy to prepare metal oxide nanomaterials. Take the main methods of preparing nano zinc sulfide crystals in aqueous and non-aqueous systems by radiation as examples. For the non-aqueous system, analytical pure zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) is used as the source of zinc ions and carbon disulfide is the source of sulfur, which is dissolved in a mixed solvent of ethanol and glycerol. The density of the prepared solution is 1.5 g/mL, isopropyl alcohol must be added as the trapping agent of free radical OH^* to fully dissolve the whole system to form a homogeneous phase. The dose of cobalt source is 1.11×10^{16} Bq, carbon disulfide is conducive to eliminating the precipitation generated during irradiation and generating sulfur radicals. The colloidal suspension will be formed during irradiation, after the irradiation is complete, wait for the precipitate to settle completely. Take out the precipitate, wash it repeatedly with anhydrous ethanol several times to remove the by-products, and dry it to constant weight under vacuum. For the aqueous system, the analytical pure zinc sulfate heptahydrate and sodium thiosulfate are prepared into the homogeneous aqueous solution in proper proportion. The remaining operation steps are the same as those in the non-aqueous system, but the period for drying under vacuum is two hours in the final step. The nanoparticles prepared by the above two methods were analyzed by TEM, XRD, UV–vis, etc. The results showed that the morphology of the particles was amorphous spherulites, the particle size of nano zinc sulfide prepared in the aqueous system was 38 nm, and that in the absolute alcohol system was 42 nm.

Urea is used as the template for preparing silver nanowires, which plays a key role in the formation of silver nanowires. Dissolve 0.01 mol urea in 50 mL water at 60 °C. Quickly add 0.01 mol of silver nitrate, add isopropanol as the hydroxyl radical trapping agent after dissolution, and fully mix them. Cool to room temperature at a cooling rate of 1 °C/min, and irradiate the system in a cobalt source for 5 h until the accumulated dose reaches 15 kGy. The size of the prepared silver nanowires is 6000 nm × 70 nm. The fibrous nickel nanowires are prepared with nickel sulfate and silver nitrate as raw materials, add the surfactants polyvinyl alcohol and sodium dodecyl benzene sulfonate. Under the acidic condition with a pH value of 6, the product is black, and silver can be obtained by the X-ray, but no nickel can be obtained. When the pH value is 10–11, nickel can be obtained under alkaline conditions at pH 10–11. Silver is the crystal nucleus of nickel in the formation of fibrous nanopowder, so characteristic peaks of silver will appear in X-ray diffraction analysis.

In the preparation of nano-poly(N-isopropylacrylamide) organic polymer materials by photoinitiation, the amide group has a strong hydrogen bonding ability. Thus, the water absorption capacity changes regularly with temperature. This kind of polymer has the characteristics of temperature sensitivity and a lower critical solution temperature (LCST). When the temperature is lower than LCST, the polymer microgel is fully dissolved by water to form a homogeneous system. When the temperature is higher than LCST, hydrophobicity will be shown, and phase separation occurs between the polymer microgel and the surrounding dispersion medium. With the change of molecular weight and polymer composition of the acrylamide-based polymer, LCST generally changes between 32 and 38 °C, which is close to the human body temperature. Therefore, it has many unique applications in biology and

medicine, mainly used in immune technology, cytology, protein antibody, drug fixed carrier, and medical diagnostics, and it is also used in the intelligent drug delivery system. When the microgel particles coated with specific therapeutic drugs are less than 50 nm, they can pass through the liver endothelial cells and reach the spleen, bone marrow, tumor tissues, and other diseased sites through lymphatic circulation. In addition, the particle size in the nanometer range is more convenient for the intelligent microgel to realize the transportation and release of drugs and living organisms in vivo.

The key to the preparation of such biological and medical materials by radiation is the preparation of the polymerization system, that is, uniformly mix the monomer with auxiliaries, stabilizers, emulsifiers, and suitable solvents to form a system. After gas extraction, inert gas is introduced to saturation, and the system is irradiated at normal temperature. Polymerization can be achieved at a lower temperature. Strictly controlling the stirring speed and the nano-microgels can be obtained. Kaetsu Kaoru even achieved the polymerization of such monomers at low or ultra-low temperatures (− 100 °C) by radiation initiation, thus controlling the implosion phenomenon that often occurs during the polymerization of such monomers. In addition, nano-microgel particles with different pore sizes can be prepared by adjusting the monomer concentration to meet different needs.

The preparation of biological and medical functional materials using acrylamide derivatives as monomers is a hot area in the research of radiation chemistry.

5.4.4 Applications of Functional Materials Prepared by the Radiation Method

Nanomaterials have quantum size effect, giant magnetoresistance, surface effect, etc., and have a wide range of applications in the field of science and materials. The decrease in the size of metal or semiconductor solids results in a blue shift of the light absorption peak. The phenomenon that the energy gap increases when the material size is reduced to the limit of the movement of electrons is called the quantum size effect. The phenomenon that the resistance has a large change under a very weak external magnetic field is called the giant magnetoresistance effect. The resistance value of the two layers of magnetic materials with opposite magnetization directions is obviously greater than that with the same magnetization direction. The main uses of nanomaterials or other new materials prepared by the radiation method are as follows.

1. **Catalysis**

As the size decreases, the number of atoms in the outer layer increases, the degree of unsaturation of the surface atomic coordination and specific surface energy also increase dramatically, which is an important reason for the high catalytic activity and instability of small-size nanoclusters. Another characteristic brought by the

increase of specific surface area is that the content of heterogeneous interface in the composite material increases greatly, which will have a greater impact on the structure of the electronic energy band and dielectric properties of the composite material. By the adjustment of the energy band structure during the interface recombination of semiconductor materials, the photoinduced catalytic behavior of the catalyst can be modified.

2. **Sensors and chips**

The preparation of metal nanowires such as palladium and titanium by radiation is a very mature technology. Therefore, the sensor based on palladium metal nanowires with a fast response to hydrogen and its isotopes can be developed, and its response speed can reach the millisecond level. The working principle is that the volume expansion of palladium metal nanowires after hydrogen absorption leads to a reduction of the distance between nanowires, which increases the conductivity of the sensor. Similarly, nanomaterials sensitive to specific substances can also be used to prepare corresponding nanosensors for the detection of target substances, toxic and harmful chemicals, dangerous goods, bacteria, viruses, etc.

Silicon carbide is an ideal chip material. The silicon carbide prepared by the conventional method has many problems, such as high hardness, many impurities, and excessive bubble voids. In particular, the existence of oxygen leads to the extreme deterioration of the performance of silicon carbide, thus reducing or even losing its application value. Adopting the radiation method to prepare silicon carbide nanomaterials can effectively solve the above problems, and can be used to prepare microelectronic chips instead of monocrystalline silicon, which has better performance than monocrystalline silicon.

3. **Structural materials**

Silicon carbide fiber is a kind of heat-resistant and wave-absorbing material for satellites, missiles, and high-tech weapons. It can withstand up to 1800 °C in a long time, while in a short time, it can even withstand higher temperatures. The radiation method has obvious advantages in preparing the silicon carbide fiber over other methods, especially in controlling the content of oxygen impurities in materials. Oxygen in the material seriously affects the capacity of temperature resistance of the material. It is reported that the existence of trace oxygen will reduce the capacity of temperature resistance from 1800 to 1200 °C, significantly reducing the application performance of the material.

4. **Nano functional microspheres**

The nanospheres prepared by radiation include magnetic microspheres, microspheres carrying radionuclides, microspheres carrying anti-cancer drugs, etc., which can be used for high-density magnetic recording, targeted therapeutic drugs, the intelligent drug delivery system, etc. Intelligent drug delivery can be used to release controlled

substances with the change of acidity in scientific experiments, and to control the intelligent release of insulin according to the change in the condition of diabetics.

There are many uses for nanomaterials prepared by radiation, and only a few main applications are listed above.

5.4.5 Prospects of Nanomaterials Prepared by the Radiation Method

The preparation of nanomaterials by radiation has developed from nanoparticles to nanofibers, nanoalloys, nano colloids, and nano oxides and has expanded from precious metals to light metals.

1. **Nanoalloys**

In the early days, nanomaterials synthesized by γ-ray radiation were mainly precious metals. At present, through the study of its preparation and the discussion of its mechanism, the preparation of nanoalloys is gradually realized. Overcome the difference in reduction potential of different metals and prepare uniform alloy materials is the key problem to be solved in the future.

2. **More active light metal nanomaterials**

Hydrated electrons have the advantage of high reducibility, which is stronger than that of conventional chemical reductants. Therefore, the radiation method can be used to prepare active light metal nanomaterials that cannot be prepared by conventional reducing methods, such as rare earth metal nanopowders.

3. **Nanocomposites such as compounds containing sulfur and oxygen**

Nanocomposites have become the main research field of nanomaterials, including inorganic nanomaterials and polymer nanomaterials. Metal compounds such as sulfide (ZnS), oxide (TiO_2), carbonate, sulfate, and other nanomaterials are being developed. Since the preparation of the radiation method is completed in solution, coupling agents, electrostatic scavengers, dispersants, anti-oxidation coatings (anhydrous solvent system), surfactants, etc. can be selected and added to the solution, so that the surface of the prepared nanomaterials is automatically wrapped with a layer of additives. Due to the existence of these additives, the problems of easy agglomeration and poor dispersion of nanomaterials can be solved, which is difficult to be achieved by other preparation methods.

4. **Other nanomaterials**

In addition to nanoparticles and fibers, the radiation method can also be used to prepare nano films and nano amorphous powder. Select the appropriate carrier, and

the nano atoms are deposited on the lining film from the solution to obtain the nano film. The preparation principle of nano amorphous powder is that when the material diffuses rate to the surface of the nucleus faster than the growth rate of the nucleus, and the atoms and ions on the nucleus surface cannot be arranged in an orderly manner, the deposited atoms randomly stacked together to form an amorphous powder, that is, the amorphous.

The preparation of cluster materials by radiation is also one of the important directions for the preparation of nanomaterials by radiation chemistry. One or several silver ions are surrounded by water molecules to form cluster compounds, which can be as small as 1 nm.

With a further understanding of nanomaterials and the development of science and technology, more new nanomaterials with broad application prospects can be prepared by radiation.

5.5 Radiation Degradation

Radiation degradation is the effect that the main chain of polymer polymer breaks under the action of high-energy radiation. The result of radiation degradation is that the molecular weight of the polymer decreases with the increase of radiation dose until some polymer molecules break down into monomer molecules. The role of both radiation degradation and thermal cracking is to deconstruct the polymer and reduce its molecular weight. The difference between the two is that during radiation degradation, a single chain break results in two shorter polymer molecules, leading to a decrease in the average molecular weight, while during thermal cracking, polymer molecules are decomposed into monomer molecules, the total amount of polymer is reduced, but the average molecular weight of the residual part remains essentially unchanged. Thermal cracking will produce a large number of original monomers that make up the polymer, while radiation degradation generally does not produce monomer molecules, even if there are monomer molecules, they are very small.

If there are quaternary carbon atoms in the molecule of the polymer main chain, the radiation degradation process will be dominant under the action of high-energy rays. The quaternary carbon contains two substituents R, which are located on one C of the main chain, producing sterospecific blockade and conjugation effect, weakening the C–C bond of the main chain. Once irradiated by high-energy rays, the main chain will break.

The mechanism of radiation degradation is generally the 1 free radical reaction, but the detailed process is not completely understood. The temperature has an effect on the radiation degradation of some polymers, and the breakage of main chains generally increases with the increase of temperature, which is strong evidence that the radiation degradation proceeds according to the free radical mechanism. However, not all radiation degradation is carried out based on the free radical mechanism, and

there are other mechanisms. For example, according to the effects of cationic retarders such as polyethyleneimine and triethylamine and the analysis of products, the reaction mechanism of radiation degradation of poly(α-methylstyrene) and polypropylene sulfide is the ionic reaction.

Chitosan is the product of partial deacetylation of chitin. In a solid or aqueous solution, its radiation degradation rate is different. The degradation rate of solid chitosan is much lower than that in solution. However, due to the low solubility of chitosan in the solvent, it can only be made into a dilute solution, so most of the energy of radiation is absorbed by the solvent. Therefore, the actual degradation effect is not ideal.

Under the action of γ-rays, chitosan can be degraded in two ways. One is direct action, that is, the bonding electrons of glycosides are excited by the action of γ-rays, causing the breakage of valence bonds. The other is indirect action, that is, the action of radiation and solvent generates electrons, free radicals, stimulated small molecules, etc., these charged particles and stimulated small molecules can accelerate the degradation of glycosides.

Chitosan and other natural polymer degradation products are excellent intermediates for the preparation of drugs, as well as food and cosmetic additives, which is an important direction of research. In addition, radiation degradation of organic halogenated waste is also a research hotspot. For example, chlorophenol is an important chemical raw material and intermediate, which is toxic to any organism. With the increase of chlorine content, the toxicity increases and is difficult to be biodegraded. Its natural degradation process is long, and the effects of chemical and optical degradation methods commonly used, such as photochemistry, photocatalysis, electrocatalytic oxidation, ion radiolysis, etc. are not obvious. However, effective degradation of 4-chlorophenol, for example, can be achieved by using the radiation method and selecting appropriate radiolysis conditions.

The degradation mechanism of chlorophenol (represented by R-Cl) is that water is irradiated to generate hydrated electrons (e_{eq}^-), H^+, $H^{\cdot}$, $OH^{\cdot}$, and various excited molecules, particles, ions, etc. These particles will attack the chlorophenol molecule, and the reaction is as follows.

$$\text{R-Cl} + e_{aq}^- \dashrightarrow \text{R}^+ + \text{Cl}^- \tag{5.42}$$

$$\text{R-Cl} + \text{H} \rightarrow \text{R}^{\cdot} + \text{H}^+ + \text{Cl}^- \rightarrow \text{RClH(H}\,adduct) \tag{5.43}$$

$$\text{R-Cl} + \text{OH} \rightarrow \text{R}^{\cdot}\text{Cl} + \text{H}_2\text{O} \rightarrow \text{RClOH(OH}\,adduct) \tag{5.44}$$

Generally speaking, there is always dissolved oxygen in the system. The existence of oxygen has a certain impact on the degradation. Oxygen attacks active particles such as e_{eq}^- and H^+, reducing the rate and effect of degradation.

$$e_{aq}^- + \text{O}_2 \rightarrow \text{O}_2^- \ (k = 2.1 \times 10^7\ \text{m}^3\ \text{mol}^{-1}) \tag{5.45}$$

$$^{*}H + O_2 \rightarrow {}^{*}HO_2 \ (k = 2 \times 10^7 \ m^3 \ mol^{-1}) \tag{5.46}$$

$$HO_2 \leftrightarrow H^+ + O_2^- \ (pH = 4.8) \tag{5.47}$$

However, the main factors affecting the radiation degradation of 4-chlorophenol are the temperature of the aqueous solution, pH value, and the type and concentration of free radical scavengers. For example, HCO_3^-, CO_3^{2-}, $^{*}OH$, etc. are strong free radical scavengers. For instance, n-butanol is used to react to eliminate the effects of $^{*}OH$, while adjusting the pH value can be adopted to eliminate the negative effects of carbonate.

The irradiation dose plays a decisive role in the degradation of 4-chlorophenol. The empirical formula is as follows:

$$G_D = \Delta R_D N_A / D(6.24 \times 10^{15}) \tag{5.48}$$

where

ΔR_D	the variation of organic solute after absorbing a certain radiation dose (mol/L);
D	radiation dose (kGy);
6.24×10^{15}	Conversion Coefficient from kGy to 100 eV/L;
N_A	Avogadro constant (6.02×10^{23}).

It can be seen from this formula that the GD value decreases with the increase in radiation dose. This is because, under the action of high dose radiation, the probability of recombination of e_{eq}^-, H^+, and other active particles increases, and the concentration of active particles decreases, leading to the decline of the radiation degradation efficiency of chlorophenol.

The end product of chlorophenol degradation is extremely critical, and it is desirable that the product generated can be non-toxic and harmless. Through the action of radiation, chlorophenols are decomposed into products without chlorine or products with low chlorine content. The most ideal product is chlorine-free organic molecules, which greatly reduces toxicity.

Studying the radiation degradation mechanism of polymer is conducive to formulating countermeasures to prevent degradation. For example, wires and cables used in aerospace navigation, nuclear industry, and other fields need to withstand the effects of cosmic rays, neutrons, γ-rays, high temperature, strong corrosives, mechanical friction, and large torque force. Special polymers can meet some of the above requirements. However, under such harsh conditions for a long time, special polymers are prone to radiation degradation, which leads to the aging of the insulation layer of wires and cables, and the loss of protection on the cable core under the action of external factors, and the equipment cannot work normally. Therefore, preventing radiation degradation is the main research direction of polymer materials. Most studies show that radiation degradation occurs in the amorphous region of polymer materials, while a large number of defects will be produced in the crystal region under the action of

high-energy rays, forming new amorphous regions and accelerating the degradation of the polymer. A better way to solve the degradation is to realize the crosslinking of polymers. In addition, preventing the formation of amorphous regions or improving the crystallinity of the polymer are also commonly used methods to reduce or eliminate the concentration of oxygen in the irradiation atmosphere. The presence of oxygen can accelerate the degradation of molecular chains. Another type of method is to add free radical blockers in the formula of material, that is, free radical absorbers constantly absorb highly-active free radicals generated in the radiation process, thus avoiding the damage of free radicals to the main chain of polymers. For polymers, the rate and effect of degradation can be reduced by adding ion blockers and reducing the ion concentration, so that the polymer can maintain normal function within the designed working life.

Radiation degradation is sometimes desirable. For example, the radiation-degraded PTFE powder added to the lubricating oil can greatly reduce friction and prolong the service life of mechanical equipment. The electrical, mechanical, and thermal aging properties of low-density polyethylene (LDPE) can be significantly improved by adding PTFE powder.

At present, radiation degradation of natural material is the main research field. For example, the radiation degradation product of cotton fiber is an important raw materials for explosives, which has unique advantages over the traditional cotton fiber nitration technology. It inhibits the oxidation caused by the decrease of polymer molecular weight in the esterification process and does not use sulfuric acid in nitration, thus improving the safety of explosives. Wood, grass, and other fibers are degraded into sugar and even ethanol after irradiation. On the one hand, it solves environmental problems, and on the other hand, it can create certain benefits to solve the problem of shortage of funds in the field of environmental protection. The biggest obstacle to application is the high cost and the difficulties of practical application. But with the progress of science and technology, as well as the reduction of costs, more technologies will gradually be applied. For example, the radiation degradation of the shells of marine organisms can produce many useful biological materials and pharmaceutical intermediates, which are important raw materials for medicine, health products, and other industries.

5.6 Radiation Curing and Its Applications

In a broad sense, radiation curing is the mixed effect of radiation polymerization, radiation crosslinking, or radiation grafting. The difference lies in that after the formula formation of monomer and auxiliary agent, after the polymerization, crosslinking, or grafting of monomer or prepolymer is initiated by radiation, the liquid low molecular weight monomer or prepolymer will be solidified into a solid, and the soluble and fusible linear molecules are transformed into an insoluble and non-fusible three-dimensional network structure, forming a solid surface film with excellent performance. Radiation curing can be divided into ultraviolet curing and electron beam

curing according to the specialty. As the components do not contain organic solvents or the content of organic solvents is small, and some solvents can participate in the radiation curing reaction, and the curing is carried out at room temperature, radiation curing is called "green processing technology", becoming the main direction of coating research and coating technology development.

5.6.1 Basic Principle of Radiation Curing

The unsaturated monomer (M) in the component produces active particles or free radicals under the action of rays. Under the guidance of active particles or free radicals, the monomer chains expand continuously, and strong chemical bonds are formed between the chains to achieve curing.

Under the action of the ray, the monomer generates active particles, and the mechanism of curing initiated by active particles is as follows:

$$M + e^{***} \rightarrow M^{+\cdot} + e + e^{**} \text{ (Generation of cations and high-energy electrons)} \tag{5.49}$$

$$M^{+\cdot} + e \rightarrow M^{*} \text{ (Electronically excited states of M) (Single, triplet states)} \tag{5.50}$$

$$M^{+\cdot} \rightarrow H^{\cdot} + M^{+} \; or \; H^{+} + M^{\cdot} \text{ (Break into carbon cations or free radicals)} \tag{5.51}$$

$$e \rightarrow substrate \; or \; O_2 \; electron \; capture \tag{5.52}$$

where

e^{***} high-energy electron;
$M^{+\cdot}$ free radical cation;
e low energy electrons, that is, thermal (moderated) electrons generated by monomer M.

1. **Free radical curing mechanism**

For electron beam radiation curing of surface coatings, the intermediate particles formed under the action of electrons include thermalized electrons, free radical cations, and excited molecules. Different curing conditions lead to different mechanisms of radiation curing reaction, sometimes multiple mechanisms are involved. The mechanism of γ-ray initiated curing is mainly free radical polymerization and anionic polymerization. If cyclohexanol (HOR) is added to the curing system, it will inhibit the anionic polymerization, and the curing mechanism is mainly a free radical reaction.

The more successful research on radiation curing is the curing system based on acrylic acid derivatives, which has been successfully industrialized. The main curing mechanism is the thermal electronic reaction. When the electron beam irradiates the acrylic acid curing system, solvated electrons are generated, which are added to the unsaturated bond to obtain free radical anions of acrylic acid derivatives, as shown in Eq. (5.56).

$$XM \xrightarrow{EB} XM^{\cdot -} + e^{-}_{solv} \tag{5.53}$$

$$e^{-}_{solv} + \mathrm{CH_2} = \mathrm{CHCO_2R} \rightarrow (\mathrm{CH_2} = \mathrm{CHCO_2R})^{\cdot -} \tag{5.54}$$

Some compounds with electron trapping ability can inhibit radiation curing. For example, when 1,4-benzoquinone is added to the curing system of isodecanol acrylate (IDA), as the benzoquinone can capture free radicals or electrons, the curing speed of IDA is significantly reduced, and the trapping of free radicals or electrons by benzoquinone will be gradually consumed. After benzoquinone is consumed, the curing rate of IDA will return to the expected speed. Dinitrobenzene is also an electron-trapping agent. The o-dinitrobenzene and the m-dinitrobenzene have stronger electron-trapping ability than dinitrobenzene because the efficiency of electron trapping increases with the increase of dipole distance. Conventional organic pigments and dyes have electron-trapping capabilities, so the addition of these components should be avoided when designing the formula for radiation curing.

Acrylate derivatives are difficult to cure when containing aromatic groups. If the aromatic group contains halogens that can be easily removed, the curing reaction can be accelerated. With the removal of halogen, dissociative free radicals are generated on the aromatic nucleus, and the concentration of free radicals initiating curing becomes the largest, which is conducive to curing.

The principles of free radical curing are summarized as follows:

a. primary reaction

$$Oligomer\ or\ reactive\ monomer\ (AB) + e^{-} \dashrightarrow AB^{+} + e^{-}_{th} + e^{-}_{k} \tag{5.55}$$

$$\rightarrow AB^{*} + e^{-}_{k} \tag{5.56}$$

where

e^{-}_{k} electrons with kinetic energy;
e^{-}_{th} thermalized electronics.

Generate ionized resin, thermalized electron e^{-}_{th}, or excite an electron to a higher energy level, so that the resin molecule becomes an excited state.

b. secondary process

$$\boxed{\begin{aligned} AB^+ &\rightarrow A^{+\cdot} + B^{\cdot} \\ AB^* &\rightarrow A^{\cdot} + B^{\cdot} \\ AB + e^- &\rightarrow AB^{-\cdot} \\ AB^- &\rightarrow A^{\cdot} + B^{-\cdot} \\ A^{+\cdot} + B^{-\cdot} &\rightarrow AB^* \end{aligned}} \tag{5.57}$$

Most important process is the capture of thermalized (moderated) electrons:

$$AB + e_{th}^- \rightarrow AB^{-\cdot} \tag{5.58}$$

If there are compounds in the system that can take away hydrogen, then.

$$\mathrm{CH_2 = CHCOOR} + e_{th}^- \rightarrow (\mathrm{CH_2 = CHCOOR})^{-\bullet} \tag{5.59}$$

$$(\mathrm{CH_2 = CHCOOR})^{-\bullet} + \mathrm{SH} \rightarrow \mathrm{CH_3}\overset{\bullet}{\mathrm{C}}\mathrm{HCOOR} + \mathrm{S}^- \tag{5.60}$$

$$\mathrm{CH_3\,CHCOOR} \xrightarrow{\bullet} \text{polymer} \tag{5.61}$$

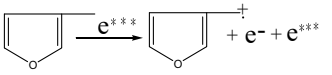
2. **Cationic curing mechanism**

The free radical curing mechanism is applicable to the polymerization of acrylic unsaturated monomers. For the curing system with epoxy as the matrix, electron beam curing is usually used, but the efficiency is low, so the initiator must be added to the formula. The initiator is generally a cationic salt, so its mechanism is cationic curing.

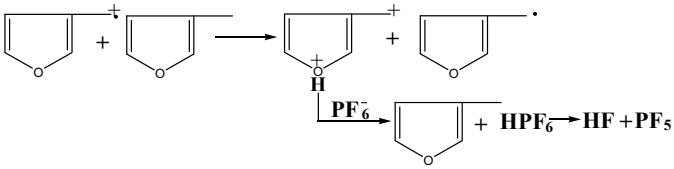
Iodonium salts and sulfonium salts capture thermalized (moderated) electrons during electron beam irradiation and decompose to produce free acids, that is,

$$\begin{aligned} Ph_2IPF_6 + e^- &\rightarrow PhI + Ph^{\cdot} + PF_6^- \\ Ph_3SPF_6 + e^- &\rightarrow Ph_2S + Ph^{\cdot} + PF_6^- \end{aligned} \tag{5.62}$$

The polymerization of tetrahydrofuran (THF) is.



(5.63)



(5.64)

After the initiator is added, three small molecules HF, HPF_6, and PF_5 can be produced under the radiation of the electron beam. These three small molecules can promote curing and significantly increase the rate of curing. When iodonium salt, sulfonium salt, and ferrocenium salt are added to the epoxy system as initiators, the decomposition rate of initiators is related to the dose of irradiation and the ionization constant of the medium. The decomposition order can be obtained experimentally as iodonium salt > sulfonium salt > ferrocenium salt.

Since epoxy compounds are not affected by free radicals and low-dose high-energy electrons, it is generally necessary to add initiators that can produce protons (H^+), such as iodonium salts. After absorbing the energy of electrons, molecules in the formula will ionize and generate thermalized (moderated) electrons, which will interact with initiators and cause the trapping of dissociated electrons. At the same time, the ionized epoxy molecule snatches the active hydrogen of adjacent molecules to generate cation, which is stabilized by the PF_6^- anion. On the other hand, the cation reacts with the epoxy functional group of the epoxy molecule to open the epoxy bond and initiate polymerization of the monomer molecule.

5.6.2 Main Components of Radiation Curing Formulas and Curing Processes

The formula of electron beam or ultraviolet curing is the basis of radiation curing, which is usually composed of monomers, prepolymers/diluents, initiators (depending on the type of prepolymer), pigments, fillers and antioxidants, etc. The main materials are multifunctional monomers and prepolymers with relatively low molecular weight. The range of functionality is 1–6, the selected functionality in the formula is 2–4, and the relative molecular weight is between 200 and 2000. Unsaturated groups in prepolymers and monomer molecules are the reaction sites of radiation-initiated polymerization. The double bond is opened by high-energy rays, which initiates a chain reaction, turning small molecules into long-chain molecules. The three-dimensional network structure is to achieve the hardening and curing of the system.

1. **Monomer (prepolymer)**

Monomer plays a decisive role in the performance and quality of radiation curing coatings. At present, the monomer base resins used for radiation curing include (meth) acrylate, unsaturated polyester, polyolefin/thiol/silicone, cationic resin, and other systems. These monomers are polymerized or crosslinked to form a three-dimensional network of polymer skeletons. There are two kinds of mature or promising monomers, namely the unsaturated polyester system and the thermosetting systems.

The main chemical composition of the unsaturated polyester system is the unsaturated polyester (also known as oligomer) and vinyl-based reactive monomers, which are formed by condensation of binary acid and polyol. Unsaturated groups can be

end groups, side groups, or intermediate double bonds. Generally speaking, the intermediate double bond is introduced by maleic anhydride, others such as 1,2-styrene, cinnamic acid, allyl, acrylamide, norbornene groups, and acrylate can also be used as the intermediate double bonds. The groups in some monomers have very high activity and are easy to copolymerize with styrene to significantly reduce the curing rate, but styrene is one of the cheapest products among organic compounds. Therefore, the maleic anhydride/styrene system is still one of the important systems in the research of radiation curing, and it has become the main coating for radiation curing. The curing process of the unsaturated polyester radiation curing system is greatly affected by oxygen. The presence of O_2 inhibits the curing reaction, thus a small amount of paraffin oil (0.2–2%) can be added to the formula. With the curing process, paraffin oil continuously overflows and migrates to the surface of the paint film, preventing O_2 from penetrating the interior of the paint film. Another solution is to introduce the allyl ether group into the polyester backbone. Compared with the method of adding paraffin oil, this method has significantly increased the cost, but it is rarely used in practice.

The higher the unsaturation and molecular weight in the polymer, the faster the formation of the gel. However, the increase in molecular weight leads to an increase in the viscosity of the system, making it difficult to coat. Adding monomers containing unsaturated groups in the system is conducive to curing. The unsaturated polyester is cured with the following monomers under radiation, and the rate of forming gel is in the order of methyl methacrylate < ethyl acrylate < styrene. For styrene with substituents on the benzene ring, the substituents will slow down the curing speed (Fig. 5.19).

The radiation dose required to treat the unsaturated polyester coating is about 10–100 kGy, and the thickness of the coating is generally between 0.025 and 0.2 mm. The energy required for the electron beam to penetrate such thickness is 25–150 keV. There is a distance between the beam outlet window of the accelerator and the coating, in order to overcome the resistance of the air, the energy of the electron beam needs to be increased to 150–600 keV. With the increase in distance, the energy of the electron beam should also be increased. With the process of curing, the viscosity of the system increases, forming a gel effect, which is conducive to the curing reaction and accelerates the overall speed of curing (including polymerization, crosslinking, copolymerization, grafting, etc.).

The rate of curing depends on the average dose rate. It is found that the gelling rate of the coating is higher when the total radiation dose is achieved in several times than

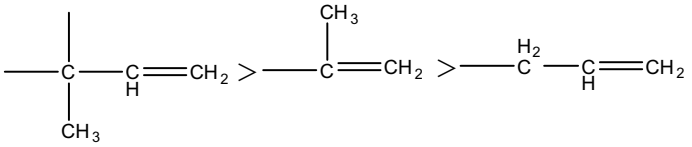
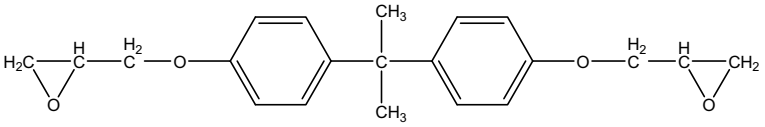


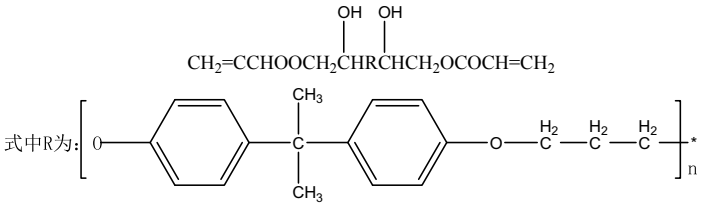
Fig. 5.19 Order of radiation sensitivity of unsaturated bonds in oligomers

when that of one enough time, indicating that fractionated irradiation is conducive to curing, but the effect of the dose rate is not fully understood.

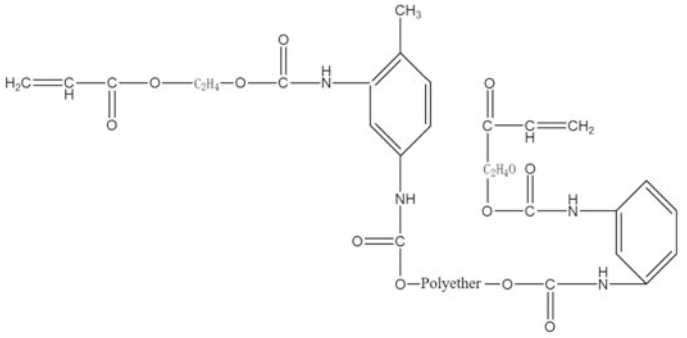
If there are different substituent groups on the main chain, oligomers with better performance such as methyl, epoxy, polyurethane, polyester (ether), and other substituents can be generated. Their structures are shown in Fig. 5.20.



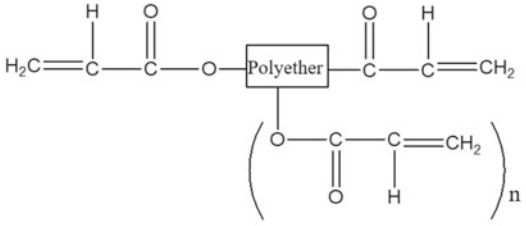
a. Bisphenol A



b. Acrylic oligomer containing bisphenol A



c. Polyurethane zwitterion



d. Polyether oligomer

Fig. 5.20 Acrylate oligomers with different substituents

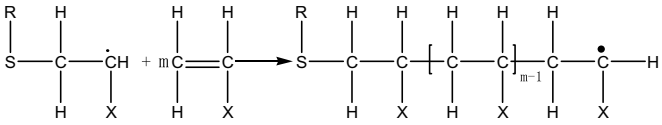
Increasing the content of unsaturated bonds in the skeleton of the main chain is beneficial to the increase of crosslinking density, which leads to an increase in the hardness and solvent resistance of the cured paint film. But at the same time, the bending property and impact resistance is reduced. Compared with the heat-cured acrylate paint film, the radiation-cured paint film shows no change after being exposed to a carbon arc lamp for 2000 h, while the heat-cured paint film is obviously yellow.

Compared with other systems, the polyolefin/thiol/silicone system has low viscosity and is easy to coat. The speed of radiation curing in this system is fast, and the influence of oxygen on the curing speed can be ignored. The coating is hydrolysis resistant and temperature resistant, with high sealing and high mechanical strength. The main mechanisms of the reaction are as follows.

$$Ph_2 + RSH \xrightarrow{h\nu} Ph_2\dot{C}OH + RS^{\cdot} \tag{5.65}$$

$$RS^{\cdot} + CH_2 = CHX \longrightarrow RSCH_2CH_2X + RS^{\cdot} \tag{5.66}$$

$$RSCH_2\dot{C}HX + RSH \longrightarrow RSCH_2CH_2X + RS^{\cdot} \tag{5.67}$$



(5.68)

In the above formulas, R is the alkyl group and X is the silicone, halogen, hydroxyl, sulfonic acid, and other groups.

The above four reaction steps are the main processes determining the curing reaction of the polyolefin/thiol/silicone system. The radiation curing speed of dithiol, trithiol, dienes, and trienes monomers is fast, and the mechanism is similar to the traditional condensation polymerization, forming the polythioether with high hardness and high elasticity. Compared with the ester bond ($R-\overset{\overset{O}{\|}}{C}-O-R'$) and the ether bond (R—O—R′), the system has better thermal stability and lower shrinkage.

Other curing systems, some of which are at the exploratory stage, and some of which are rarely used in the actual curing process, will not be introduced.

2. **Diluent**

Multi-functional group monomer/diluent. In the radiation curing system, the monomer has a high viscosity. When formulating, it is difficult to achieve uniform blending of materials. Therefore, diluents must be added to the system to reduce the viscosity of the system, increase the density of crosslinking, and control the adhesion and flexibility of the cured film.

Diluents mainly include acrylate monomer and vinyl monomer. Acrylates have high reactivity, and the hydrogen on the acrylate monomer is easily replaced by other groups to form a series of derivatives, which can improve the performance of acrylates, such as ethylene glycol diacrylate, butylene glycol diacrylate, phenoxyethyl acrylate, hydroxyethyl acrylate, etc. Although acrylate is a very good diluent, it has a strong smell and is irritating and harmful to the body surface, causing redness, swelling, rash, etc., or even cancer in serious cases. Therefore, the development of low-toxic or non-toxic acrylate ester has become the focus of research. Tripropylene glycol diacrylate, propylene oxide acrylate, and oxidized trihydroxypropane triacrylate have been successfully developed. The curing speed of vinyl is much slower than that of acrylate. However, due to cost and other factors, vinyl is still well used at present.

Diluents are not only used to reduce viscosity but also can increase the speed of curing, improve various mechanical properties of the paint film, and resistance to chemical solvents. The diluent is easy to volatilize during processing, causing adverse effects on operators and the environment. In addition to reducing the viscosity of the system before curing to facilitate construction, the diluent can also react with monomers to enter the curing system during curing. Therefore, after curing, the diluent will not migrate out during placement and use to endanger human health and pollute the environment and will not cause deterioration of the performance of the paint film.

3. **Stabilizers and other additives**

In addition to the above main components, stabilizers should be added to the curing system to prevent oxidation and aging of oligomers and monomers during irradiation. The cured paint film will be degraded under the action of acid, alkali, salt, organic solvent, heat, sunlight, etc. In order to improve the rigidity of the paint film in some formulas, it is required to add inorganic fillers such as TiO_2, Fe_3O_4, $CaCO_3$, etc. in the components. To obtain different colors of paint films, various pigments or pigment master batches can be added to the components. In this way, a relatively complete radiation curing material formula is formed.

4. **Curing process**

The process of radiation curing is relatively simple compared with thermal curing, but it is more efficient and environmentally friendly. The main process is shown in Fig. 5.21. Each step can adopt the continuous automatic process, which can realize the whole-process control by computer with controllable and adjustable parameters.

The curing parameters of a typical formula system of radiation curing such as unsaturated polyester, require an irradiation dose of 10–100 kGy. Polytetramethylene glycol dimercaptoacetate and acetyl triallyl citrate started to gel after irradiation for 0.7 h at 10^3 Gy/h. After 3 h, curing will be basically completed. If irradiation is continued, little gel will be produced.

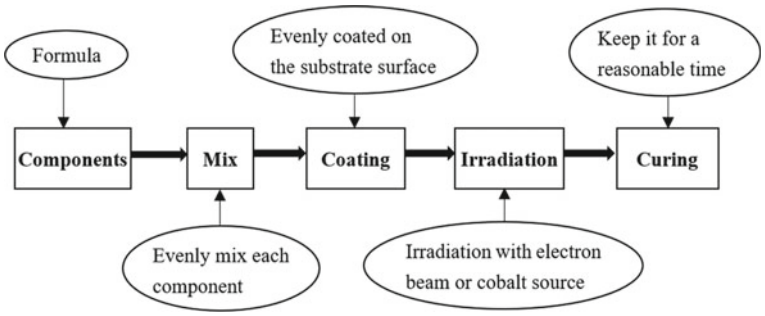


Fig. 5.21 Process diagram of electron beam or cobalt source radiation curing

5.6.3 Application of Radiation Curing

With the development of material formulation chemistry, radiation curing has gradually replaced traditional thermal curing in some fields, and its application is more and more extensive. The surface treatment of high-quality paper and wood has become the main direction of radiation curing. For example, the paper used for packaging can realize radiation curing of the double-sided coating. After radiation curing, it has low permeability, few chemical residues, low odor, and non-pollution, and it can also kill bacteria under the action of radiation. These advantages are particularly critical to the packaging of food and cosmetics. The radiation curing technology of wood plastic composite can improve the strength and quality of wood, and transform low-quality wood into high-quality wood, which is a key technology for the wood industry. For example, the inferior wood is digested with solvent, dried, and immersed in the radiation curing formula system composed of monomers, diluents, and additives, so that the monomers are filled with wood holes or infiltrated into wood fiber tissue for radiation. After solidification, low-quality wood becomes high-quality wood, the quality and luster of wood can be improved, the application of wood can be expanded, and the service life of wood products can be extended. In addition, it can save a lot of wood, which is conducive to the protection of natural resources such as forests. Radiation curing focuses on realizing that organic monomers such as styrene, acrylonitrile, acrylate, etc. can enter the defects, holes, or fiber tissues inside the wood evenly, effectively, and repidly.

Radiation curing can be used to prepare adhesives, such as pressure-sensitive adhesives and laminated adhesives, which can significantly improve the performance of adhesives. The magnetic medium adopts radiation curing to accurately bond small oxide particles on the surface, improving the efficiency of magnetic recording. The radiation curing of optical fiber coating effectively reduces the loss of light in the transmission process and has been widely used in the optical fiber manufacturing industry.

Electron beam radiation curing in the automotive industry is more widely used, such as the use of carbon fiber impregnated monomer zwitterionic, X-ray radiation

curing preparation of high-strength automotive fenders, radiation curing of car paint, and the use of electron beam radiation curing technology on the surface of automotive parts, which achieves rapid pollution-free production and provides high-quality products.

The optimization of material formulas and the popularization of low-cost compact low-energy electron accelerators capable of emitting curtain electron beams are the main technical bottlenecks in the development of radiation curing. In the formula of materials, it is required to focus on solving the problems of toxicity of each component and release of irritating gas, the ability to cure in an air atmosphere (currently, electron beam curing is generally carried out in a nitrogen atmosphere to reduce or eliminate the inhibition of oxygen), reducing radiation dose, improving the adhesion of the coating to base materials (such as metals, plastics, etc.), and realizing radiation curing of various special-shaped structural parts.

The direction of radiation technology development is currently focused on the environment and energy, such as natural polymers or biopolymers from waste that needs to be treated and transformed into products with greater application value. Radiation technology has also become a hot spot for research in marine plastic pollutant traceability, irradiation treatment, and ecosystem recycling. Besides, movable electron accelerators have become the focus of archaeological research on fragile and immovable cultural relics.

Exercise

1. What is radiation processing? What are the main types of rays used in industrial radiation processing (electron beam, γ-ray, X-ray, and UV light)?
2. What is the main mechanism of crosslinking of the linear polymer under the action of rays?
3. What are the ranges of radiation dose for the radiation crosslinking, radiation grafting, radiation degradation, and radiation curing?
4. Correctly write down the mechanism of preparing metal nanomaterials by radiation. Which step is the key reaction that affects the preparation of nanomaterials? Why?
5. What types of reactions are included in radiation curing?
6. In order to improve the wrinkle resistance of silk, 50 g silk is irradiated with a 10 kGy electron beam and placed in a 100 mL acrylonitrile (molecular weight is about 67) solution for grafting. $k_1 = 3 \times 10^{-3}$ mol/s, $k_2 = 5 \times 10^{-1}$ mol/mL/s. The free radical formed by every 100 Gy irradiation is 1, and it reacts for 30 min at room temperature. Calculate the weight of the graft product.
7. Briefly describe the possible main reactions of the polycarbosilane precursor in the radiation process and thermal cracking process.
8. What are the four main processes of polyolefin/thiol/silicone radiation curing system? Please list them using chemical 1 equations.

Bibliography

Ai, K. K., Xin, L. H., & Zhou, R. M. (2003). Zai Shui He Yichun Tixi Zhong Yong Fushe Jishu Zhibei Nami ZnS Jingti [Preparation of ZnS nanocrystals in water and ethanol system by radiation technique]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 21*(1), 35–39.

Berejka, A. J., & Cleland, M. R. (2011). *Industrial radiation processing with electron beams and X-rays*. IAEA International Atomic Energy Agency (p. 115).

Biancolli, A. L. G., Barbosa, A. S., Kodama, Y., de Sousa, R. R., Lanfredi, A. J. C., Fonseca, F. C., Santiago, E. I., et al. (2021). Unveiling the influence of radiation-induced grafting methods on the properties of polyethylene-based anion-exchange membranes for alkaline fuel cells. *Journal of Power Sources*, 512. https://doi.org/10.1016/j.jpowsour.2021.230484

Biancolli, A. L. G., Bsoul-Haj, S., Douglin, J. C., Barbosa, A. S., de Sousa, R. R., Rodrigues, O., Santiago, E. I., et al. (2022). High-performance radiation grafted anion-exchange membranes for fuel cell applications: Effects of irradiation conditions on ETFE-based membranes properties. *Journal of Membrane Science*, 641. https://doi.org/10.1016/j.memsci.2021.119879

Caldera-Villalobos, M., Herrera-González, A. M., & del Pilar Carreón-Castro, M. (2021). Improving the adsorption capacity of *Opuntia ficus-indica* fruit peels by graft-copolymerization using gamma radiation. *Radiation Physics and Chemistry*, 189. https://doi.org/10.1016/j.radphyschem.2021.109653

Charlesby, A. (1960). Atomic radiation and polymers. *Pergamon*. https://doi.org/10.1016/c2013-0-07861-9

Deng, H., & Yang, J. H. (1998). Gaojuwu Fushe Jiezhi De Fazhan Ji Yingyong [Development and application of polymer radiation grafting]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 16*(2), 65–69.

Ge, X. W., Ni, Y. H., Liu, H. R., Ye, Q., Xu, X. L., & Zhang, Z. C. (2001). Yizhong Caiyong Fuzhao Mubanfa Zhibei Yingnamidai De Xinfangfa [A new method for the preparation of silver nanoribbons using irradiated template method]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 19*(2), 118–121.

Golubenko, D. V., Van der Bruggen, B., & Yaroslavtsev, A. B. (2021). Ion exchange membranes based on radiation-induced grafted functionalized polystyrene for high-performance reverse electrodialysis. *Journal of Power Sources*, 511. https://doi.org/10.1016/j.jpowsour.2021.230460

Gong, N. R., Liu, J. H., & Chang, D. H. (1999). Fushe Jiangjie Mianxianweisu De Yanjiu Xianzhuang [Current status of research on radiation degradation of cotton cellulose]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 22*(1).

Hu, J., & Wang, J. L. (2005). Lvfenlei Wuranwu De Fushe Jiangjie Yanjiu Jinzhan [Progress in the study of radiation degradation of chlorophenolic pollutants]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 23*(3), 135–139.

Imanian, Z., Hormozi, F., Torab-Mostaedi, M., & Asadollahzadeh, M. (2022). Highly selective adsorbent by gamma radiation-induced grafting of glycidyl methacrylate on polyacrylonitrile/polyurethane nanofiber: Evaluation of CO_2 capture. *Separation and Purification Technology*, 289. https://doi.org/10.1016/j.seppur.2022.120749

Kang, B., Qi, Z. Q., Wu, Y. J., Tang, X. B., Chang, S. Q., Zhang, P. G., Fang, M. H., & Dai, Y. D. (2006). Γfushe Jiangjiefa Zhibei Xiaofenzi Shuirongxing Kejutang [Preparation of small-molecule water-soluble chitosan by γ-radiation degradation]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 24*(2), 83–86.

Li, W., Wang, W. F., Qian, S. P., & Yao, S. D. (2002). Nami JuN-yibingji Bingxixianan Weiningjiao De Guang Yinfa Juhe [Photoinitiated polymerization of nano-poly-N-isopropylacrylamide microgels]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 20*(2), 118–122.

Liu, Y. P., Zhang, M. W., Qian, Y. T., & Wang, C. S. (1997). Fushe Huaxue Hecheng Nami Cailiao De Yanjiu Jinzhan He Zhanwang [Research progress and prospect of synthesis of nanomaterials by radiation chemistry]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 15*(4), 8.

Shafiq, M., Hussain, S. N., Sabir, A., Wasim, M., Khan, S. M., & Khan, R. U. (2021). Radiation grafting of vapour grown carbon nanofibers on cellulose acetate/halloysite nanotubes matrix

membrane for $MgSO_4$ rejection. *Journal of Environmental Chemical Engineering, 9*(6). https://doi.org/10.1016/j.jece.2021.106804

Torkaman, R., Maleki, F., Gholami, M., Torab-Mostaedi, M., & Asadollahzadeh, M. (2021, December 1). Assessing the radiation-induced graft polymeric adsorbents with emphasis on heavy metals removing: A systematic literature review. *Journal of Water Process Engineering*. https://doi.org/10.1016/j.jwpe.2021.102371

Ueki, Y., Seko, N., & Maekawa, Y. (2021). Machine learning approach for prediction of the grafting yield in radiation-induced graft polymerization. *Applied Materials Today*, 25. https://doi.org/10.1016/j.apmt.2021.101158

Valencia-May, E. G., Rivera, E., Novelo-Peralta, O., & Burillo, G. (2022). Comparative analysis of two hydrogel architectures synthesized by gamma radiation based on dimethylacrylamide and acrylic acid grafted on polyethylene. *Radiation Physics and Chemistry*, 194. https://doi.org/10.1016/j.radphyschem.2022.109975

Wang, M., Yang, R. Y., Zhu, Z. Y., & Wang, W. F. (2005a). 4-Lvfen De γshexian Fuzhao Jiangjie Yanjiu [Study on the degradation of 4-chlorophenol by gamma irradiation]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 23*(1), 19–24.

Wang, S. L., Zhang, Z., Li, M., Sun, X. Y., Li, W. Z., Ni, Y. M., Wang, W. F., & Yao, S. D. (2004). Shuixiang Zhong Kuilin De Fujie Jili Yanjiu [Study on the radiation degradation mechanism of quinoline in aqueous phase]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 22*(6), 334–338.

Wang, S. L., Zhu, D. Z., Sun, X. Y., Li, W. Z., Zeng, K. L., Ni, Y. M., Wang, W. F., & Yao, S. D. (2005b). 4-Lvfen De Fushe Jiangjie Jili Yanjiu [Study on the mechanism of radiation degradation of 4-chlorophenol]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 23*(2), 70–71.

Xu, Y. S., Fu, Y. B., Song, Y. C., & Huang, R. L. (1999). Qifen dui γShexian Fuzhao Jutan Guiwan Taoci Xianqusi De Huaxue Jiegou He Rejie Texing De Yingxiang [Effect of atmosphere on the chemical structure and pyrolytic properties of γ-ray irradiated polycarbosilane ceramic precursor filaments]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 17*(3), 145–150.

Yin, Y. D., Xu, X. L., Ge, X. W., Wu, H. K., & Zhang, Z. C. (1999). Xianweizhuang Nami Niefen De γShexian Fushe Hecheng [γ-ray radiation synthesis of fibrous nickel nanopowders]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 17*(1), 19–23.

Zhang, H. M., Li, X. R., Yang, K. B., Xiong, R. L., Chen, C., & Xu, J. J. (1999a). Dianzishu Fuzhao Dui Nilong610 Xingneng De Yingxiang [Effect of electron beam irradiation on the properties of nylon 610]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 17*(4), 249–251.

Zhang, H. M., Liu, G. Y., Chen, C., Lu, T., Chen, T. X., & Liu, G. L. (1998). Fushe Jiaolian CB/EVA Daodian Fuhewu Reyang Wending Yanjiu [Thermal and oxygen stabilization study of radiation cross-linked CB/EVA conductive complexes]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 16*(2), 80–83.

Zhang, H. M., Luo, S. Z., Zhao, P. J., Li, H. Q., & Luo, M. R. (1995). Naiwen Baoqixing Rerongjiao De Yanzhi [Development of temperature-resistant and gas-preserving hot melt adhesive]. *Zhongguo Jiaonianji, 4*(4), 10–12.

Zhang, H. M., Yang, K. B., Xiong, R. L., Chen, C., Xu, J. J., & Li, X. R. (1999b). Luhuatong Dui Nilong610 Fushe Xiaoying De Yingxiang [Effect of copper halide on the radiation effect of nylon 610]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao, 17*(3), 156–158.

Zhang, H. M., Yang, K. B., Xu, J. J., & Li, X. R. (2000). Boli Xianwei Tianchong Nilong610 De Fushe Xiaoying [Radiation effects of glass-filled nylon 610]. *Xiandai Suliao Jiagong Yingyong, 12*(1), 18–19.

Zhao, W. Y., & Pan, X. M. (2003). *Fushe Jiagong Jishu Jiqi Yingyong: Gaojishu Lvse Jiagong Chanye* [Radiation processing technology and its applications: high tech green processing industry]. Bingqi Gongye Chubanshe.

Chapter 6
Application of Nuclear Technology in Medicine



Medicine is one of the important areas of nuclear technology application. More than 80% of the radioisotopes produced in the world are used in medicine. The application of nuclear technology for preventing, diagnosing, and treating diseases has formed an important part of modern medicine—nuclear medicine.

Nuclear medicine is a discipline that uses nuclides (radionuclides and stable nuclides)-labeled tracers for medical (diagnosis and therapy) and biological (in vivo and in vitro) research purposes, and its development can be traced back to the late nineteenth century. Roentgen's discovery of X-rays in 1895 began the rapidly expanding uses of radiation and radioactivity in medicine. Becquerel discovered radioactivity the following year, and Marie Curie coined the term "radioactivity" shortly thereafter. These pioneers laid the groundwork for scientific principles that now take for granted, such as atomic structure. The first few decades of the twentieth century were a hotbed of discoveries, including artificial radioactivity by Irène and Frédéric Joliot-Curie and the invention of the cyclotron by Lawrence, leading to the production of radionuclides for medical applications (e.g. ^{131}I, ^{99m}Tc). De Hevesy presented the "radiotracer principle", which states that radiopharmaceuticals can participate in biological processes but do not alter or perturb them. Kamon and Rubin's discovery of ^{14}C was critical for its role in life science research. After World War II, nuclear science research used for destruction was quickly channeled into medicine. ^{131}I was successfully applied to treat Graves' disease and thyroid cancer. The ^{99}Mo/^{99m}Tc generator was developed by scientists at Brookhaven National Laboratory. The invention of the gamma camera, single-photon emission computed tomography (SPECT), and positron emission tomography (PET) instrumentation boomed from the 1950s to the 1970s. Fluorine-18-labeled 2-deoxy-2-[^{18}F]fluoro-D-glucose (or [^{18}F]FDG) was approved by the U.S. Food and Drug Administration (FDA) in 1999 and is now the primary tracer for PET scans throughout the world. As of June 2022, FDA has approved a total of 60 radiopharmaceuticals, including 20 drugs for positron diagnostic, 28 drugs for single-photon diagnostic, and 12 drugs for

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6_6

radiotherapy. Novel research in developing instrumentation, radionuclide production, radiochemistry strategies, and radiotracers continues in the quest to improve human health.

In addition to the creation of radionuclides, the development of imaging instrumentation was essential for the expansion of nuclear medicine. In the second half of the twentieth century, the rapid development of electronics technology, computer technology, and image reconstruction technology provided strong technical support for the development of nuclear medicine. The invention and continuous improvement of the gamma camera and emission computed tomography imaging have made nuclear medicine enter a period of rapid development.

With the development of computer technology, the image fusion technology of CT, MRI, and ECT have been developed, which can integrate the information obtained from various imaging technologies to accurately determine the size range of lesions and their relationship with surrounding tissues, to obtain functional parameter maps with more physiological significance. Nuclear medicine has a unique advantage in the clinical diagnosis of diseases. In the future, the development of nuclear medicine still depends on the development of imaging technology, radionuclides, radiopharmaceuticals, molecular biology, etc.

6.1 Medical Radionuclides

Radiopharmaceuticals are a group of pharmaceutical drugs/medicinal formulations containing radioisotopes that are used as diagnostics and therapeutic agents.

The selection of radionuclides depends on both their application and the target vector. According to different ways of applications, radiopharmaceuticals can be divided into two categories: in vitro and in vivo agents. The former is analytical agents used in radioimmunoassay (RIA), immunoradioassay (IRMA), radioreceptor assay (RRA), radioligand binding assay (RBA), etc. The latter is used to diagnose certain medical problems through the biodistribution and metabolism of radiotracers in a patient's body, or treat certain diseases via radionuclide radiation.

6.1.1 Radionuclides for Diagnosis

The radionuclide for SPECT imaging should preferably emit only monoenergetic γ-rays and no charged particles. This is because the charged particles add unnecessary internal exposure to the patient without contributing to the imaging. The energy of γ-ray is preferably between 100 and 300 keV. The energy loss increases throughout the body with too low energy, while the thickness of the collimator needs to be increased with too high energy.

The radionuclides for PET imaging are best to emit only β^+-particles and no γ-rays because the latter increases the occasional conformance count and decreases

the signal-to-noise ratio. The half-life of this type of nuclide is preferably 10 s to 80 h. Nuclides with too short half-lives cannot be carried to the target by the carrier before they decay rapidly. If its half-life is too long, the high radioactivity remaining in the body causes additional irradiation to the patient after imaging. Nuclides with a suitable half-life can be sufficient to acquire enough data in a short period and decay quickly, which is conducive to obtaining a high-quality image.

The ideal medical radionuclide should be an isotope of the main constituent elements (such as C, H, N, O, S, P, etc.) or similar elements (such as F, Cl, Br, I, and other halogens replacing H) in the organism. However, few such radionuclides can be found. For medical metal radionuclides, it is required to form thermodynamically stable or dynamically inert complexes with the carrier molecules. In addition, medical radionuclides should be readily available, inexpensive, and easily made into preparations with a highly specific activity. Some radionuclides suitable for SPECT and PET imaging are listed in Tables 6.1 and 6.2, respectively.

Considering various factors, ^{99m}Tc is the preferred nuclide for SPECT imaging. Currently, ^{99m}Tc labeled radiopharmaceuticals accounted for 80% of all radiopharmaceuticals. ^{18}F is the optimal nuclide for PET imaging, and its representative drug is ^{18}F-FDG.

Table 6.1 Radionuclides suitable for SPECT imaging and their production methods

Radionuclide	$T_{1/2}$	Decay mode	Primary ray energy /keV	Production mode
^{67}Ga	3.261 d	EC	93.311 (39.2)	^{67}Zn (p, n), ^{66}Zn (d, n)
^{99m}Tc	6.008 h	IT	140.511 (88.5)	^{99}Mo (β^-)
^{111}In	2.805 d	EC	245.4 (94.09)	^{111}Cd (p, n), ^{109}Ag (α, 2n)
^{123}I	13.27 h	EC	158.97 (83.3)	^{123}Te (p, n), ^{121}Sb (α, 2n)
^{125}I	59.41 d	EC	35.4919 (6.67)	^{124}Xe (n, γ), ^{123}Sb (α, 2n)
^{201}Tl	72.91 h	EC	167.43 (10.0)	Hg (d, x), ^{203}Tl (p, 3n), ^{201}Pb (EC)

Table 6.2 Radionuclides suitable for PET imaging and their production methods

Radionuclide	$T_{1/2}$/min	Primary ray energy/keV	Production mode
^{11}C	20.39	511 (≤199.52)	^{14}N (p, α), ^{10}B (d, n)
^{13}N	9.965	511 (≤199.84)	^{16o} (p, α), ^{10}B (α, n)
^{15}O	2.037	511 (≤199.8)	^{14}N (d, n), ^{16o} (^{3}He, α)
^{18}F	109.77	511 (≤193.46)	^{18o} (p, n), ^{20}Ne (d, α)
^{62}Cu	9.67	511 (≤194.86)	^{62}Ni (p, n), ^{62}Zn (EC)
^{68}Ga	67.629	511 (≤178.2)	^{68}Zn (p, n), ^{68}Ge (EC)
^{82}Rb	1.273	511 (≤190.94)	^{85}Rb (p, 4n), ^{82}Sr (EC)

6.1.2 Therapeutic Radionuclides

Radionuclides suitable for treatment should meet the following requirements:

(a) Only α, β, and Auger electrons are emitted;
(b) No or only a small amount of weak γ-rays are emitted;
(c) Half-life ranges from several hours to dozens of days;
(d) Daughter nuclides are stable;
(e) Radioactive agents with high specific activity can be obtained.

Linear energy transfer (**LET**) is the average (radiation) energy deposited per unit path length along the track of an ionizing particle, with the unit of keV/μm. High LET is a typical characteristic of high ionizing radiation, indicating dense deposition of energy and great biological and chemical damage to biological tissues. The range of LET and the action of particles in biological tissues is related to the types of radionuclides and are greatly affected by decay types and energies. The significant differences in mass, energy, and charge among β-particles, α-particles, and Auger electrons lead to markedly different consequences when they interact with biological tissues. The LET of β-particles is about 0.2 keV/μm, and its emission range in biological tissues is 1.5–19 mm, about 500–1000 cell diameter. The LET of α-particles is about 50–230 keV/μm, and its range in biological tissues is about 16–75 μm, about 2–10 cell diameter. The LET of Auger electrons is 10–25 keV/μm, and its range in biological tissue is 1–10 nm, which is close to that of α-particle and belongs to high LET.

If a radiopharmaceutical can selectively enter a tumor cell, the α-particles and Auger electrons emitted by it can kill the tumor cells. In addition, α-particles also cause additional damage to proximal or distal tumor cells through radiation-induced bystander effects. However, compared with long-range β-particles, α-particles have a smaller bystander effect and less indirect damage to normal cells in the nearby tumor microenvironment, suggesting lower toxicity. Table 6.3 lists the radionuclides currently considered suitable for the treatment of tumors (Fig. 6.1).

6.2 Diagnostic Radiopharmaceuticals

In the past few decades, with the development of radiopharmaceutical chemistry and nuclear medicine, a batch of radiopharmaceuticals with excellent performance has been screened from thousands of synthesized radiolabeled compounds and used for imaging. So far, suitable imaging agents are available for almost all organs in the body.

Table 6.3 Radionuclides suitable for the treatment of tumors and their production methods

Radionuclide	$T_{1/2}$	Decay mode	Primary ray energy/keV	Production mode
^{32}P	14.262 d	β^-	1710.3 (100.0)	^{31}P (n, γ); ^{32}S (n, p)
^{35}S	87.38 d	β^-	166.84 (100.0)	^{34}S (n, γ); ^{35}Cl (n, p)
^{67}Cu	2.58 d	β^-	391 (57.0); 483 (22.0); 576 (20.0)	^{67}Zn (n, p); ^{68}Zn (γ, p); ^{70}Zn (p, α); ^{68}Zn (p, 2p)
^{89}Sr	50.53 d	β^-	1495.1 (99.99)	^{88}Sr (n, γ); ^{89}Y (n, p)
^{90}Y	2.667 d	β^-	2280.1 (99.99)	^{90}Sr (β^-); ^{89}Y (n, γ)
^{109}Pd	13.701 h	β^-	1027.9 (99.9)	^{108}Pd (n, γ)
^{114}In	71.9 s	β^-	1988.7 (99.36)	^{113}In (n, γ)
^{131}I	8.0207 d	β^-	606.3 (89.9)	^{131}Te (β^-)
^{153}Sm	46.284 h	β^-	635.3 (32.2); 808.2 (17.5)	^{152}Sm (n, γ)
^{161}Tb	6.88 d	β^-	517.5 (66); 460.3 (26.0)	^{160}Gd (n, γ); ^{161}Gd (d, x)
^{165}Dy	2.334 h	β^-	1286.7 (83.0)	^{164}Dy (n, γ)
^{166}Ho	26.763 h	β^-	1853.9 (50.0); 1773.3 (48.7)	^{165}Ho (n, γ)
^{169}Er	9.40 d	β^-	350.9 (55); 342.5 (45)	^{168}Er (n, γ)
^{177}Lu	6.734 d	β^-	497.8 (78.6)	^{176}Lu (n, γ); ^{176}Yb (n, γ); ^{177}Yb (β^-)
^{188}Re	17.005 h	β^-	2120.4 (71.1)	^{187}Re (n, γ); ^{188}W (β^-)
^{186}Re	3.7183 d	β^-	1069.5 (70.99)	^{185}Re (n, γ); ^{186}W (p, n); ^{186}W (d, 2n)
^{198}Au	2.695 17 h	β^-	960.6 (98.99)	^{197}Au (n, γ)
^{211}At	7.214 h	A; EC	5869.5 (41.8)	^{209}Bi (α, 2n)
^{212}Bi	60.55 min	β^-; α	2248 (55.46); 6050.78 (25.13)	^{208}Pb (^{18}O, ^{14}N)
^{213}Bi	45.59 min	β^-; α	1422 (65.9); 5869 (1.94)	^{213}Pb (β^-)
^{223}Ra	11.4 d	α	5716.23 (52.6); 5606.73 (25.7)	^{226}Ra (n, γ); ^{227}Ra (β^{-227}); Ac (β^-)

(continued)

Table 6.3 (continued)

Radionuclide	$T_{1/2}$	Decay mode	Primary ray energy/keV	Production mode
^{225}Ac	10.0 d	β^-; α	5830 (50.7); 5793.1 (18.3)	^{226}Ra (d, 2n); ^{232}Th (p, x)
^{227}Th	18.72 d	α	6038.01 (24.2); 5977.72 (23.5); 5756.87 (20.4)	^{227}Ac (β^-)

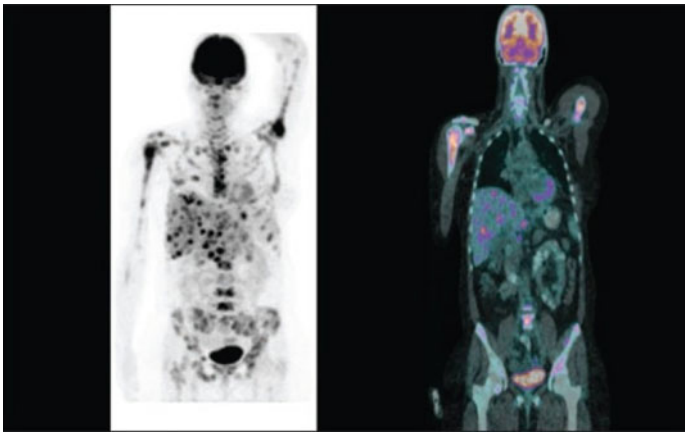


Fig. 6.1 MIP image (left panel) and coronal fused images (right panel) of ^{18}F-FDG PET/CT showed extensive hepatic and bony metastases

6.2.1 Cardiovascular Imaging Agents

1. **Myocardial perfusion imaging agents**

Myocardial perfusion imaging is a plane or tomographic imaging of the myocardium using a gamma camera or SPECT. The principle is to use the mechanism by which normal or functional cardiomyocytes can selectively take up certain metal ions or nuclide-labeled compounds. The functional myocardium is visualized, while the necrotic myocardium and ischemic myocardium cannot be visualized (defective) or the image is faded (sparse), to achieve the purpose of diagnosing myocardial disease and understanding the myocardial blood supply. Clinically, myocardial perfusion imaging is used for the early diagnosis of myocardial ischemia in coronary heart disease, the diagnosis of myocardial infarction and cardiomyopathy, and the assessment of myocardial viability.

The ideal myocardial imaging agent should meet the following requirements:

(a) Higher myocardial uptake and longer residence time;
(b) Fast blood clearance and high heart/liver, heart/blood, and heart/lung ratios;

(c) Myocardial uptake proportional to myocardial blood flow;
(d) Myocardial redistribution characteristics.

There are many drugs currently used for myocardial perfusion imaging. Two categories of agents are commonly used. One is single photon emission imaging agents, such as ^{201}TlCl, ^{99m}Tc-MIBI, ^{99m}Tc-TEBO, ^{99m}Tc-P_{53}, ^{99m}Tc-Q_{12}, and ^{99m}Tc-NOET (Table 6.4, Fig. 6.2), the other is myocardial perfusion imaging drugs for positron emission imaging, such as ^{13}N-NH_3, ^{15}O-H_2O, ^{82}Rb, etc.

Since its radius is similar to K^+, $^{201}Tl^+$ can participate in the active transport system of Na^+/K^+-ATPase and be concentrated in the myocardium. A significant advantage of $^{201}Tl^+$ is redistributable. The exercise load delayed imaging method was used. The patients are asked to exercise first and then be injected with ^{201}TlCl. The early and delayed imaging was performed at 10 min and 3 h, respectively. The perfusion

Table 6.4 Main characteristics of several SPECT myocardial perfusion imaging agents

Imaging agent	^{210}TlCl	^{99m}Tc-MIBI	^{99m}Tc-TEBO	^{99m}Tc-P_{53}	^{99m}Tc-Q_{12}	^{99m}Tc-NOET
Structural formula	–	I	II	III	IV	V
Metal oxidation state	+ I	+ I	+ III	+ V	+ III	+ V
Myocardial uptake	3–4%	1–2%	1–3.4%	0.8–1.3%	1.0–2.6%	3–5%
Redistribution	Y	N	N	N	N	Y
Uptake mechanism	Na^+/K^+ pump	Passive diffusion	Passive diffusion	Passive diffusion	Passive diffusion	Inconclusive
Imaging time	10 min, 3 h	1 h	2 min	15 min	30 min	30 min, 3.5 h

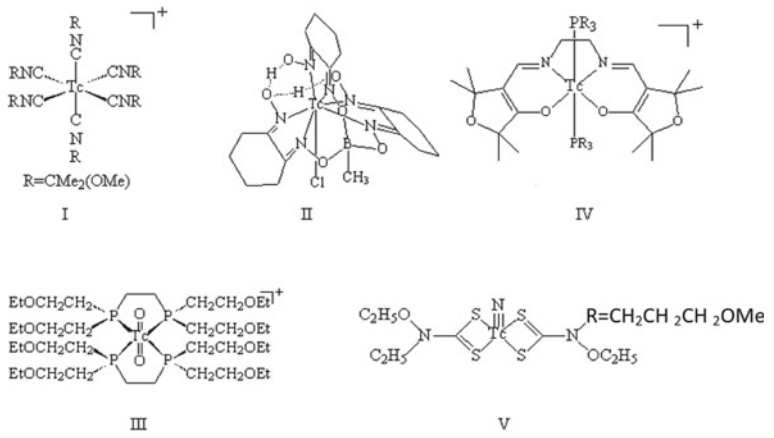


Fig. 6.2 Structural formulae for myocardial perfusion visualizers in Table 6.4

of ischemic myocardium during exercise is worse than that of normal myocardium, manifested as radioactive sparseness or defects. After 3 h, $^{201}Tl^{+}$ entered the original ischemic myocardium with blood perfusion and showed normal distribution in the image. This property of $^{201}Tl^{+}$ is redistribution. Differences between ischemic myocardium and normal myocardium are observed even in the resting imaging modality but are not as clear as in the previous method.

In the images acquired 10 min after injection, the former showed radioactive sparse or defective. After 3 h, the former differs very little from the latter, after which the clearance of ischemic myocardium is slower than that of normal myocardium. The disadvantage of ^{201}Tl is that the energy of γ-rays is low, the half-life is long, and the price is high.

^{99m}Tc-MIBI (^{99m}Tc-sestamibi) is currently the most widely used myocardial perfusion imaging agent. And its sensitivity and specificity for the diagnosis of coronary heart disease can be compared with ^{201}TlCl. The imaging agent can also be used to determine myocardial function using the first-pass method or the gating circuit method. The disadvantage is that there is no redistribution and it needs to be visualized in the resting and motion states, respectively. In addition, due to high hepatic absorption and slow clearance, a fatty meal is required after the injection of the drug to facilitate drug excretion from the hepatobiliary system. $[^{99m}Tc(CO)_3(MIBI)_3]+$ retains the advantages of ^{99m}Tc-MIBI. The results of animal experiments show that the heart/liver and heart/lung ratios are significantly improved, which is expected to be used in clinical.

^{99m}Tc-TEBO is a BATO complex, which is rapidly absorbed and cleared from the myocardium. Therefore, imaging must be started 2 min after injection. To acquire sufficient data in a short time, multi-probe SPECT is required.

^{99m}Tc-P_{53} (^{99m}Tc-tetrofosmin) is a complex containing $[TcO_2]^{+}$ core. It can be prepared at ambient temperature for easy hospital application. Meanwhile, it has good myocardial uptake and retention properties and can be rapidly cleared from the liver, lungs, and blood, which has been applied clinically. Figure 6.3 is an example of ^{99m}Tc-P53 myocardial tomographic imaging.

^{99m}Tc-Q_{12} (^{99m}Tc-furifosmin) is a Tc(III) complex, its coordination polyhedron is a quadrangular bipyramid. Due to the stabilization effect of the two trimethoxypropyl groups in the axial direction, the complex has good stability in vivo, fast myocardial uptake, and a long retention time. Moreover, it can be quickly cleared from the blood, liver, and lungs.

^{99m}Tc-NOET is a complex containing a $[Tc{\equiv}N]^{2+}$ core with redistribution properties. $[Tc{\equiv}N]^{2+}$ core intermediates are usually prepared by reacting $^{99m}TcO_4^{-}$, methyl hydrazinodithiocarboxylate (providing N), sodium tris-p-sulfonate phenylphosphine or $SnCl_2$, and sodium ethyl ethoxysulfonate. $[Tc{\equiv}N]^{2+}$ core complexes are more stable to hydrolysis and redox reactions than that of $[Tc=O]^{3+}$ core complexes. One of the characteristics of this imaging agent is the high rate of myocardial uptake, but the mechanism of uptake is still unclear.

After injection of positron emission imaging agents such as ^{13}N-NH_3, ^{15}O-H_2O, and ^{82}Rb, PET should be used for tomographic imaging. It is mainly used in conjunction with myocardial glucose metabolism imaging to understand the matching of

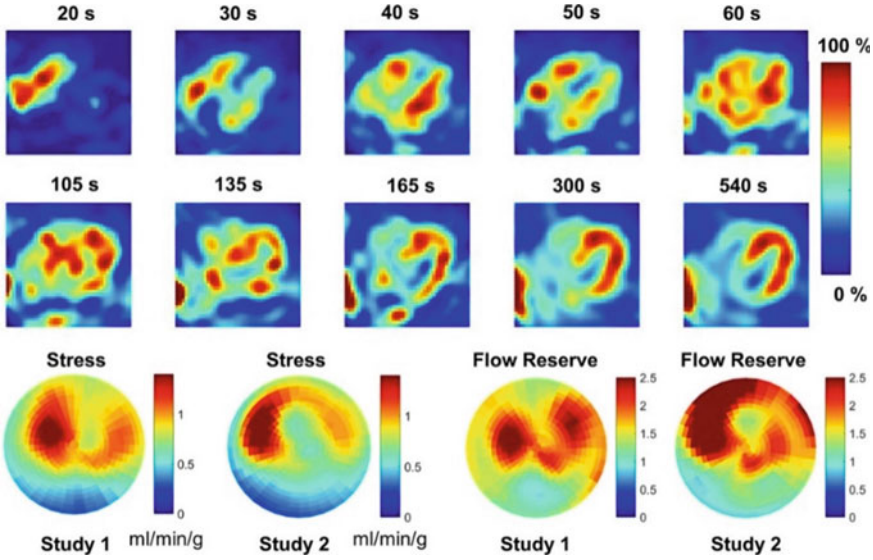


Fig. 6.3 ^{99m}Tc-tetrofosmin myocardial tomographic image

blood perfusion and metabolism to determine the activity of myocardial cells in the lesion area.

^{13}N is produced by a cyclotron with a half-life ($T_{1/2}$) of 10 min. ^{13}N-NH_3 is carried into myocardial cells by free diffusion, and its uptake rate in the first passage in the myocardium is close to 100%. ^{13}N-NH_3 is involved in cellular metabolism and can be converted into glutamate or glutamine under the action of glutamine synthase, but the first-pass uptake rate is not affected by metabolism. PET myocardial perfusion imaging was performed 3 min after intravenous injection of ^{13}N-NH_3.

^{15}O-H_2O is a cyclotron-produced imaging agent with a half-life of 2 min. With a blood flow of 80–100 mL/100 mg/min, the yield of first-pass uptake was 96%. Myocardial uptake of ^{15}O-H_2O is positively correlated with coronary blood flow. Its disadvantage is that the half-life is very short and the technical requirements are high.

^{82}Rb is produced by the ^{82}Sr/^{82}Rb generator. The half-life ($T_{1/2}$) of ^{82}Sr is 25 d, and it decays into ^{82}Rb by electron capture. The uptake mechanism of ^{82}Rb by the myocardium is similar to that of potassium ions, and it is actively transferred into cells through Na^+-K^+-ATPase. Under normal conditions, the initial uptake rate of ^{82}Rb by cardiomyocytes is 65–70%.

2. **Myocardial hypoxia imaging agents**

Due to insufficient blood supply to the myocardium, some of the myocardium will be in a state of hypoxia. If the patient is not treated promptly, it may lead to myocardial necrosis. Currently, clinical approaches such as thrombolysis, angioplasty, or reconstruction techniques can reduce mortality and improve prognosis. Therefore, it

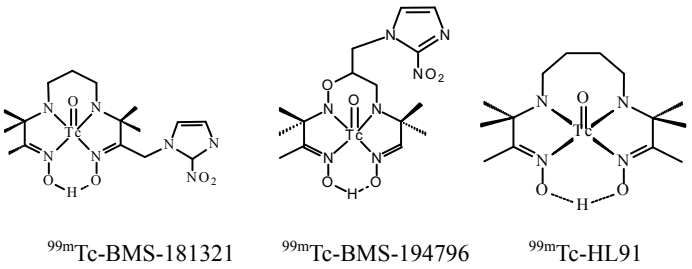


Fig. 6.4 Structural formulae of several myocardial hypoxia imaging agents

is important to distinguish between myocardial ischemia and necrosis before cardiac "bypass" surgery.

After the hypoxic imaging agent is taken up by ischemic cells, it can be catalyzed and reduced by xanthine oxidase under hypoxic conditions and retained in hypoxic cells. Under normal oxygen supply conditions, it will not be reduced, so it is difficult to stay in normal cardiomyocytes. However, necrotic cells have no uptake function for imaging agents. Thus, hypoxic imaging agents can differentiate between normal, ischemic, and necrotic myocardium. Currently, ^{99m}Tc-BMS-181321, ^{99m}Tc-BMS-194796, and ^{99m}Tc-HL91 are considered good hypoxic imaging agents, and their structures are shown in Fig. 6.4.

3. **Cardiac metabolism imaging agents**

The energy of the myocardium mainly comes from the metabolism of fatty acids, so radionuclide-labeled fatty acids can be used for imaging myocardial metabolic function. Myocardial metabolism imaging agents are mainly used for the diagnosis of myocardial injury and myocardial ischemia and the distinction between myocardial ischemia and myocardial necrosis.

The myocardial metabolism imaging agents labeled with ^{123}I include ^{123}I-IHA, ^{123}I-IPPA, ^{123}I-BMIPP, etc. Methods for indirect labeling of fatty acids with ^{99m}Tc via bifunctional chelators are under investigation. The myocardial metabolism imaging agents for PET imaging include ^{11}C-PA (^{11}C-palmitic acid) and ^{18}F-FDG.

4. **Cardiac blood pool imaging and cardiac function measurement**

Generally speaking, ^{99m}Tc-RBC and ^{99m}Tc-HAS are used as imaging agents of the heart blood pool. In cardiovascular dynamic imaging, the imaging agent is injected into the vein of the subject in the form of a "bolus". Then the gamma camera is used to continuously collect data for 20 s to obtain a dynamic image of the imaging agent passing through the heart and great vessels for the first time with the blood flow. Ventricular function parameters, such as left and right ventricular ejection fraction, peak ejection rate, etc., can be obtained. These data can be used to understand the location and shape of the heart and great vessels, as well as information on whether the circulation channels and circulation sequence are normal. This has clinical value for the diagnosis of congenital heart disease, left ventricular aneurysm and

large aneurysm, superior vena cava occlusion syndrome, and evaluation of valvular regurgitation.

In cardiac blood pool imaging, imaging agents are injected intravenously into blood vessels. After the imaging agent is evenly mixed with the blood, the R wave of the patient's electrocardiogram is used as the start and end signal of the data acquisition, and the image is repeatedly acquired during the R-R period. From the obtained images, systolic and diastolic functional indicators, ventricular volume load indicators, local ventricular wall motion, functional indicators, and phase and amplitude diagrams of contraction can be calculated. These indicators can be used clinically for the early diagnosis of coronary heart disease, the diagnosis of myocardial infarction and cardiomyopathy, and the evaluation of cardiac conduction and ventricular function.

5. **Thrombus imaging agent**

The formation of blood clots can lead to serious consequences such as myocardial infarction, angina pectoris, stroke, and sudden death. Therefore, thrombosis imaging agents are currently a research hotspot for radiopharmaceuticals.

Thrombosis is formed by the aggregation of intravascular fibrin, platelets, and red blood cells, and its formation process is regulated by fibrinogen. Fibrinogen binds to GP IIb/IIIa receptors through a matrix of the Arg-Gly-Asp (RGD) sequence in the polypeptide, and the RGD unit has a high affinity for the GPIIb/IIIa receptor antagonist DMP757. Therefore, thrombus imaging can be performed by labeling DMP757 with ^{99m}Tc. In addition, P280 and P748 are also GP IIb/IIIa receptor thrombus imaging agents, the former can be used for venous thrombosis imaging and has been used clinically, and the latter can be used for pulmonary embolism imaging research.

6.2.2 Brain Imaging Agent

1. **Cerebral perfusion imaging agent**

Cerebral perfusion imaging agents are mainly used to measure regional cerebral blood flow (rCBF). Therefore, the distribution of radiopharmaceuticals in the brain needs to be proportional to rCBF. This requires cerebral perfusion imaging agents to cross the blood–brain barrier (BBB) into the brain tissue. This requires that such imaging agent molecules meet the following five conditions: certain lipid solubility ($\log P = 0.5$–2.5, P is the distribution ratio of the drug between n-octanol and water), electric neutrality, molecular weight less than 500, a suitable residence time in the brain, and a definite regional distribution.

There are three possible retention mechanisms for cerebral perfusion imaging agents:

(a) ^{99m}Tc complexes bind to intracellular components, proteins, or other macromolecules;

(b) The neutral ^{99m}Tc complex is converted into a charged substance that cannot diffuse out of the cell;
(c) ^{99m}Tc complex is decomposed into other substances that cannot diffuse out of the cell.

However, it is not easy to determine the accurate retention mechanism of cerebral perfusion imaging agents.

The lipophilic ^{99m}Tc-D,L-hexamethylene-propylene amine oxime (^{99m}Tc-HMPAO, Certec®) was the first approved ^{99m}Tc-labeled cerebral perfusion imaging agent for clinical use. While its poor in vitro stability and low brain/blood ratio limit its applications, its analogs ^{99m}Tc-D,L-cyclobutylpropylene amine oxime (^{99m}Tc-CBPAO) has better in vitro stability and lipid solubility and improved performance.

^{99m}Tc-L,L-Ethyl cysteinate dimer (^{99m}Tc-L, L-ECD, Nurolite®) has high in vitro stability and lipid solubility. Its brain uptake and retention are relatively high, but the retention time is short. The retention mechanism of this compound in the brain is inferred to be the enzymatic hydrolysis of one of the two ethyl ester groups to a carboxylic acid, thereby changing the polarity, ester solubility, and charge state of the entire molecule. Since the enzymatic reaction is stereoselective, the D,D configuration has poorer retention properties than the L,L configuration. Since the brain retention properties of ^{99m}Tc-L,L-ECD are controlled by enzymatic hydrolysis, its brain retention is related to the concentration distribution of hydrolase, not entirely determined by rCBF.

The four coordinating atoms of $^{99m}TcO^{3+}$ of the aforementioned imaging agents are all on the same molecule (tetradentate ligand). If a tridentate ligand and a monodentate ligand are used together to replace the tetradentate ligand, i.e., a "3 + 1" hybrid design scheme, there will be more flexibility in changing the types of coordinating atoms and adjusting the structure of the ligand. The experimental results show that this approach is feasible, and it is possible to develop new brain imaging agents with excellent performance.

2. **Brain receptor imaging agents**

Receptors have a prominent role in brain function, as they are the effector sites of neurotransmission at the postsynaptic membrane. They have a regulatory role on presynaptic sites for transmitter reuptake and feedback and are modulating various functions on the cell membrane. The distribution, density, and activity of receptors in the brain can be visualized by radioligands labeled for SPECT and PET, and the receptor binding can be quantified by appropriate tracer kinetic models, which can be modified and simplified for particular applications. Selective radioligands are available for the various transmitter systems, by which the distribution of these receptors in the normal brain and changes in receptor binding during various physiologic activities or resulting from pathologic conditions can be visualized. Quantitative imaging for several receptors has gained clinical importance. For example, dopamine (D2) receptors for differential diagnosis of movement disorders and assessment of receptor occupancy by neuroleptics drugs; serotonin (5-hydroxytryptamine, 5-HT) receptors

and the 5-HT transporter in affective disorders and for assessment of activity of antidepressants; nicotinic receptors and acetylcholinesterase as markers of cognitive and memory impairment; central benzodiazepine-binding sites at the gamma-aminobutyric acid A (GABAA) receptor complex as markers of neuronal integrity in neurodegenerative disorders, epilepsy, and stroke and as the site of action of benzodiazepines; peripheral benzodiazepine receptors as indicators of inflammatory changes; opioid receptors detecting increased cortical excitability in focal epilepsy but also affected in the perception of and emotional response to pain; and several receptor systems affected in drug abuse and craving. Further studies of the various transmitter/receptor systems and their balance and infraction will improve the understanding of complex brain functions and will provide more insight into the pathophysiology of neurologic and psychiatric disease interaction.

(1) Dopamine System

Dopaminergic neurotransmission has a central role in many brain functions, which is necessary for proper movement coordination. Degeneration of the nigrostriatal dopamine system will lead to Parkinson's disease and is involved in multisystem atrophy. Pulsatile dopamine secretions elicit pleasant feelings and form a strong reward system that also appears to play a central role in drug abuse. The presynaptic nigrostriatal projection is the main location of the pathologic process in Parkinson's disease, therefore, the assessment of disturbed dopamine synthesis is the main target for clinical studies. Postsynaptic receptors may also be involved in neurodegenerative disorders. They are functionally changed in the course of Parkinson's disease and by the treatment with antiparkinson drugs. Besides, they also play an eminent role in schizophrenia and the effect of neuroleptics. There are 2 major dopamine receptor types (D1 and D2), and the 3 other types (D3, D4, and D5) detected in molecular genetic studies are related to these families—D3 and D4 are close to D2, and D5 is close to D1. Only D1 and D2 receptors have been imaged in humans, but the applied radioligands usually bind also to the other subtypes.

(2) Serotonin (5-Hydroxytryptamine, 5-HT) System

5-HT is the transmitter in the central nervous system involved in sleep, eating, sexual behavior, impulse control, circadian rhythm, and neuroendocrine function, and it is also the precursor of the hormone melatonin. Serotonergic neurotransmission is altered in many neurologic and psychiatric disorders, particularly in depression and compulsive disorders, as well as in Alzheimer's and Parkinson's disease, autism, and schizophrenia. There is great heterogeneity in the postsynaptic 5-HT receptors, which belong to 7 major classes and contain more than 16 subtypes. Suitable radioligands are only available for 5-HT_{1A} and 5-HT_{2A} receptors.

PET of the 5-HTT sites has been possible with ^{11}C-McN5652 (hexahydro-6-[4-(methylthio)phenyl]pyrrolo-[2,1-a]-isoquinoline), but reliable quantification was obtained only in areas with high receptor density (midbrain, thalamus, striatum). The 403U76 derivative ADAM exhibits high affinity and selectivity for 5-HTT, which is an excellent SPECT tracer for the visualization of 5-HTT in humans. ^{11}C-Labeled derivatives 3-amino-4-(2-dimethylaminomethylphenylsulfanyl)benzonitrile (DASP)

and *N,N*-dimethyl-2-(2-amino-4-methylphenylthio)benzylamine (MADAM) exhibit high affinity and selectivity for 5-HTT and have proven to be excellent PET tracers for visualization of 5-HTT in human brains.

(3) Cholinergic System

Acetylcholine receptors were originally divided into two main classes: nicotinic and muscarinic, and with multiple heterogeneous subtypes. Nicotinic receptors belong to the ligand-gated ion channels, and muscarinic receptors operate via several second messengers.

Nicotinic receptors have been implied in many psychiatric and neurologic diseases, including depression and cognitive and memory disorders, such as Alzheimer's and Parkinson's disease. Thus, ^{11}C-labeled nicotine was used to visualize and quantify nicotinic receptors in the brain. High binding was reported in several cortical and subcortical regions, and low density was found in the pons, cerebellum, occipital cortex, and white matter. Higher uptake was observed in smokers than in nonsmokers, indicating the increased density of nicotinic binding with chronic administration of nicotine. However, the high nonspecific binding and its rapid washout have limited the clinical application of this tracer. More specific ligands such as epibatidine and derivatives labeled with ^{11}C or ^{18}F showed high uptake in the thalamus and hypothalamus or midbrain, intermediate uptake in the neocortex and hippocampus, and low uptake in the cerebellum, which corresponds with the known distribution of nicotinic receptors.

(4) Gamma-Aminobutyricyric Acid (GABA) System

GABA is the most important inhibitory neurotransmitter. Its transmission is altered in epilepsy and is also altered in anxiety and other psychiatric disorders. Because the GABA receptor is abundant in the cortex and is very sensitive to damage, it represents a reliable marker of neuronal integrity (e.g., in ischemic brain damage and various neurodegenerative diseases). Part of the GABA receptor complex that gates the Cl^- channel is the central benzodiazepine receptor, which specifically mediates all pharmacologic properties of the benzodiazepines (sedative, anxiolytic, anticonvulsant, myorelaxant). The tracer most widely used for central benzodiazepine-binding sites is the antagonist flumazenil labeled with ^{11}C or ^{123}I.

As an antagonist of GABA, glutamate is the main excitatory neurotransmitter in the cortex, and alterations of glutamatergic neurotransmission are associated with many neurologic diseases. At higher concentrations, glutamate has neurotoxic potential and is involved in the cascade of neuronal damage in ischemia and degenerative disorders. So far, the tracers used to study this system (^{11}C-MK 801, ^{18}F-fluoroethyl-TCP, ^{11}C-ketamine, and ^{18}F-memantine) have only a low specificity to the NMDA receptor, and relevance for clinical studies has not been established.

(5) Adenosine Receptors

The adenosine receptors (A1 and A2A) play a role in neuromodulation and are functionally altered in epilepsy, stroke, movement disorders, and schizophrenia. The labeled xanthine analogs ^{18}F-CPFPX and ^{11}C-MPDX are ligands for the A1 receptor,

which shows high density in the putamen and mediodorsal thalamus, intermediate density in most cortical regions, and low density in the midbrain, brain stem, and cerebellum. The A2A receptors have also been visualized recently in the human brain. These tracers might have the potential for predicting severe tissue damage in the early stages of ischemic stroke.

(6) Opioid Receptors

Morphine, codeine, heroin, and pethidine were labeled with ^{11}C but, because of the complex metabolism of these compounds and nonspecific binding, these tracers are not well suited for opioid receptor imaging. Successful PET tracers have been obtained with ^{11}C-carfentanyl, a potent synthetic μ opiate antagonist, and ^{11}C-diprenorphine and ^{18}F-cyclofoxy, which bind to all types of opioid receptors.

^{11}C-Carfentanyl, the ligand for the μ receptors, which are the primary site for pleasurable reward feeling, reaches the highest concentrations in the basal ganglia and thalamus. With ^{11}C-diprenorphine, the ligand for μ and non-μ-receptor sites, high naloxone-replaceable concentrations can be obtained in the striatum and in the cingulate and frontal cortex, including the cortical projections of the medial pain system. ^{18}F-Cyclofoxy, an antagonist to μ and k subtypes, is distributed similarly to the distribution of naloxone in the caudate, amygdala, thalamus, and brain stem.

6.2.3 Tumor Imaging Agent

1. **Small molecule tumor imaging agents**

Due to the vigorous growth of tumor cells, their demand for nutrients (glucose, amino acids, etc.) is much higher than that of normal cells. Therefore, radionuclide-labeled glucose, amino acids, etc. can be used as tumor imaging agents.

For example, the distribution of ^{18}F-FDG in the body is similar to that of glucose, but it cannot be metabolized like glucose. ^{18}F-FDG can be concentrated in tumor tissue in vivo, and its concentration increases with the increase of malignancy of the tumor. Therefore, it can be used for the early diagnosis of tumors, the distinction between benign tumors and malignant tumors, the grading of tumors, and the evaluation of the efficacy of surgery, radiotherapy, and chemotherapy. The disadvantage of ^{18}F-FDG for tumor imaging is that the specificity is not high enough, and other methods are often required to confirm the diagnosis of abnormal imaging sites. The uptake mechanism of ^{18}F-FDG is similar to that of ^{99m}Tc-glucoheptonic acid (^{99m}Tc-GH), which was used in the early diagnosis of lung and liver cancer.

The protein synthesis rate of tumor tissue is accelerated, and the uptake rate of amino acids is also increased accordingly. While amino acids play a lesser role than glucose in the metabolism of inflammatory cells (primarily neutrophils), measuring the uptake of radiolabeled amino acids provides a more accurate estimate of tumor growth rate than measuring glucose consumption. Based on this, ^{11}C-L-tyrosine, ^{11}C-L-methionine, and ^{11}C-L-leucine are suitable for detecting protein synthesis

in tumor cells and provide useful information for tumor diagnosis and treatment. Since its metabolite $^{11}CO_2$ is rapidly cleared from tissues, it has no effect on PET measurements of ^{11}C in tumor cells. The tumor uptake of ^{123}I-methyltyrosine is related to the activity of tumor cells, but not to the cell density, and can be used for the diagnosis and treatment of glioma.

The Ga^{3+} in ^{67}Ga-Gallium Citrate is similar to Fe^{3+} and can combine with transferrin, lactoferrin, etc. in the blood. The conjugates can bind to specific receptors on the surface of tumor cells and partially enter the lysosomes of tumor cells and infiltrating inflammatory cells. The radiolabeled molecule can be used for localization diagnosis and clinical staging of malignant lymphoma and Hodgkin's disease, localization diagnosis and differential diagnosis of lung and mediastinal tumors, and prognosis evaluation of lymphoma and lung cancer by radiotherapy and chemotherapy.

$^{99m}TcO_4^-$ labeled dithiosuccinic acid (DMSA) was reduced with Sn(II) under weak alkaline conditions, and the oxidation state of ^{99m}Tc in the obtained product was +V, namely ^{99m}Tc(V)-DMSA. Because of its pro-tumor properties, it can be used for the diagnosis and postoperative follow-up of medullary thyroid carcinoma, the differential diagnosis of soft tissue tumors, the detection of metastases, and the follow-up of recurrence. It can also be used for auxiliary characterization and localization of head and neck malignancies other than thyroid, diagnosis of lung tumors, and qualitative diagnosis of bone lesions.

The corresponding + 1-valent metal ions in ^{201}Tl, ^{99m}Tc-MIBI, and ^{99m}Tc-P_{53} also have tumor affinity. Among them, ^{201}Tl+ is similar to K^+ and can enter cancer cells via Na^+/K^+ ATPase. Since the tumor is rich in blood supply, the uptake of the imaging agent is facilitated. The tumor-affinity mechanism of ^{99m}Tc-MIBI and ^{99m}Tc-P53 is still inconclusive. Some researchers believe that it is related to the membrane potential, mitochondrial metabolism, and blood supply of tumor cells. These imaging agents can be used clinically for the differential diagnosis and localization of lung and craniocerebral tumors, the differential diagnosis of benign and malignant breast masses, the examination of pulmonary mediastinal lymph node metastases, and the observation of the curative effect of lung cancer after radiotherapy and chemotherapy.

Ischemia and even necrosis are common in many tumors, especially near the core of solid tumors. These tumors can be diagnosed using tissue hypoxia imaging agents. Several hours after the injection of the agent, most of the radioactivity in the normal tissue was cleared, and the hypoxic tumor still retained a high level of radioactivity, which appeared as an area of increased radioactivity concentration during imaging.

2. **Peptide-based tumor imaging agents**

Peptide-based tumor imaging agents are radionuclide-labeled peptides that can recognize receptors overexpressed on tumors and bind with high affinity and specificity.

Peptide tumor imaging agents are radionuclide-labeled polypeptides that can recognize high-affinity specific binding of overexpressed receptors on tumors, showing the number, function, and distribution of receptors through imaging devices.

The number, function, and distribution of receptors can be visualized by imaging equipment. Peptide imaging agents have the characteristics of fast reaching the target, fast blood clearance, and strong tissue penetration. Therefore, a high-contrast tumor image can be obtained in a relatively short time, and there is almost no human immunogenic response.

Most radioactive metal nuclides (such as ^{99m}Tc, ^{68}Ga, and ^{111}In, etc.) cannot be prepared into stable labeled compounds by direct labeling. Instead, it needs to be indirectly labeled on the peptide molecule by a bifunctional chelator (BFCA). BFCA binds covalently to peptides with one of its groups and chelates metal ions with another functional group. To maximize the biological activity of the labeled compound, a spacer group is often inserted between the BFCA and the peptide. Monoclonal antibodies can also be radiolabeled with radioactive metal nuclide via BFCA. Figure 6.5 lists several examples of BFCA.

Currently, there are five kinds of imaging agents used in clinical practice, including two kinds of ^{111}In-labeled compounds, two kinds of ^{68}Ga-labeled compounds, and one kind of ^{64}Cu-labeled compounds. Among them, the most successful peptide tumor imaging agent is the ^{68}Ga-labeled somatostatin (SST) imaging agent. Its diagnostic sensitivity and specificity for neuroendocrine tumors are above 90%, which is superior to conventional imaging examinations and traditional somatostatin receptor (SSTR) SPECT imaging. As a result, the diagnosis and treatment strategy of 50–60% of neuroendocrine tumor patients have been changed.

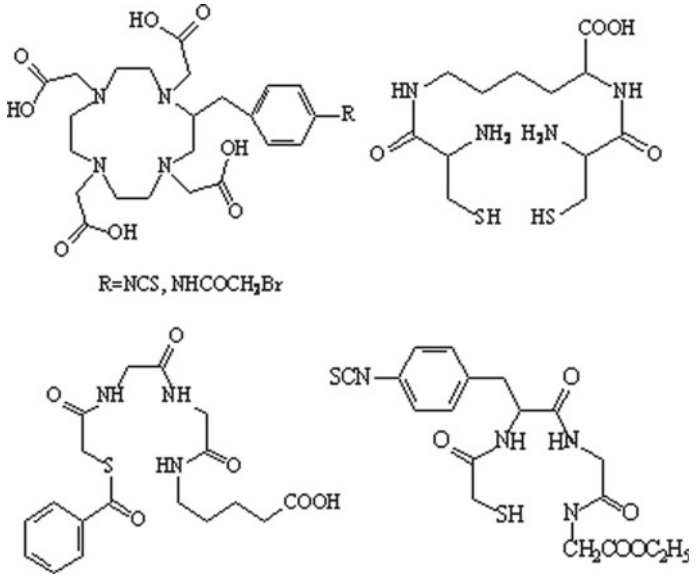


Fig. 6.5 Structural formulae of several BFCAs

^{68}Ga-DOTA-TATE (Netspot) and ^{68}Ga-DOTA-TOC were launched in the US in 2016 and 2019, respectively. Currently, there are many related clinical studies on the widely used ^{68}Ga-DOTA-TATE, ^{68}Ga-DOTA-TOC, and ^{68}Ga-DOTA-NOC.

^{68}Ga PET/CT SSTR imaging has become the "gold standard" for imaging diagnosis of neuroendocrine tumors. However, it still has some shortcomings, one of the prominent problems is the low detection rate of insulinoma. The sensitivity of SSTR imaging for the diagnosis of insulinoma is only about 30–50%, which is due to the low expression of SSTR in insulinoma itself. Glucagon-like peptide-1 (GLP-1) receptor imaging well compensates for this deficiency.

Since the case of GLP-1 receptor imaging for the diagnosis of insulinoma was reported in 2008, clinical studies on the diagnosis of insulinoma by GLP-1 receptor imaging labeled with ^{111}In, ^{99m}Tc, and ^{68}Ga have been reported. A prospective clinical study of ^{68}Ga PET/CT GLP-1 receptor imaging (^{68}Ga-exendin-4) showed that the sensitivity of ^{68}Ga-exendin-4 in diagnosing insulinoma patients was 98.96%, and the positive predictive value for lesions was 100%. It has great clinical significance and reference value. With the popularization and application of this technology, the imaging diagnosis pattern of insulinoma will change.

In addition, due to the similar coordination chemical properties between ^{68}Ga, ^{90}Y, and ^{177}Lu, the same compounds labeled with ^{90}Y and ^{177}Lu can be used for polypeptide receptor radionuclide therapy (PRRT), thereby realizing the theranostics. This can more accurately screen patients, formulate treatment strategies, calculate the dose of radionuclide treatment and evaluate the efficacy, and realize individualized diagnosis and treatment.

3. **Monoclonal antibody tumor imaging agent**

When exogenous substances with larger molecular weight enter the organism, the organism will produce a protein called an antibody that fights against the antigen. Antibodies have a high affinity with the corresponding antigens, and after combining them to form complexes, the harmful effects of foreign substances can be weakened or eliminated. This process is called the immune response, which is a kind of self-protection reaction of organisms. Immunoglobulin G (IgG) present in the human body is the most common type of antibody. Antibodies consist of two parts, each consisting of a light chain (L chain) and a heavy chain (H chain), which are linked by disulfide bonds. The front end of the H and L chains is the recognition site with the antigen, which is called the determinant of the antibody. If cleaved with an appropriate enzyme, fragments such as Fab or $F(ab')_2$ can be obtained, the latter containing the hinge region (Hinge). The molecular weights of intact antibodies or fragments are rough as follows: Fab, 70–90 kD; $F(ab')_2$, 150–200 kD; Fc, 70–90 kD; whole antibody 220–280 kD.

Since the creation of B lymphocyte hybridoma technology by German scientist H Köhler and Argentine scientist G Milstein in 1975, various McAbs have been prepared one after another.

With the advancement of biotechnology, after 40 years of development, monoclonal antibodies have gone through murine antibodies, chimeric antibodies, humanized antibodies, and now fully human antibodies. This process gradually eliminates

the immunogenicity brought by the mouse-derived part and avoids the risk of immune rejection or hypersensitivity caused by McAb. The advantage of McAb as a drug carrier is its high specificity and high affinity for its specific antigen. Radioimmunoassay is SPECT or PET imaging using monoclonal antibodies labeled with single-photon emitting nuclides or positron emitting nuclides. Radioimmunotherapy (RIT) is the labeling of therapeutic radionuclides on monoclonal antibodies for internal radiation therapy. The radionuclide-labeled McAbs are called "biomissiles", in which the McAb acts as a targeting carrier to deliver the radionuclide as a warhead to the target cells.

Radionuclide-labeled intact McAbs have some disadvantages as tumor imaging agents. The first is that the blood circulation time in the body is too long, and it takes 48–72 h to reach the tumor. This makes McAb unsuitable for imaging radionuclides with short half-lives. Secondly, McAb cells have low permeability and metabolize for too long in the body, resulting in high blood toxicity. The third is that its large molecular weight leads to high uptake in the liver, which affects the uptake in target tissues.

To date, there are mainly two approaches to improving the biological effects of McAbs in vivo. One is the enzyme digestion technology, and the other is the pretargeting technology. The former can be used to obtain the targeted functional fragment Fab or $F(ab')_2$ of McAb and reduce its molecular weight. As a result, the metabolism of the antibody fragment in vivo is accelerated, and the time for reaching the target is shortened. This method is suitable for the labeling of short half-life nuclides (such as ^{99m}Tc). There are four strategies for the realization of the latter method: (a) Avidin (AV)-Biotin strategy; (b) Bispecific antibody strategy (bsAbs); (c) In vivo bioorthogonal reaction strategy; (d) DNA analog complementation pairing strategy. Taking the AV-Biotin strategy as an example, AV is a tetramer formed from a glycoprotein extracted from egg white, which can specifically bind to Biotin, and each AV tetramer can bind to 4 biotins. Its binding constant is as high as 1015 L/mol, which is much higher than the antibody-antigen binding constant (10^5–10^{11} L/mol). This is done by conjugating AVs to McAbs and injecting them intravenously into the body, and a portion of the McAb-AVs bind to the surface of tumor cells. After the free McAb-AV in the blood was cleared, radiolabeled biotin was injected. It binds with high specificity to McAb-AV already bound to the surface of tumor cells. The disadvantage of the AV-Biotin conjugation strategy and the bispecific antibody strategy is that there is still the problem of immune resistance. Pretargeting techniques are also applicable to radioimmunotherapy.

6.2.4 Other Organ Imaging Agents

Radionuclide-labeled imaging agents can also be used for imaging other organs. In addition, ^{131}I-labeled radiopharmaceuticals tend to be gradually replaced by ^{99m}Tc labels.

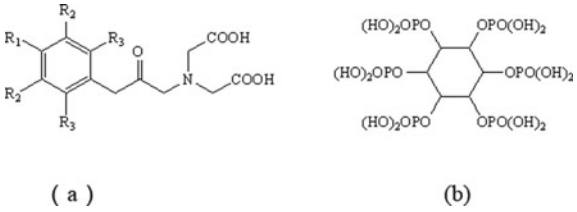


Fig. 6.6 Structural formulae of several hepatobiliary imaging agents

1. **Hepatobiliary imaging agents**

The ^{99m}Tc-iminodiacetic acid derivative can be used for hepatobiliary imaging. The imaging mechanism is that it can be taken up from the blood by hepatocytes, and then secreted into the capillary bile ducts and excreted into the intestine together with bile. The general formula of these drugs is shown in Fig. 6.6a. Changes in the substituents on the benzene ring can modulate the lipophilicity of the entire molecule. Lipophilic molecules are beneficial for hepatobiliary imaging.

The widely used ^{99m}Tc-iminodiacetic acid derivative for hepatobiliary imaging include ^{99m}Tc-IDA (R1 = R2 = H, R3 = CH3), ^{99m}Tc-EHIDA (R1 = R2 = H, R3 = C_2H_5), ^{99m}Tc-TMBIDA (R1 = R3 = CH_3, R2 = H and Br) and ^{99m}Tc-DISIDA (R3 = i-C_3H_7, R1 = R2 = H). ^{99m}Tc-labeled phytate (Fig. 6.6b) forms an insoluble chelate with Ca^{2+} in blood. Because of its small particle size (about 20–40 nm), it can be phagocytosed by hepatic reticuloendothelial cells and then enter the liver, which can be used for liver imaging.

^{99m}Tc-pyridoxal-5-methyltryptophan (^{99m}Tc-PMT) is a specific imaging agent for hepatocellular carcinoma. Well-differentiated hepatocellular carcinoma cells have the function of secreting gallstones of some normal hepatocytes and can take up ^{99m}Tc-PMT, while benign and malignant tumors of other organs do not have this function.

2. **Renal imaging agents**

(1) Glomerular filtration agents

Glomerular filtration rate (GFR) is the volume of fluid filtered from the kidney's glomerular capillaries into Bowman's capsule per unit of time.

Since DTPA (diethylenetriaminepentaacetic acid) can be freely filtered from the glomerulus without being reabsorbed or secreted by the renal tubule, ^{99m}Tc-DTPA can be used for the determination of GFR. According to the imaging results, it can be used to determine renal function, diagnose urinary tract infarction, monitor the response after kidney transplantation, determine the time of renal dialysis in patients with renal failure, and check for urinary tract infections.

(2) Renal tubular imaging agent

Effective renal plasma flow (ERPF) is the amount of plasma flowing to the parts of the kidney that have a function in the production of constituents of urine. ERPF is closely related to the clearance rate of certain substances from plasma to urine when

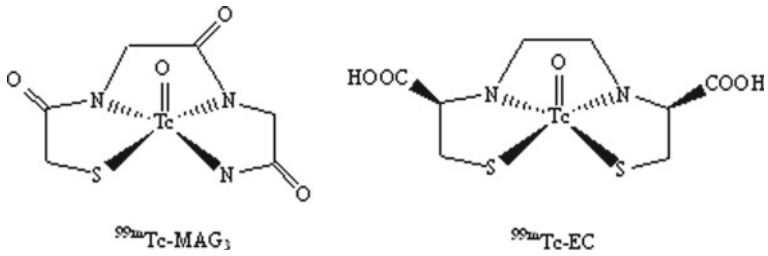


Fig. 6.7 Structural formulae of ^{99m}Tc-MAG3 and ^{99m}Tc-EC

they flow through the kidneys. Substances that are both filtered from the glomerulus and secreted from the renal tubules and not absorbed by the renal tubules can be used for the determination of ERPF after being labeled with radionuclides.

Using imaging agents such as ^{99m}Tc-mercapto-acetylglycyl-glycyl-glycine (^{99m}Tc-MAG$_3$) and ^{99m}Tc-L,L-Ethylenedicysteine (^{99m}Tc-EC) (Fig. 6.7), dynamic imaging of renal perfusion, determination of ERPF, diagnosis of renal tubular necrosis, studies of renal tubular function and monitoring of renal transplantation can be performed.

(3) Static renal imaging agents

^{99m}Tc-DMSA, ^{99m}Tc-Glu, ^{99m}Tc-GH, etc. have a high binding ability to plasma proteins. The resulting conjugates are slowly filtered in the glomerulus, reabsorbed by the tubules, and concentrated in the renal cortex, so they can be used for static imaging of the kidney. Clinically, it can be used to evaluate the function of the renal cortex, diagnose infection, observe the position, shape, and size of the kidney, and diagnose diseases such as renal atrophy or space-occupying lesions.

3. **Bone imaging agents**

All kinds of tumors eventually metastasize to the bone, causing severe bone pain. Bone imaging agents are used for early diagnosis of tumor bone metastases. It can detect bone metastases 3 to 6 months earlier than X-rays. In addition, bone scintigraphy has clinical value in the diagnosis of primary osteoma, avascular necrosis of the femoral head, and osteomyelitis, and in monitoring the survival of bone grafts. The main component of bone is hydroxyapatite crystals, and its Ca^{2+}, OH^-, and PO_4^{3-} can be exchanged with the same radioactive ions in the blood. Radionuclide-labeled compounds can also be enriched in bone by chemisorption.

Commonly used bone imaging agents include ^{99m}Tc-pyrophosphate P (^{99m}Tc-PY), ^{99m}Tc-methylene diphosphonic acid (^{99m}Tc-MDP), ^{99m}Tc-hydroxymethylene diphosphonic acid (^{99m}Tc-HMDP), ^{99m}Tc-diphosphonic acid Carboxypropane diphosphonic acid (^{99m}Tc-DPD), ^{99m}Tc-hydroxyethylethylenediamine trimethylenephosphonic acid (^{99m}Tc-HEDTMP) and ^{99m}Tc-hydroxyethylenediphosphonic acid (^{99m}Tc-HEDP) and so on. Among them,

the phosphonic acid type imaging agent containing the P-C-P structure is more stable in vivo than the pyrophosphate type imaging agent containing the P-O-P structure, so it develops rapidly.

6.3 Therapeutic Radiopharmaceuticals

Therapeutic radiopharmaceuticals are radioactive substances that could help in delivering radiation entirely to body tissues by the administration of radioactive substances. In essence, it uses the radiation ionization effect of rays on the organism to directionally destroy the diseased tissue or change the tissue metabolism to achieve the purpose of treatment. Therapeutic radiopharmaceuticals generally consist of two parts, a radiotherapeutic nuclide and a drug delivery system that delivers the radionuclide to the target tissue (tumor). The former can emit α-particles, β-particles, or Auger electrons to kill tumor cells. To maximize the killing of cancer cells and minimize the damage to normal cells, drug delivery systems are required to target tumors with high specificity. The highly specific uptake of therapeutic radiopharmaceuticals by tumors can increase their therapeutic efficacy.

Therapeutic radionuclides generally have the following characteristics: capable of emitting high-energy alpha or beta particles; short half-life, which can achieve the desired therapeutic effect in a short period; easy to label into suitable preparations, and stable in vitro and in vivo.

There are three main types of radionuclide carriers in therapeutic radiopharmaceuticals:

a. Small molecule compounds. Its function is similar to that of general targeting molecules, which can specifically reach the lesions. The difference is that the former can carry radionuclides, which play a therapeutic role in the lesions.
b. Biological targeting molecules. Using biological targeting molecules to specifically bind to receptors on the cell surface, radiopharmaceuticals can be concentrated on the diseased target tissue or target organ to achieve the effect of radiotherapy.
c. Colloids, microspheres, and other preparations. It is to embed colloids or microparticles containing radionuclides in the capillaries of the corresponding target organs. It does not enter or rarely enters non-target organs, resulting in local radioembolization so that the radioactivity remains in the tumor to achieve the purpose of radiotherapy.

After decades of unremitting efforts by radiopharmaceutical chemists and nuclear medicine clinicians, a limited number of radiopharmaceuticals with excellent performance have been screened out of thousands of synthesized radiolabeled compounds for nuclear medicine treatment. So far, in addition to the more researched ^{90}Y-labeled microspheres, ^{131}I, ^{32}P, ^{153}Sm, ^{186,188}Re, and other therapeutic nuclide-labeled small-molecule compounds and biological agents, the related research on ^{177}Lu, ^{161}Tb, ^{211,225}Ac, and other nuclides has also attracted extensive attention of researchers.

6.3.1 Small Molecule Radiotherapeutic Drugs

1. **^{131}I-labeled therapeutic radiopharmaceuticals**

Iodine can be selectively absorbed by the thyroid gland and is one of the important raw materials for the thyroid gland to synthesize thyroid-stimulating hormone (TSH). Since ^{131}I has the same biochemical and biological properties as stable iodine required by humans, ^{131}I radiation can be used to destroy thyroid cancer cells. The main β-ray emitted by ^{131}I has a maximum energy of 606.3 keV (90%) and a short-range in tissues, which can effectively kill cells that have ingested ^{131}I, with little damage to adjacent tissues.

Na^{131}I has been used for many years in the treatment of hyperthyroidism with good results. Autonomic high-functioning thyroid adenomas are caused by the partially increased function of thyroid nodules (adenomas), which are autonomous and are not regulated by the thyroid-stimulating hormone secreted by the pituitary gland. Hyperthyroidism occurs when the functionally autonomous thyroid tissue secretes too much thyroxine. The normal thyroid still maintains the negative feedback regulation mechanism of iodine uptake. After taking Na^{131}I, functional autonomous thyroid tumors take up a large amount of ^{131}I, while normal thyroid tissue does not, or rarely takes up ^{131}I due to inhibited function, to achieve the purpose of treatment. ^{131}I is also effective in removing postoperative residues and metastases of differentiated thyroid cancer because these cells are iodine-rich.

Since ^{131}I-metaiodobenzylguanidine (^{131}I-MIBG) can bind to adrenergic glands, it can be used to treat neuroendocrine tumors rich in this receptor, such as malignant pheochromocytoma, neuroblastoma, malignant neuroendocrine Tumors, etc. In addition, ^{131}I-5-iodo-uracil can be used to treat gastric cancer, and ^{131}I-BDP3 (^{131}I-α-amino-4-hydroxybenzylidene bisphosphonate) can be used to relieve pain in bone metastases and treat bone metastases.

2. **^{32}P-labeled therapeutic radiopharmaceuticals**

^{32}P mainly exists in the form of $Na_2H^{32}PO_4$ or $NaH_2{}^{32}PO_4$ and can enter cells by participating in the metabolism of nuclear proteins, nucleotides, phospholipids, and the synthesis of DNA and RNA. Its intracellular uptake is proportional to the rate of cell division. Polycythemia vera, essential thrombocythemia, and other conditions can be treated with ^{32}P.

Many advanced cancers (such as breast cancer, prostate cancer, lung cancer, etc.) are accompanied by bone metastases, and about 50% of patients have increased pain. In the past, nerve anesthetics were mainly used for analgesia, which was ineffective and prone to drug dependence. Osteophilic radionuclide ^{32}P has a better effect (called the palliative treatment of metastatic bone cancer), and $^{32}PO_4{}^{3-}$ is concentrated in bone tumor lesions and can be used for analgesia of bone metastases. But it also penetrates bone marrow cells and has a greater inhibitory effect on hematopoietic function.

3. ^{89}Sr-labeled therapeutic radiopharmaceuticals

Sr can be highly selectively enriched in hydroxyapatite in bone, which is in the same family as Ca in the periodic table (IIA). ^{89}Sr is an excellent radionuclide for bone tumor remission. The maximum energy of β-ray is 1.463 meV, the average energy is 0.58 meV, and the γ-ray with a branching ratio of 0.009 5% and energy of 0.909 meV can be emitted. The average range of β-rays of ^{89}Sr in soft tissue is about 2.4 mm, which is an ideal radionuclide for bone tumor radiotherapy Currently. Since the Ca^{2+} of Sr^{2+} and hydroxyapatite, the main inorganic component of bone, are similar, Sr^{2+} can be highly concentrated in the skeletal system of the human body. ^{89}Sr compounds that can exist in the form of Sr^{2+} in the blood can become ^{89}Sr drugs. Therefore, ^{89}Sr drugs do not require special compounds as carriers, which provides great convenience for the design of ^{89}Sr-related therapeutic radiopharmaceuticals. Currently, the clinical drug form of ^{89}Sr is $^{89}SrCl_2$ solution, which can be used for the relief of pain in the treatment of bone tumors and bone metastases.

4. ^{153}Sm-labeled therapeutic radiopharmaceuticals

^{153}Sm has a short half-life ($T_{1/2} = 46.3$ h), moderate β-ray energy $E_{\beta max}$ (640 keV and 710 keV), and simultaneously emits 103 keV γ-ray. Due to the chemical properties of Sm, it is easy to concentrate in bone tumors and causes little radiation damage to surrounding tissues. Its gamma-ray energy is suitable for in vitro imaging and can be used for tumor localization, dose estimation, and curative effect monitoring. Based on the above characteristics, ^{153}Sm has been widely used in clinical practice.

^{153}Sm-ethylenediaminetetraethylenephosphonic acid (^{153}Sm-EDTMP) is a radiopharmaceutical with good effect in the palliative treatment of bone metastases. The preparation process is as follows: adding the 0.1 N hydrochloric acid solution of $^{153}SmCl_3$ into the freeze-dried EDTMP kit. After ^{153}Sm-EDTMP is injected into the patient, about 50 to 70% of it accumulates in the bone.

5. ^{186}Re- and ^{188}Re-labeled therapeutic radiopharmaceuticals

^{186}Re and ^{188}Re have excellent properties as therapeutic nuclides (Table 6.5), so they are the preferred nuclides for radiotherapy drugs. They can be produced via reactors or generators. The specific activity of ^{186}Re reached 12.50 GBq/mg when the natural Re target was irradiated at a neutron flux of 1014 cm^{-2}/s for 14 d, while the specific activity of ^{188}Re was only 0.323 GBq/mg. Both can not only label organic small molecule compounds but can be used to label monoclonal antibodies (McAb), monoclonal antibody fragments (Fab), or receptor ligands.

The maximum energy of beta rays emitted by ^{186}Re is 1.07 meV (92%). These particles have a maximum range of 5 mm in tissue and moderate energies and are often selected as therapeutic nuclides. The energy of the γ-ray emitted by it is 137 keV

Table 6.5 Characteristics of ^{186}Re and ^{188}Re

	$T_{1/2}$/d	$E_{\beta max}$/MeV	E_γ/KeV
^{186}Re	3.7	1.07	137 (9%)
^{188}Re	0.7	2.11	155 (15%)

(9%), which can be used for SPECT imaging, so its labeled complex can be used for theranostics.

The β-ray energy emitted by ^{188}Re is 2.11 meV (79%), 1.96 meV (20%), the maximum range in tissue is 12 mm, and the average range is 2.2 mm. The γ-ray energy emitted by ^{188}Re is 155 keV (15%), which is suitable for imaging and facilitates monitoring of the distribution of its labeled compounds and estimation of absorbed dose. ^{188}Re is easily prepared from the ^{188}W-^{188}Re generator, suitable for remote transportation, and easy to use. As a generator nuclide, its half-life ($T_{1/2}$) is 16.9 h. If its labeled complex and has a short biological half-life in the human body, it will not cause serious radiation damage to the human body. But its imaging effect is not as good as ^{186}Re.

As a transition element, the main valence state of Re in the compound is +III–+VII. Its radiolabeled radiopharmaceuticals are available in many chemical forms, resulting in a specific affinity for different target organs. The chemical properties of Re are very similar to those of technetium, and the molecular geometry is almost identical. The biodistribution properties of the corresponding molecules are often very close and can be used to label a variety of compounds and biomolecules. In addition, Re has stable isotopes, which provides convenience for studying the structure and properties of Re-labeled radiopharmaceuticals.

Re often exists in the form of high valence (+VII), but the Re involved in the formation of complexes is generally in a low valence state. Re(+VII) often has multiple chemical valence states after being reduced, and its complexes often exist in the form of multiple components. How to quantitatively reduce Re(+VII) to a certain valence state has become the primary research content of Re coordination chemistry.

The key problem in basic chemical research of Re is the quantitative reduction of high-valent Re(+VII). The main reducing agent currently used is $SnCl_2$, but the Re reduced by this reducing agent often coexists in multiple valence states. As a result, Re complexes have multiple components, complex structures, and unsatisfactory biodistribution.

The researchers used the tracer method to select several new reduction systems to study the valence distribution after the reduction of high valence Re and compared it with the commonly used stannous reduction method. They tried to establish analytical methods and quantitative reduction conditions for Re in different reduction valence states. The research results will help to solve the problems of multiple compositions and complex structures of Re complexes due to the complex chemical properties and variable valences of Re. This can not only enrich the basic chemistry of Re but also provide basic technical support for the promotion and application of Re.

Re-labeled radiopharmaceuticals can be divided into two categories: one is the complex itself, such as Re-DTPA, Re-N_2S_2, Re-bisphosphonate, etc.; the other is the precursor of conversion label, such as $[ReNL_4]$, $[ReO(en)_2]Cl$, etc.

The small-molecule radiopharmaceuticals of Re are mainly osteophilic compounds, most of which are radioactive Re complexes containing $H_2PO_3^-$ ligands. If the radioactive Re is replaced by ^{99m}Tc, the corresponding molecule obtained is a bone imaging drug, which has a great reference value for the therapeutic drug of Re. The ligands of Re osteophilic drugs that have been studied include HEDP, MDP,

AEDP, HEDTMP, TTHMP, and so on. The complexes can be used for relieving bone pain and treating bone metastases. Taking the preparation of ^{186}Re- or ^{188}Re-HEDP as an example, $^{186}ReO_4^-$ or $^{188}ReO_4^-$ was added to a freeze-dried kit containing hydroxyethylene diphosphonate (HEDP), reducing agent and gentisic acid, and heated in boiling water for 15 min. ^{186}Re- or ^{188}Re-DMSA for the treatment of medullary thyroid carcinoma can also be prepared using a similar method.

6. **^{223}Ra-related therapeutic radiopharmaceuticals**

95% of the decay energy of ^{223}Ra is released in the form of α-particles, which have a shorter range and less damage to non-target cells in vivo. Since ^{223}Ra is chemically similar to Ca, the main component of bone, it is easily transferred to the bone. $^{223}RaCl_2$ is the first clinically approved α-nuclide therapy drug, which can be used for the treatment of bone metastases from prostate cancer. $^{223}RaCl_2$ is currently approved in more than 40 countries around the world, including the United States, Japan, and the European Union. The anti-tumor effect of the drug is significant and outperformed existing palliative treatments for ^{89}Sr and ^{153}Sm, improving life expectancy and quality of life.

6.3.2 Targeted Therapy Radiopharmaceuticals

If tumor cells have specific receptors on their surface, or if they are not specific, but at a much higher density than on normal cells, therapeutic radionuclides can be labeled with ligands for that receptor. Using specific interactions between ligands and receptors, radionuclides can be delivered to tumor tissues with high selectivity.

Targeted radiotherapy is to use tumor-specific and highly expressed molecules as targets, and uses ligands with high affinity and specific binding to such targets, such as antibody molecules or polypeptide molecules, as carriers to deliver radionuclides to the target. tumor site. Therefore, specific and targeted internal radiation therapy is performed on tumors by utilizing the physical killing effect of radionuclides.

Targeted radiopharmaceuticals not only kill tumor cells on the surface or superficial layer of tumor tissue through radioactive rays but use radiation to kill tumor cells inside solid tumors. Although these cells or tissues are not specific targets of radio conjugates, ionizing radiation can deposit in them. This is due to an emitted radiation particle path length that is longer than at least several cell diameters, cells, and tissue not expressing the target antigen will still be impacted by the incidental radiation, that is, the “crossfire” effect.

Compared with biological drugs and chemical drugs, targeted radiopharmaceuticals have stronger therapeutic effects. In addition, targeted radiotherapy has a significant therapeutic effect on small tumor lesions or metastases that cannot be detected by imaging diagnosis and surgery.

Targeted therapy radiopharmaceuticals can be divided into peptides and antibodies according to their carriers. Currently, clinically approved targeted therapy radiopharmaceuticals include ^{177}Lu-DOTATATE (Lutathera®), ^{90}Y-Ibritumomab Tiuxetan (Zevalin), and ^{177}Lu-PSMA-617 (Pluvicto).

As the first radiopharmaceutical for Peptide Receptor Radionuclide Therapy (PRRT), Lutathera® was approved by the EMA in 2017 and the FDA in 2018 for the treatment of somatostatin receptor (SSTR) positive gastroenteropancreatic neuroendocrine tumors. Using the concept of PRRT, Lutathera® combines the radionuclide ^{177}Lu with the somatostatin analog DOTATATE, thus delivering ionizing radiation specifically to tumor cells expressing somatostatin receptors. As a result, DNA single- and double-strand breaks are provoked, in case of double-strand breaks leading to cell death of the tumor and its SSTR-positive lesions.

^{90}Y-Ibritumomab Tiuxetan is an antineoplastic agent indicated for non-Hodgkin's lymphoma. ^{90}Y-Ibritumomab Tiuxetan, a monoclonal antibody, is currently unavailable in generic form due to its patented brand name, Zevalin. In February of 2002, Zevalin became the first "radioimmunotherapeutic" pharmaceutical product to exist under FDA approval Zevalin is specifically indicated for previously untreated follicular non-Hodgkin's lymphoma (NHL) as well as relapsed or refractory B-cell NHL. Ibritumomab Tiuxetan, the monoclonal antibody, is therefore coupled with a radioactively cytotoxic agent capable of directly targeting cancer cells. Once in the body, Ibritumomab Tiuxetan then binds with the CD20 receptor of B-cells, inducing apoptosis, or cell death, thereby reducing the growth of cancerous cells. The role of ^{111}Indium in Zevalin is to function as a tracer, determining whether the drug has been delivered to the correct tissues. After correct distribution is confirmed, ^{90}Yttrium provides specificity for cancer cells, exposing them to radioactive beta emission.

Pluvicto™ (formerly ^{177}Lu-PSMA-617) is a radioligand therapy that was approved by the FDA in March 2022 to treat progressive, PSMA-positive metastatic castration-resistant prostate cancer. Pluvicto™ is being further developed by Novartis (originally acquired from the Purdue startup company Endocyte) for other prostate cancer indications. Pluvicto™ utilizes a high affinity targeting ligand to direct potent radiotherapy to prostate cancer cells. The specific targeting of this therapy comes from the "ligand" portion of the therapeutic, which is a small molecule designed to bind to Prostate Specific Membrane Antigen, or, PSMA, a protein highly expressed on the cell surface of most prostate cancer cells but absent on most normal cells. The PSMA targeting ligand in Pluvicto™ is chemically attached to a therapeutic radioactive atom called Lutetium-177 (^{177}Lu), which releases an energetic beta particle to precisely deliver cell-killing radiation to the site of disease. Unlike traditional external beam radiotherapy, Pluvicto™ is administered as a systemic injection where it can directly target multiple sites of PSMA-positive prostate cancer throughout the body, including the bone and soft tissue while bypassing the PSMA-negative healthy cells. The expression of PSMA before treatment with Pluvicto™ can be determined using whole-body PSMA-directed imaging, allowing for the personalization of treatment so that the best course of therapy might be selected. It is estimated that approximately 80% of men with metastatic castration-resistant prostate cancer (mCRPC) express PSMA on their cancer cells.

6.3.3 *Colloidal and Microsphere Formulation-Based Radiotherapeutic*

Rhenium [^{188}Re] sulfur suspension for injection is a colloidal therapeutic radiopharmaceutical. Its main component $^{188}Re_2S_7$ is a colloid. The preparation method is basically to reduce $^{188}ReO_4^-$ with H_2S under a certain pH condition. It is a radioactive synovectomy agent for intra-articular injection. Because of its suitable particle size, it can stay in the joint cavity for a long time with little leakage. Therefore, it will not cause damage to other tissues and can treat various arthritis. Colloid therapy radiopharmaceuticals are also used in other indications. Some researchers disperse ^{188}Re compounds in the organic phase and use interfacial polymerization to make ^{186}Re microcapsules. The microcapsule solution was injected into the lice-bearing artery of mouse melanoma, the tumor was embolized, and more than 90% of the radioactivity was retained in the tumor. Such techniques are also of interest in localizing tumors for therapy.

^{90}Y-resin microspheres are representative of microsphere radiopharmaceuticals. It can target the liver for selective internal radiation therapy for unresectable hepatoma. This treatment is also known as radioembolization. It is to inject ^{90}Y-adsorbed resin microspheres directly into liver tumor blood vessels. These microspheres can penetrate the small branch blood vessels of liver tumors, embolize at the liver lesions, and play a killing effect through high-dose high-energy β-radiation so that the radiotherapy can continue to work. The radiation coverage area of ^{90}Y microspheres is larger than that of traditional external radiation therapy, which can remove the cancer cells around the liver tumor and greatly reduce the chance of tumor recurrence. And ^{90}Y can only emit beta rays, and its radiation distance to the tissue is less than 1 cm, with an average value of 0.25 cm. It has a strong lethality to the surrounding tumor cells, and its influence decreases beyond this range, so it is relatively less harmful to the normal cells adjacent to the tumor. The radiation energy of ^{90}Y microspheres will naturally attenuate by 84% after one week of implantation, and less than 3% will remain after two weeks. The radiation damage to the surrounding environment and personnel can be minimized.

6.4 Nuclear Medical Imaging Techniques and the Equipment

Nuclear medicine is a specialized area of radiology that uses very small amounts of radioactive materials, or radiopharmaceuticals, to examine organ function and structure. Nuclear medical imaging is a combination of many different disciplines. These include chemistry, physics, mathematics, computer technology, and medicine. This branch of radiology is often used to help diagnose and treat abnormalities very early in the progression of a disease, such as thyroid cancer.

Because X-rays pass through soft tissue, such as intestines, muscles, and blood vessels, these tissues are difficult to visualize on a standard X-ray, unless a contrast agent is used. This allows the tissue to be seen more clearly. Nuclear imaging enables visualization of organ and tissue structure as well as function. The extent to which a radiopharmaceutical is absorbed, or "taken up", by a particular organ or tissue may indicate the level of function of the organ or tissue being studied. Thus, diagnostic X-rays are used primarily to study anatomy. Nuclear imaging is used to study organ and tissue function.

A tiny amount of a radioactive substance is used during the procedure to assist in the exam. The radioactive substance, called a radionuclide (radiopharmaceutical or radioactive tracer), is absorbed by body tissue. Several different types of radionuclides are available. These include forms of the elements technetium, thallium, gallium, iodine, and xenon. The type of radionuclide used will depend on the type of study and the body part being studied.

After the radionuclide has been given and has collected in the body tissue under study, radiation will be given off. This radiation is detected by a radiation detector. The most common type of detector is the gamma camera. Digital signals are produced and stored by a computer when the gamma camera detects the radiation.

By measuring the behavior of the radionuclide in the body during a nuclear scan, the healthcare provider can assess and diagnose various conditions, such as tumors, infections, hematomas, organ enlargement, or cysts. A nuclear scan may also be used to assess organ function and blood circulation.

The areas where the radionuclide collects in greater amounts are called "hot spots." The areas that do not absorb the radionuclide and appear less bright on the scanning image are referred to as "cold spots".

In planar imaging, the gamma camera remains stationary. The resulting images are two-dimensional (2D). Single photon emission computed tomography (SPECT), produces axial "slices" of the organ in question because the gamma camera rotates around the patient. These slices are similar to those performed by a CT scan. In certain instances, such as Positron Emission Tomography (PET) scans, three-dimensional (3D) images can be performed using the SPECT data.

6.4.1 SPECT

Single photon emission computed tomography (SPECT) is a medical imaging technique. A type of nuclear imaging that allows doctors to see how well a patient's internal organs are functioning with the help of radioactive substances and special gamma cameras. The technique creates a 3-D scan of the patient's "insides" at different angles and provides information about how different parts of the body are working to identify any problems.

While a patient may think a SPECT scan is a simple process, it takes considerable skill to generate SPECT images that are suitable for real-life applications. From brain scans to diagnosing cardiac conditions, a SPECT scan can be used in a variety of

ways in the medical field. SPECT scans are available at most hospitals, clinics, and imaging centers, and provide doctors with a way to evaluate patients' health through accurate imaging.

SPECT imaging/scan monitors the level of biological activity in the body to create a 3-D image. To create this image, a radioactive "tracer" is injected into the patient's bloodstream. While inside the body, the "tracer" produces gamma rays that can be detected by a special gamma camera. The gamma camera rotates around the patient's body, picks up the signal from the tracer found within the body, and a computer converts that signal into a picture. Through the use of a tomographic reconstruction algorithm, these 2-D image slices can then produce a 3-D image/data set.

A SPECT scan provides information about the functionality of internal organs and tissue. It produces an image that can give a "glimpse" inside the body to see if things are working as intended, or if there is a potential problem. The image is a primary view of how the blood flows through arteries and veins in the body and can detect reduced blood flow in injured or compromised sites.

6.4.2 PET

Positron emission tomography (PET) is a type of nuclear medicine procedure that measures the metabolic activity of the cells of body tissues. PET is a combination of nuclear medicine and biochemical analysis. Used mostly in patients with brain or heart conditions and cancer, PET helps to visualize the biochemical changes taking place in the body, such as metabolism (the process by which cells change food into energy after food is digested and absorbed into the blood) of the heart muscle.

PET differs from other nuclear medicine examinations in that PET detects metabolism within body tissues, whereas other types of nuclear medicine examinations detect the amount of a radioactive substance collected in body tissue in a certain location to examine the tissue's function.

Since PET is a type of nuclear medicine procedure, this means that a tiny amount of a radioactive substance, called a radiopharmaceutical (radionuclide or radioactive tracer), is used during the procedure to assist in the examination of the tissue under study. Specifically, PET studies evaluate the metabolism of a particular organ or tissue, so that information about the physiology (functionality) and anatomy (structure) of the organ or tissue is evaluated, as well as its biochemical properties. Thus, PET may detect biochemical changes in an organ or tissue that can identify the onset of a disease process before anatomical changes related to the disease can be seen with other imaging processes such as computed tomography (CT) or magnetic resonance imaging (MRI).

PET is most often used by oncologists (doctors specializing in cancer treatment), neurologists and neurosurgeons (doctors specializing in the treatment and surgery of the brain and nervous system), and cardiologists (doctors specializing in the treatment of the heart). However, as advances in PET technologies continue, this procedure is beginning to be used more widely in other areas.



Fig. 6.8 PET/CT device

PET may also be used in conjunction with other diagnostic tests, such as computed tomography (CT) or magnetic resonance imaging (MRI) to provide more definitive information about malignant (cancerous) tumors and other lesions. Newer technology combines PET and CT into one scanner, known as PET/CT. PET/CT shows particular promise in the diagnosis and treatment of lung cancer, evaluating epilepsy, Alzheimer's disease, and coronary artery disease.

Originally, PET procedures were performed in dedicated PET centers, because the equipment to make the radiopharmaceuticals, including a cyclotron and a radiochemistry lab, had to be available, in addition to the PET scanner. Now, radiopharmaceuticals are produced in many areas and are sent to PET centers, so that only the scanner is required to perform a PET scan.

Further increasing the availability of PET imaging is a technology called gamma camera systems (devices used to scan patients who have been injected with small amounts of radionuclides and are currently in use with other nuclear medicine procedures). These systems have been adapted for use in PET scan procedures. The gamma camera system can complete a scan more quickly, and at less cost, than a traditional PET scan (Fig. 6.8).

6.5 Neutron Capture Therapy

Boron neutron capture therapy (BNCT) is a targeted therapy whose principle is based on the property of the isotope ^{10}B to capture thermal neutrons with high probability (high effective cross-section: 3835 b), decaying into a He and a Li nucleus by the

capture reaction $^{10}B(n,\alpha)7Li$. If this reaction occurs in tissues, both particles effectively destroy cells due to their high linear energy transfer (LET) properties. Due to the short range of both particles (about 5–9 μm) in tissue, cell damage remains almost entirely confined to those cells containing ^{10}B atoms. Neighboring cells containing little or no boron will not be damaged. Therefore, if ^{10}B can be selectively enriched in tumor cells by suitable transport molecules, targeted destruction of malignant cells while sparing healthy tissue is possible.

The idea of BNCT is therefore to enable highly individualized tumor treatment, limiting the therapeutic effect exclusively to the patient-specific tumor spread. Developing this principle into a treatment option requires a compound that selectively, but with sufficiently high concentrations, accumulates ^{10}B in or close to the nucleus of all tumor cells but is not toxic to healthy cells and is not toxic systemically. Both individual components of this binary treatment, namely a suitable ^{10}B-containing compound and low-energy neutrons, have little or no biological effect of their own. Only the combination of both components triggers the boron neutron capture reaction and thus leads to the therapeutic effect.

Development of this principle in a treatment modality is challenging as the irradiation dose is applied by BNCT in the patient, and thus the effect of BNCT depends on the amount of ^{10}B in different tissues. Even more, BNCT is not only highly precise by limiting the antineoplastic effect to malignant cells but is also highly personalized: (1) the ^{10}B-uptake via a specific targeting mechanism depends on the molecular characteristics of single tumor cells; (2) the radiation dose depends on the ^{10}B concentration in single cells; (3) spatial dose distribution depends on the subcellular ^{10}B-distribution; and (4) the optimal time points of drug-application and irradiation depend on patient-specific pharmacokinetics and pharmacodynamics of the ^{10}B-delivering agent (irradiation must take place at the time point when the ^{10}B-concentration is highest in the tumor cells and lowest in the healthy tissue). The possibility of imaging and measuring these highly individual dependencies is thus a prerequisite for the further development of BNCT.

Currently, the ^{10}B-concentration in tissue can technically not be determined at the time of irradiation. It is exclusively possible to measure the ^{10}B concentration in the blood and to assume that the accumulation in the tissue, be it the tumor or organ at risk, is the same for each patient according to an experimentally determined factor. The two compounds currently used in clinical applications for BNCT, namely BPA (^{10}B-p-boronophenylalanine, $C_9H_{12}{}^{10}BNO_4$) and BSH (Sodium mercaptoundecahydro-closo-dodecaborate, $Na_2{}^{10}B_{12}H_{11}SH$) (Fig. 6.10), such factors have been determined in healthy tissues, so that safe application of BNCT seems possible within narrow limits within clinical trials. However, larger controlled prospective studies are completely lacking. The well-known heterogeneity of tumor tissues in a single individual, but also between different patients, makes the accurate estimation of the dose, and therefore the prediction of the expected effect, impossible.

The recent emergence of accelerator-based facilities for BNCT placed in hospitals makes the modality independent of nuclear research reactors and thus available for routine clinical use. This evolving market makes the development of new boron compounds a matter of urgency.

A theranostic approach offers the potential to overcome these challenges and to make BNCT a real precision therapy. The term "theranostics" is used for a material that combines the modalities of therapy and diagnostic imaging. A compound, which could serve as a ^{10}B-delivering agent during treatment but also for diagnostic imaging of the macroscopic ^{10}B-distribution and possibly allow for quantification, could enormously help further developments. This principle has been used in the therapy of thyroid tumors for the last 70 years. Among the most successful examples of more recent theranostic concepts in nuclear medicine are peptide receptor scintigraphy (PRS) and peptide receptor radionuclide therapy (PRRT) for imaging and treating cancer, i.e., neuroendocrine tumors.

BNCT is a treatment modality of precision medicine. Its success depends on the optimized customization of dose applications to a given individual patient. To fully exploit the potential of BNCT, one challenge is to use omic methods to identify biomarkers that allow the definition of subgroups of patients for whom specific targeting ^{10}B-carriers are appropriate. The approach with ^{18}F-labeled BPA is the first step in addressing this issue. However, this approach is not sufficient because it does not capture the heterogeneity of tumors and the individual dynamics of the uptake of boron carriers into target cells. To make optimal use of BNCT, ways must be found to evaluate the boron concentration in the tumor and the organs at risk as precisely as possible in direct temporal relation to the irradiation. The principles of theranostics offer the possibility to achieve this goal. New boron carriers should be designed a priori so that their distribution in the body and their concentration in specific tissues can be determined directly before (or even during) irradiation.

Research efforts are underway to identify new candidates for BNCT that have better tumor selectivity, longer cell retention, and whose accumulation in the patient's internal organs can be monitored by various techniques, with a focus on PET. The 4-^{10}B-Borono-2-^{18}F-fluoro-l-phenylalanine ([^{18}F]FBPA) was the first compound developed for monitoring the pharmacokinetics of 4-^{10}B-borono-phenylalanine, which is still used in BNCT. MRI can be alternatively used to monitor the tumor before and after BNCT treatment and different preclinical studies have reported the detection of compounds containing both B and Gd or Fe as a new generation of theranostic BNCT agents. Fluorescence imaging mainly applied in vitro found an application in BNCT in vivo with a nonpeptidic RGD-mimetic integrin ligand and a cyanine dye. An alternative approach is the conjugation of BSH with CPPs. When BSH, linked with a short oligoarginine peptide, was conjugated with 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) and labeled with a positron emitter ^{64}Cu, the monitoring of the compound in vivo in U87ΔEGFR brain tumor-bearing mice by PET was possible. Proteins, growth factors, antibodies, and nanoparticles were conjugated to increase the selectivity and delivery of a large amount of ^{10}B. When a maleimide-closo-dodecaborate was linked to albumin lysin and cysteine Cys34 residues, the compound was selectively accumulated in colon-26 tumor-bearing mice. The boronate-mAb conjugate (BD-C225) demonstrated a specific accumulation in tumor cells expressing the EGFR in vitro. Nanoparticular entities (i.e., boronated porphyrin complex with a ^{64}Cu isotope or a liposome for a carborane-containing cholesterol derivative bearing a GdIII complex) were

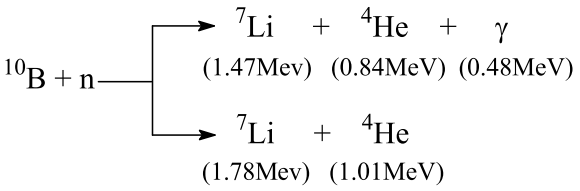


Fig. 6.9 Basic principles of boron neutron capture therapy

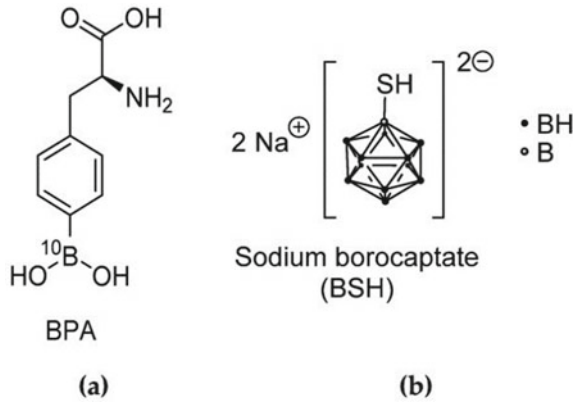


Fig. 6.10 The two compounds currently used in clinical applications for BNCT **a** ^{10}B-p-boronophenylalanine (BPA). **b** Sodium mercaptoundecahydro-closo-dodecaborate (BSH)

used without satisfying tumor uptake for BNCT. These results indicate the need for further optimization of the shape and size of the gold nanoparticles. Moreover, a future approach will involve Omics Technologies, combined with computational tools allowing the development of the so-called Systems Medicine. In particular, BNCT could take advantage of the methodological setups of molecular profiling to improve the understanding of the effects of novel compounds and their combination with neutron radiation. The most relevant aspect emerging from the work here described is the increasing effort toward new theranostic agents that may help to create breakthroughs in the BNCT field (Figs. 6.9 and 6.10).

6.6 Radiotherapy

Radiotherapy, also known as radiation therapy, is a cancer treatment that uses focused radiation to kill cancer cells or damage them so they cannot grow or spread. Different forms of radiotherapy may use different kinds of radiation including X-rays, gamma rays, or proton beams.

Radiotherapy uses radiation—rays of very powerful energy—to kill cancer cells in a specific area. It is an effective treatment for many cancers, but certain cancers respond better to radiation, for example, cancers of the head and neck.

Radiotherapy is a localized cancer treatment. This means that it targets only the area affected by cancer. The medical team will plan the treatment to minimize damage to healthy, cancer-free cells and organs around the cancer.

Like other cancer treatments, radiotherapy can be used in different ways:

a. Curative radiotherapy is used to cure cancer or send it into remission (making it undetectable for a long time).
b. Adjuvant or neo-adjuvant radiotherapy is used before, after, or together with other cancer treatments, such as surgery and chemotherapy, to make the treatments more effective.
c. Palliative radiotherapy does not aim to cure cancer but is used to decrease pain or other symptoms associated with cancer by making cancer smaller or stopping it from spreading.

Radiotherapy may be given in a few different ways:

External beam radiotherapy is administered from outside the body using equipment that sends out radiation beams. When receiving this treatment, patients will sit or lie on a special bed underneath the machine. Patients will need to stay very still so the radiation only affects the area around their cancer. The medical team will make sure the patient is in exactly the right position each time before starting the machine. Depending on the area being treated, patients may be supported with boards, wedges, beanbags, or a special face mask. Radiotherapy usually only takes a few minutes in each session and it does not hurt.

Treatment is usually given on an outpatient basis, meaning that patients can go home between sessions. Sessions are often scheduled daily from Monday to Friday, with a break over weekends.

Internal beam radiotherapy uses small devices such as wires, needles, or pellets that have a sealed radiation source inside them. These are inserted inside the patient's body, close to or inside cancer, to give off radiation and kill the cancer. The patient may have a local anesthetic to numb the area or receive a general anesthetic while the devices are inserted. One benefit of this treatment is that it can be given in a specific area—even areas deep inside the patient's body—with minimal effect on healthy cells. The radioactive devices may be left inside the patient's body temporarily or permanently, depending on the dose of radiation being used and the type of cancer being treated.

Radiotherapy itself does not hurt but may have other temporary or permanent side effects. This might happen if radiation damages healthy cells close to the cancer cells being treated. The kinds of side effects patients may experience, and how significant they are, can vary and depend on the patient's general health, the dose of radiotherapy given, the part of the patient's body being treated, and any other cancer treatments patients may be receiving.

Some people who receive radiotherapy feel few side effects or even none and can carry on with everyday activities. Others experience more significant side effects. Usually, people have side effects due to radiotherapy after a few weeks of receiving treatment. They can continue for a while—even after treatment is complete.

6.6.1 Mechanism of Action

Radiation therapy works by damaging the DNA of cancerous cells. This DNA damage is caused by one of two types of energy, photon or charged particle. This damage is either direct or indirect ionization of the atoms which make up the DNA chain. Indirect ionization happens as a result of the ionization of water, forming free radicals, notably hydroxyl radicals, which then damage the DNA.

In photon therapy, most of the radiation effect is through free radicals. Because cells have mechanisms for repairing single-strand DNA damage, double-stranded DNA breaks prove to be the most significant technique to cause cell death. Cancer cells are generally undifferentiated and stem cell-like; they reproduce more than most healthy differentiated cells and have a diminished ability to repair sub-lethal damage. Single-strand DNA damage is then passed on through cell division; damage to the cancer cells' DNA accumulates, causing them to die or reproduce more slowly.

One of the major limitations of photon radiation therapy is that the cells of solid tumors become deficient in oxygen. Solid tumors can outgrow their blood supply, causing a low-oxygen state known as hypoxia. Oxygen is a potent radiosensitizer, increasing the effectiveness of a given dose of radiation by forming DNA-damaging free radicals. Tumor cells in a hypoxic environment may be as much as 2 to 3 times more resistant to radiation damage than those in a normal oxygen environment. Much research has been devoted to overcoming hypoxia including the use of high-pressure oxygen tanks, blood substitutes that carry increased oxygen, hypoxic cell radiosensitizers drugs such as misonidazole and metronidazole, and hypoxic cytotoxins (tissue poisons), such as tirapazamine. Newer research approaches are currently being studied, including preclinical and clinical investigations into the use of an oxygen diffusion-enhancing compound such as trans sodium crocetinate (TSC) as a radiosensitizer.

Charged particles such as the proton, boron, carbon, and neon ions can cause direct damage to cancer cell DNA through high-LET (linear energy transfer) and have an antitumor effect independent of tumor oxygen supply because these particles act mostly via direct energy transfer usually causing double-stranded DNA breaks. Due to their relatively large mass, protons and other charged particles have little lateral side scatter in the tissue—the beam does not broaden much, stays focused on the tumor shape, and delivers a small dose of side effects to the surrounding tissue. They also more precisely target the tumor using the Bragg peak effect. See proton therapy for a good example of the different effects of IMRT and charged particle therapy. This procedure reduces damage to healthy tissue between the charged particle radiation source and the tumor and sets a finite range for tissue damage after the tumor has been reached. In contrast, IMRT's use of uncharged particles causes its energy to damage healthy cells when it exits the body. This exiting damage is not therapeutic, can increase treatment side effects, and increases the probability of secondary cancer induction. This difference is very important in cases where the close proximity of other organs makes any stray ionization very damaging (such as head and neck cancers). This X-ray exposure is especially bad for children, due to their growing bodies, and they have a 30% chance of a second malignancy after 5 years post initial RT.

6.6.2 Teletherapy

Teletherapy is the use of radioactive material, such as ^{60}Co, for the production of an external beam of gamma rays for treatment at a distance from the radioactive source (tele, meaning "at a distance"). The term is historical and in contrast to brachytherapy, in which the radioactive source is placed in or on the treatment volume (brachy, meaning "close"). Gamma rays are emitted from a daughter nucleus formed after the radioactive decay of an unstable parent nucleus. Each gamma ray has a unique energy that relates to the immediately preceding nuclear transformation, and this unique energy can be used to identify the daughter (and therefore the parent). ^{226}Ra, ^{137}Cs, and most commonly ^{60}Co have been used for teletherapy. ^{137}Cs and ^{60}Co are manufactured and became available by neutron activation and as a byproduct of fission after the invention of the nuclear reactor. The use of ^{60}Co as a source of gamma rays for treatment was pioneered by H. E. Johns and represented a major step in obtaining high-energy photons above 1 meV, "megavoltage" photons. At that time, electronic means of photon production from high-energy X-ray tubes were limited to 300 keV maximum because of electrical arcing at higher accelerating potentials. Specialized particle accelerators were required to produce potentials above 300 keV.

1. **Stereotactic Radiation Therapy (SRT)**

Stereotactic Radiation Therapy (SRT), also known as "Stereotactic Radiosurgery, Cyberknife, or Gammaknife," is an advanced type of radiation therapy delivery that uses a variety of specialized technology to precisely delivering a very high dose of radiation to a tumor, while simultaneously protecting and sparing the normal surrounding tissues. With SRT, the total dose of radiation is divided into several smaller doses given over several days.

Like other forms of radiation therapy, stereotactic radiation therapy does not involve the removal of the tumor. Instead, SRT causes the tumor to shrink by causing sufficient damage to the cells of the tumor to make them unable to grow. The damage accomplished through SRT procedures tends to produce results within a few months, indicated by the shrinkage of the mass.

SRT relies on thorough imaging with three-dimensional digital treatment monitoring to deliver extremely accurate and precise radiation dosage. Imaging provides the precise size and shape of the tumor to pinpoint treatment.

The main distinguishing feature of stereotactic radiotherapy treatment, from other types of external radiation therapy, is the division of the daily doses of radiation into fractions. The number of fractions used for a treatment program can vary from between 3 and 30 fractions, depending on the individual situation and circumstances of treatment.

In addition to carefully calculated dosages and targeting, SRT often requires immobilization devices to assist in limiting, monitoring, or adjusting any patient movement during treatment. Immobilization of the head is done through the use of a mask, specifically formed to fit the patient's head, which helps to position the head in the same precise location for each fraction. Other types of molds can be made

to immobilize other body parts as well. This is critical to provide a higher level of accuracy without damaging nearby tissue.

The Benefits of Stereotactic Radiation Therapy are as follows:

a. Painless, non-invasive, and non-surgical.
b. Ideal for well-defined small tumors, especially those that are close to critical organs.
c. Can treat small tumors in the brain, that might otherwise be inoperable.
d. Typically completed in two—eight treatments, in contrast to longer-term traditional radiation regimens.
e. Treatments delivered with extreme accuracy, minimizing harmful side effects to nearby organs.
f. Available as an outpatient option at various Compass locations.

2. **Medical Linear Accelerator (Linac)**

A medical linear accelerator, or linac, is a particular type of machine that produces high-energy X-ray or electron beams for use in radiation therapy. This method of treatment is commonly referred to as "external-beam radiation therapy" because the radiation beams are generated at a distance outside the patient's body.

(1) **How does a linac work?**

(a) Electron acceleration

First, a tungsten filament is heated to a high temperature so that it continuously emits electrons. Some of these electrons are then injected into a long tube called a waveguide where they are accelerated to high (megavoltage, or MV) energies by electromagnetic waves at microwave frequencies. As the electrons accelerate down the waveguide, they are also focused into a narrow beam by magnets. The beam of high-energy electrons emerging from the end of the waveguide is then steered in the direction of treatment delivery.

Before any radiation reaches the patient, however, the narrow electron beam must be modified to produce the type of treatment beam needed. A linac can deliver either an electron beam or a photon beam at a given time; it can't deliver both types of beams at once.

(b) Electron beam generation

If the patient is receiving electron-beam therapy—typically prescribed for certain types of lesions within a few cm of the skin surface—the narrow electron beam is sent through a series of metallic foils which scatter the electrons into a wide beam, and the wide beam is then shaped (or "collimated") by special devices attached to the linac head so that only the part of the patient requiring therapy is irradiated.

(c) Photon (X-ray) beam generation

If the patient is receiving photon-beam therapy, the narrow electron beam is instead directed at a thick metal target to produce a shower of X-rays. (The energies of these X-rays are 15–150 times higher than in a typical chest X-ray exam.) The wide beam of X-rays is then shaped down by a series of thick moveable blocks inside the linac treatment head to irradiate only the part of the patient requiring therapy. The X-ray beam is often then further shaped by a system of thin metal blocks called multi-leaf collimators (MLCs). The MLCs block radiation to prevent healthy tissue near the tumor from being irradiated.

(d) Radiation delivery

Most modern-day linacs are mounted on a gantry that can rotate in a full circle around the patient. Electron-beam treatments are generally delivered with the gantry in a fixed position whereas photon-beam treatments may be delivered either with the gantry at a fixed position or as it rotates. Most linacs can deliver photon and electron beams of various energies, which enables the doctor to choose a beam with the penetrating power most appropriate for treatment. Photon beams penetrate deeper into the patient than electron beams, and higher energies penetrate deeper than lower energies.

(2) **What is the treatment process with a linac?**

In the majority of cases, linacs are used to deliver a computerized treatment plan which is prepared in advance. After a medical doctor (radiation oncologist) prescribes a course of radiation treatment, a dosimetrist or medical physicist creates a plan on a computer to meet the prescription. The radiation oncologist then examines and approves the plan, and a medical physicist reviews and performs safety checks for the plan. Once the plan is deemed satisfactory it is transferred to linac through a computer network. The patient is set up on the treatment table by radiation technology therapists (RTTs) and, using marks on the patient's body and/or X-ray imaging devices, moved into a position that corresponds to the computerized treatment plan. When the patient is in the correct position, the RTTs can direct the linac to deliver the programmed treatment plan.

The number of treatment sessions (which can be referred to as "fractions") and total radiation dose that a patient receives depends on the tumor type, the amount of dose tolerated by organs surrounding the tumor nearby, and the goal of treatment. The radiation for a single treatment session can often be delivered within a few minutes, but the total time for each treatment will vary depending on the time needed for patient set-up, the treatment method, and the total radiation dose delivered.

6.6.3 Brachytherapy

Brachytherapy is radiation treatment that is given directly to the patient's body. It is placed as close to cancer as possible. The radiation is given using tiny devices such

as wires, seeds, or rods filled with radioactive materials. These devices are called implants.

Brachytherapy lets doctors use a higher total dose of radiation over a shorter time than is possible with external beam therapy. The radiation dose is focused on the cancer cells and does less damage to the nearby normal cells.

This treatment may be done along with external beam therapy to help destroy tumor cells for certain types of cancer. It is often used in the treatment of the following cancers: breast, cervix eye, head and neck, prostate, uterus, and vagina. However, the therapy may also be used to treat many other types of cancers.

Brachytherapy can be given in 3 ways:

a. Intracavitary treatment. The implants are placed inside body cavities such as the vagina, uterus, or breast.
b. Interstitial treatment. The implants are placed directly into the tumor and may stay in permanently.
c. Unsealed internal radiation therapy. A medicine with radioactive materials is injected into a vein or a body cavity.

Brachytherapy implant placement may be either permanent or temporary:

a. Permanent brachytherapy. This is also called low-dose rate brachytherapy. Permanent brachytherapy uses implants called pellets or seeds. These implants are very small, about the size of a grain of rice. A doctor inserts the seeds directly into a tumor with thin, hollow needles. The seeds are left in place after the radiation has been used up. Their small size causes little or no discomfort.
b. Temporary brachytherapy. In temporary brachytherapy, implants are removed after the treatment has ended. Implants, such as hollow needles, catheters (hollow tubes), or balloons filled with fluid, are inserted into or near cancer for a period of time, then removed. Either high-dose or low-dose brachytherapy may be used (Fig. 6.11).

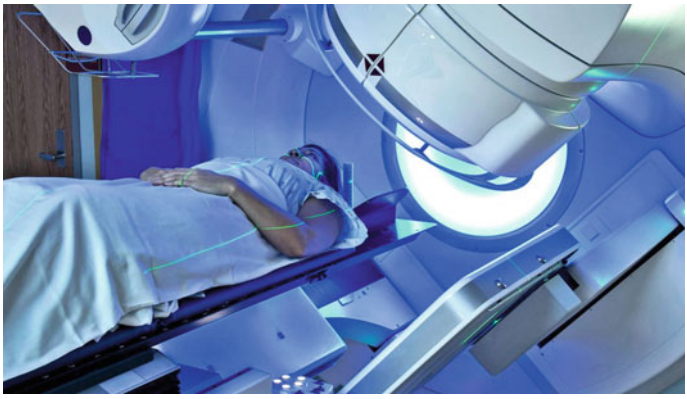


Fig. 6.11 Radiation therapy

6.7 Application Prospect of Nuclear Technology in Medicine

Nuclear medical devices are constantly being improved and updated in developed countries and gradually popularized in developing countries.

The continuous updating and expanding application of advanced medical imaging instruments such as PET, SPECT, PET/CT, and SPECT/CT, as well as the continuous development of new radiological diagnostic and therapeutic drugs, has provided a strong impetus for the development of nuclear medicine.

Nuclear medical imaging mainly provides functional and metabolic information, and it is far inferior to CT in the display of anatomical morphology. Therefore, the fusion of nuclear medical images and CT images led to the emergence of SPECT/CT and PET/CT, which brought nuclear medical images into a new era. PET/CT shows the powerful advantages of fused images, and also heralds the development direction of medical imaging. MRI has better soft tissue contrast and sub-millimeter spatial resolution than CT. Its detection of soft tissue lesions such as the brain, liver, breast, and uterus is significantly better than CT. A PET/MRI scan is a two-in-one test that combines images from a positron emission tomography (PET) scan and a magnetic resonance imaging (MRI) scan. This new hybrid technology harnesses the strengths of PET and MRI to produce some of the most highly detailed pictures of the inside of a patient's body currently available. Doctors use those pictures to diagnose medical conditions and plan their treatment. For example, PET/MRI scans of the brain are useful in the care of Alzheimer's disease, epilepsy, and brain tumors.

There are major benefits to PET/MRI scans:

a. More accurate diagnosis and treatment options: PET/MRI scans of the brain can detect abnormal findings that PET/CT misses in more than 50% of patients scanned.
b. Improved safety from significantly reduced radiation exposure: Compared to PET/CT scans, PET/MRI exposes patients to about 50% less radiation.
c. Convenience of two scans in one: PET/MRI eliminates the need for separate appointments.

Miniaturization is another direction for the development of nuclear medical imaging equipment. Small animal nuclear medical imaging equipment is tomographic imaging equipment specially developed for small animals based on nuclear medicine clinical diagnosis technology, mainly including Micro-PET, Micro-SPECT, and Micro-CT.

Micro-PET and micro-SPECT mainly provide information such as functional metabolism and biodistribution. Micro-CT mainly provides anatomical information, and its images have high spatial resolution and accurate anatomical structure, positioning, and adjacent relationship information.

With the increasing development and maturity of various technologies, small animal imaging equipment has gradually developed from monofunctional to bifunctional imaging equipment (Micro-PET/CT, Micro-SPECT/CT) and trifunctional

(Micro-SPECT/PET/CT) imaging equipment and other multi-functional imaging platforms.

Small animal imaging devices have higher sensitivity and spatial resolution than clinically applied devices. It can perform live and quantitative inspections of small animals to obtain dynamic information in vivo. The obtained experimental results can be directly analogized to the clinic. At the same time, the small animal imaging instrument breaks through the traditional experimental method of killing experimental animals at different time points for measurement, without sacrificing a large number of experimental animals. This shortens the experimental period and provides new methods for biomedical research.

Nuclear medical imaging has gradually transformed into a fusion of complementary advantages of various imaging technologies, which can significantly improve the level of nuclear medicine diagnosis and treatment.

The research and development of SPECT radiopharmaceuticals with a focus on ^{99m}Tc continued around the three diseases of brain, myocardium, and tumor.

The distribution of radiopharmaceuticals in different organs in the body is regulated by changing the valence state of the radionuclide and the characteristics of the ligand group. The specific binding of the labeled targeting molecule to the receptor can also be used to direct the radionuclide to the lesion site, which significantly improves the diagnostic effect.

The research of brain imaging agents is mainly based on receptors related to neurological and psychiatric diseases, such as dopamine receptor imaging agents, 5-HT receptor imaging agents, opioid receptor imaging agents, AD plaque imaging agents, etc.

The research on myocardial imaging agents mainly focuses on hypoxic imaging agents, atheromatous plaque imaging agents, and thrombus receptor imaging agents for the diagnosis of tumors and ischemic tissues. The research on tumor imaging agents goes deep into radionuclide-labeled peptides, tumor receptor imaging, tumor multidrug resistance imaging, and regulatory blockade research. At the same time, the research on imaging agents of inflammation and infection receptors has gradually attracted the attention of researchers.

The development of radiopharmaceuticals for PET imaging is the main development direction of imaging agents in nuclear medicine in the future. The focus of research will continue to focus on ^{18}F, ^{11}C, etc. At the same time, researchers will continue to develop new methods and new technologies for the automated and rapid synthesis of such drugs. In addition, the development of new metal PET nuclide generators, such as ^{62}Zn-^{62}Cu generator, ^{68}Ge-^{68}Ga generator, etc., and the development of corresponding technologies will also continuously improve the diagnostic quality of nuclear medicine, and even expand its diagnostic field.

Excellent therapeutic radiopharmaceuticals labeled with ^{131}I, ^{188}Re, ^{90}Y, and ^{177}Lu are being intensively researched and developed. Targeted therapy radiopharmaceutical research and evaluation techniques are booming. New types of radiopharmaceuticals such as nano-drugs and magnetically guided drugs are being promoted and applied. The development and research of new therapeutic nuclides such as ^{165}Dy, ^{166}Ho, ^{169}Er, ^{161}Tb, ^{211}At, ^{225}Ac, and their labeled complexes are also in full swing.

All of these will greatly promote the rapid development of nuclear medicine technology, and further promote the seamless connection of radiological diagnosis and treatment, adding fresh impetus to the continuous development of nuclear medicine.

Diseases have been classified into six levels: gene abnormality, gene expression, metabolic alteration, dysfunction, structural compensation, and symptoms. The earlier a disease is diagnosed, the easier it is to treat. The application of nuclear medicine at the genetic level can provide accurate diagnoses of diseases and improve the level of treatment. The combination of nuclear medicine and molecular biology technology has created a new branch of nuclear medicine—molecular nuclear medicine.

It is the application of nuclear medicine tracer techniques to study diseases at the molecular level. It can detect changes in the density and function of receptors in diseased tissue, abnormal gene expression, and changes in biological metabolism and cell signaling. Thus, it can provide molecular-level information for clinical diagnosis, treatment, and disease research. As far as imaging technology is concerned, molecular nuclear medicine is no longer limited to receptor imaging. It has been extended to antisense nucleic acid imaging, transduction gene expression imaging, multidrug resistance imaging, apoptosis imaging, etc. In the research of receptors, genes, antigens, antibodies, enzymes, neurotransmitters, and various biologically active substances, nuclear medicine is one of the irreplaceable methods. In particular, cardiac nuclear medicine and nerve conduction nuclear medicine will receive more attention from the nuclear medicine community in the future. Meanwhile, nuclear medical imaging technology from the molecular level to the sub-molecular level will enable the clear diagnosis of many subclinical diseases and hidden genetic diseases, indicating that molecular nuclear medicine has broad prospects for development.

Currently, although the application of molecular nuclear medicine in tumor clinical is not mature, it is an important development direction. Receptor imaging has been paid attention to and developed, and gene imaging needs further study in the future. In particular, gene imaging, as clinical gene therapy matures, can be used to observe its transgenic expression to monitor its effectiveness and success rate. Application of positron labeling drugs, PET imaging, and interventional gene imaging will play a greater role.

In recent years, with the rapid development of precision radiotherapy, various stereotactic radiosurgery techniques are gradually replacing traditional radiotherapy techniques. Stereotactic radiosurgery techniques include X-knife, gamma knife, three-dimensional conformal radiotherapy (3D-CRT), intensity modulated radiation therapy (IMRT), etc. The four-dimensional conformal radiotherapy technology that can solve the problems of organ movement, anatomy, and tumor volume change during radiotherapy is also developing. Meanwhile, neutron and proton therapy has been carried out in a few countries around the world. Bioconformal radiotherapy technology is also developing in exploration.

Nuclear medicine will play an important role in cancer prevention and research in the past, present, and future so that the research and development of its related fields continue to enter a new era.

Exercise

1. Compare the characteristics of radionuclides for diagnosis and radionuclides for treatment.
2. Briefly describe the classification and characteristics of emission computed tomography.
3. What are the main preparation methods for radionuclide markers? And try to illustrate.
4. What conditions are required to meet as an ideal brain perfusion imaging drug?
5. What are therapeutic radiopharmaceuticals. What are the main categories of such drugs?

Bibilography

Almeida-Parra, Z., Peñalver, M., & Mendez, L. E. (2006). Cervical carcinoma. In *Clinical gynecology* (pp. 651–663). https://doi.org/10.1016/B978-0-443-06691-7.50049-2

Almuhaideb, A., Papathanasiou, N., & Bomanji, J. (2011). 18F-FDG PET/CT imaging in oncology. *Annals of Saudi Medicine, 31*(1), 3. https://doi.org/10.4103/0256-4947.75771

Ayesa, S. (2021). Renal imaging in nuclear medicine. *Radiopaedia.Org*. https://doi.org/10.53347/RID-91098

Badria, F. A. (2021). Radiopharmaceuticals: On-going research for better diagnosis, therapy, environmental, and pharmaceutical applications. *Radiopharmaceuticals—Current Research for Better Diagnosis and Therapy*. https://doi.org/10.5772/INTECHOPEN.99204

Bauer, A., Holschbach, M. H., Meyer, P. T., Boy, C., Herzog, H., Olsson, R. A., Coenen, H. H., & Zilles, K. (2003). In vivo imaging of adenosine A1 receptors in the human brain with [18F]CPFPX and positron emission tomography. *NeuroImage*, *19*(4). https://doi.org/10.1016/S1053-8119(03)00241-6

Bressan, R. A., & Pilowsky, L. S. (2000). Imaging the glutamatergic system in vivo—Relevance to schizophrenia. *European Journal of Nuclear Medicine, 27*(11). https://doi.org/10.1007/s002590000372

Chaturvedi, S., & Mishra, A. K. (2016). Small molecule radiopharmaceuticals—A review of current approaches. *Frontiers in Medicine*, *3*(FEB), 5. https://doi.org/10.3389/FMED.2016.00005/BIBTEX

Doonan, M. (2020). Hepatobiliary imaging. *Journal of Nuclear Medicine Technology, 48*(4), 304–310. https://doi.org/10.2967/JNMT.120.257436

Erwin, W. D., & Esmaeli, B. (2009). Estimation of yttrium-90 Zevalin tumor-absorbed dose in ocular adnexal lymphoma using quantitative indium-111 Zevalin radionuclide imaging. *Nuclear Medicine Communications, 30*(9), 681–686. https://doi.org/10.1097/MNM.0B013E32832A6E4D

Fan, Y., Lu, M., Yu, X. A., He, M., Zhang, Y., Ma, X. N., Kou, J., Yu, B. Y., & Tian, J. (2019). Targeted myocardial hypoxia imaging using a nitroreductase-activatable near-infrared fluorescent nanoprobe. *Analytical Chemistry, 91*(10), 6585–6592. https://doi.org/10.1021/ACS.ANALCHEM.9B00298

Frost, J. J., Wagner, H. N., Dannals, R. F., Ravert, H. T., Links, J. M., Wilson, A. A., Burns, H. D., Wong, D. F., Mc Pherson, R. W., Rosenbaum, A. E., Kuhar, M. J., & Snyder, S. H. (1985). Imaging opiate receptors in the human brain by positron tomography. *Journal of Computer Assisted Tomography*, *9*(2). https://doi.org/10.1097/00004728-198503000-00001

Fukmitsu, N., Ishii, K., Kimura, Y., Oda, K., Sasaki, T., Mori, Y., & Ishiwata, K. (2005). Adenosine A1 receptor mapping of the human brain by PET with 8-dicyclopropylmethyl-111C-methyl-3-propylxanthine. *Journal of Nuclear Medicine*, *46*(1).

Gratz, M. J., Stavrou, S., Kuhn, C., Hofmann, S., Hermelink, K., Heidegger, H., Hutter, S., Mayr, D., Mahner, S., Jeschke, U., & Vattai, A. (2018). Dopamine synthesis and dopamine receptor expression are disturbed in recurrent miscarriages. *Endocrine Connections, 7*(5), 727–738. https://doi.org/10.1530/EC-18-0126

Heiss, W. D., & Herholz, K. (2006). Brain receptor imaging. *Journal of Nuclear Medicine, 47*(2).

Hochberg, A. R., & Young, G. S. (2012). Cerebral perfusion imaging. *Seminars in Neurology, 32*(4), 454–465. https://doi.org/10.1055/S-0032-1331815

Ishiwata, K., Mizuno, M., Kimura, Y., Kawamura, K., Oda, K., Sasaki, T., Nakamura, Y., Muraoka, I., & Ishii, K. (2004). Potential of [11C]TMSX for the evaluation of adenosine A 2A receptors in the skeletal muscle by positron emission tomography. *Nuclear Medicine and Biology*, *31*(7). https://doi.org/10.1016/j.nucmedbio.2004.06.003

Lin, M., Paolillo, V., Le, D. B., Macapinlac, H., & Ravizzini, G. C. (2021). Monoclonal antibody based radiopharmaceuticals for imaging and therapy. *Current Problems in Cancer*, *45*(5). https://doi.org/10.1016/J.CURRPROBLCANCER.2021.100796

Mack, J. T. (2007). Ibritumomab tiuxetan. In *XPharm: The comprehensive pharmacology reference* (pp. 1–8). https://doi.org/10.1016/B978-008055232-3.63712-2

Malik, T. N., Cartailler, J. P., & Emeson, R. B. (2021). Quantitative analysis of adenosine-to-inosine RNA editing. In *Methods in molecular biology* (Vol. 2181). https://doi.org/10.1007/978-1-0716-0787-9_7

Morgan, R. B. (2018). Myocardial perfusion imaging. In *Encyclopedia of cardiovascular research and medicine* (pp. 404–424). https://doi.org/10.1016/B978-0-12-809657-4.10958-5

Owen, S. C., Doak, A. K., Ganesh, A. N., Nedyalkova, L., McLaughlin, C. K., Shoichet, B. K., & Shoichet, M. S. (2014). Colloidal drug formulations can explain 'bell-shaped' concentration-response curves. *ACS Chemical Biology, 9*(3), 777–784. https://doi.org/10.1021/CB4007584

Rizzieri, D. (2016). Zevalin® (ibritumomab tiuxetan): After more than a decade of treatment experience, what have we learned? In *Critical reviews in oncology/hematology* (Vol. 105). https://doi.org/10.1016/j.critrevonc.2016.07.008

Sadzot, B., Price, J. C., Mayberg, H. S., Douglass, K. H., Dannals, R. F., Lever, J. R., Ravert, H. T., Wilson, A. A., Wagner, H. N., Feldman, M. A., & Frost, J. J. (1991). Quantification of human opiate receptor concentration and affinity using high and low specific activity [11C]diprenorphine and positron emission tomography. *Journal of Cerebral Blood Flow and Metabolism*, *11*(2). https://doi.org/10.1038/jcbfm.1991.52

Sauerwein, W. A. G., Wittig, A., Moss, R., & Nakagawa, Y. (2012). Neutron capture therapy: Principles and applications. *Neutron Capture Therapy: Principles and Applications, 9783642313349*, 1–553. https://doi.org/10.1007/978-3-642-31334-9/COVER

Schwartz, J. B. (2004). Introduction to drug metabolism. *Principles of Gender-Specific Medicine, 2*, 825–829. https://doi.org/10.1016/B978-012440905-7/50346-7

Sheth, S., Brito, R., Mukherjea, D., Rybak, L. P., & Ramkumar, V. (2014). Adenosine receptors: expression, function and regulation. *International Journal of Molecular Sciences, 15*(2), 2024. https://doi.org/10.3390/IJMS15022024

Sun, X., Li, Y., Liu, T., Li, Z., Zhang, X., & Chen, X. (2017). Peptide-based imaging agents for cancer detection. *Advanced Drug Delivery Reviews, 110–111*, 38–51. https://doi.org/10.1016/J.ADDR.2016.06.007

Taegtmeyer, H., & Dilsizian, V. (2021). Imaging cardiac metabolism. In *Atlas of nuclear cardiology* (pp. 369–401). https://doi.org/10.1007/978-3-030-49885-6_9

Taylor, A. (1982). Quantitation of renal function with static imaging agents. *Seminars in Nuclear Medicine, 12*(4), 330–344. https://doi.org/10.1016/S0001-2998(82)80014-7

Teipel, S. J., Grinberg, L. T., Hampel, H., & Heinsen, H. (2009). Cholinergic system imaging in the healthy aging process and Alzheimer disease. In *Encyclopedia of neuroscience* (pp. 857–868). https://doi.org/10.1016/B978-008045046-9.02041-6

Thomadsen, B., & Miller, R. (2014). Brachytherapy physics. *Comprehensive Biomedical Physics, 9*, 315–381. https://doi.org/10.1016/B978-0-444-53632-7.00926-6

Trandaburu, T., & Trandaburu, I. (2007). Serotonin (5-hydroxytryptamine, 5-HT) immunoreactive endocrine and neural elements in the chromaffin enteropancreatic system of amphibians and reptiles. *Acta Histochemica, 109*(3), 237–247. https://doi.org/10.1016/J.ACTHIS.2006.10.005

Tsang, M. W. K. (2016). Stereotactic body radiotherapy: Current strategies and future development. *Journal of Thoracic Disease, 8*(Suppl 6), S517. https://doi.org/10.21037/JTD.2016.03.14

Turner, P. G., & O'Sullivan, J. M. (2015). 223Ra and other bone-targeting radiopharmaceuticals—The translation of radiation biology into clinical practice. *The British Journal of Radiology*, *88*(1050). https://doi.org/10.1259/BJR.20140752

Villemagne, V. L., Horti, A., Scheffel, U., Ravert, H. T., Finley, P., Clough, D. J., London, E. D., Wagner, H. N., & Dannals, R. F. (1997). Imaging nicotinic acetylcholine receptors with fluorine-18-FPH, an epibatidine analog. *Journal of Nuclear Medicine*, *38*(11).

Waldhoer, M., Bartlett, S. E., & Whistler, J. L. (2004). Opioid receptors. *Annual Review of Biochemistry, 73*, 953–990. https://doi.org/10.1146/ANNUREV.BIOCHEM.73.011303.073940

Wambersie, A., & Gahbauer, R. A. (n.d.). *Medical applications of electron linear accelerators.*

Wells, R. G., Radonjic, I., Clackdoyle, D., Do, J., Marvin, B., Carey, C., Dekemp, R. A., & Ruddy, T. D. (2020). Test-retest precision of myocardial blood flow measurements with 99mTc-Tetrofosmin and solid-state detector single photon emission computed tomography. *Circulation: Cardiovascular Imaging*, *13*, 9769. https://doi.org/10.1161/CIRCIMAGING.119.009769

Yeong, C. H., Cheng, M. hua, & Ng, K. H. (2014). Therapeutic radionuclides in nuclear medicine: Current and future prospects. *Journal of Zhejiang University: Science B, 15*(10). https://doi.org/10.1631/jzus.B1400131

Yuille, D. L. (1979). Cardiac blood pool imaging: a review. In *CRC critical reviews in diagnostic imaging* (Vol. 11(3)).

Zanco, P., Zaroccolo, M., & Ave, S. (2019). Radionuclides diagnostic techniques. In *Critical care nephrology* (3rd ed., pp. 197–204). https://doi.org/10.1016/B978-0-323-44942-7.00036-4

Zhong, L., Li, Y., Xiong, L., Wang, W., Wu, M., Yuan, T., Yang, W., Tian, C., Miao, Z., Wang, T., & Yang, S. (2021). Small molecules in targeted cancer therapy: Advances, challenges, and future perspectives. *Signal Transduction and Targeted Therapy, 6*(1), 1–48. https://doi.org/10.1038/s41392-021-00572-w

Chapter 7
Application of Nuclear Technology in the Environment



Nuclear technology is not only widely used in industry, agriculture, and medicine but has also made rapid development in environmental science and environmental protection. Experimental or pilot studies on the treatment of waste gas, wastewater, and solid waste by nuclear technology have been carried out worldwide, such as the SO_2/HO_x removal by the electron beam. In addition, the qualitative and quantitative analysis of elements in environmental samples by nuclear technology has many irreplaceable characteristics of conventional non-nuclear technologies, such as high sensitivity, accuracy, precision, high resolution (including spatial resolution and energy resolution), non-destructive, and multi-element determination capability, etc. The nuclear analytical techniques adopted mainly include the nuclide tracer technique, nuclide activation analysis, radiation decomposition technique, and isotope measurement technique. Taking the radioactive tracer method as an example, it is widely used in the study of environmental conditions, such as the study of atmospheric diffusion behavior in the environment, the application of ^3H in the analysis of stratigraphic structure, the study of groundwater dynamics, and the analysis of surface water level change.

The application of nuclear technology in the environment can be divided into two categories: irradiation technology and nuclear analytical technique. In the field of environment, irradiation technology is mainly used for the treatment of environmental waste, and nuclear analytical technique is used for the analysis and detection of environmental samples. This chapter will focus on the above two aspects.

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6_7

7.1 Application of Irradiation Technology in the Environment

The irradiation technology uses the interaction between rays and substances. The activated atoms and activated molecules produced by ionization and excitation have a series of physical, chemical, and biological changes with the substance, resulting in the degradation, polymerization, cross-linking, and modification of the substance. In the recent 30 years, irradiation technology has been applied to environmental waste treatment, which provides a new way to purify pollutants that are difficult to be treated by conventional methods.

In terms of environmental protection, irradiation technology uses ionizing radiation exposure to change environmental pollutants, which can achieve the purpose of treatment and reuse. For example, change harmful substances to harmless or useful substances, kill bacteria and pathogens, accelerate the degradation rate of refractory substances, etc. Irradiation treatment is widely applied to the treatment of waste gas, wastewater, and solid waste, and is becoming one of the important means of environmental protection.

Irradiation technology is an emerging environmental treatment technology, its main characteristics are as follows:

(1) Good disinfection effect. It can completely kill harmful microorganisms.
(2) Secondary pollution can be avoided. Most of the irradiation process is carried out at room temperature. Without adding other chemical reagents or catalysts, harmless physical degradation of some chemical pollutants can be achieved by irradiation technology, which generally does not cause secondary pollution to the environment. Since the energy of γ-rays, X-rays and electron beams used for irradiation are lower than the threshold energy of nuclear reactions, no nuclear reactions will occur, and no radioactive contamination caused by induced radioactive substances will be produced.
(3) Problems that are difficult to solve by ordinary methods can be solved. Since the mechanism of irradiation reactions is quite different from that of ordinary chemical reactions, using irradiation technology to deal with problems that are difficult to be solved by ordinary technologies can often get satisfactory results. Examples include the treatment of high polymers, the recycling of polytetrafluoroethylene, the removal of nitrogen oxides from fuel oil and coal combustion exhaust gases, etc.
(4) Safe and reliable in use. The implementation of irradiation technology is very simple, without any manual operation. Modern science and technology can fully ensure the safety of personnel. In addition to the necessary protective barriers, the automatic interlocking system between the radioactive source and the personnel entrance is usually installed. When the entrance is opened, the source will be automatically dropped to the depth of the pool. When the background value of radioactivity in the environment exceeds the allowable level, the source will be immediately shut down, and the dose monitoring and alarm system will automatically signal personnel to leave the site.

(5) Strong adaptability and wide range of applications. Since the intensity and energy of the radioactive source are not affected by any external conditions, there are no special requirements for the external conditions during irradiation. The irradiation process only needs to control the irradiation time, distance, and orientation to control the irradiation dose.
(6) The biggest disadvantage of irradiation technology is that the cost of the source is relatively expensive. In order to ensure the absolute safety of personnel, the equipment is required to have a certain degree of automation, so the capital construction investment is also higher than that of general facilities.

In terms of environment, γ-rays and electron beams are mostly used for radiation treatment. Are carried out using, γ-rays mainly come from reactors or radionuclides produced by the reactor, and electron beams come from electron accelerators. This chapter will mainly introduce several mature applications from the radioactive source irradiation and accelerator irradiation.

7.1.1 Reactors in the Environment

Reactors and radionuclides produced by reactors can be used for the radiation treatment of environmental wastes. The most commonly used radionuclides in the industry are ^{60}Co and ^{137}Cs. The half-life of the ^{60}Co source is 5.26 a. Each decay emits two kinds of γ-rays with energies of 1.17 and 1.33 meV. ^{137}Cs has a half-life of 30 a and does not require frequent source changes in use. The reactor can also be used as an online irradiation source, where the irradiated object is placed in the cooling pond of the reactor. When the dose level at the irradiation point is known, the dose level received by the object can be determined by controlling the irradiation time.

1. **Wastewater treatment**

Nowadays, water pollution is a serious problem that the whole world pays close attention to. With the gradual diversification of production activities, the components of pollutants in wastewater are becoming more and more complex, and the allowable discharge standards for these pollutants are becoming stricter. Therefore, it is urgent to develop an economic, simple, effective sewage treatment technology that can deal with a variety of pollutants. Irradiation technology is a potential wastewater treatment technology, which has broad application prospects.

Radionuclides produced by reactors can be used for the treatment of domestic sewage and industrial wastewater, usually in the form of radioactive sources, such as ^{60}Co sources and ^{137}Cs sources. The basic principle is that water molecules will generate a series of radiolysis products with strong activity under the action of radiation, such as OH, H, H_2O_2, and other free radicals. These products can be decomposed or modified by reacting with organic substances in wastewater and sewage.

The radiation treatment that uses radioactive sources can significantly eliminate total organic carbon (TOC), biological oxygen demand (BOD), and chemical oxygen demand (COD) in urban sewage, and inactivate pathogens in sewage. For wastewater containing azo dyes and anthraquinone dyes, irradiation can completely decolorize them. The removal rate of TOC can reach 80–90%, and that of COD can reach 65–80%. Wastewater containing lignin can be easily degraded by irradiation by γ-ray irradiation under the condition of oxygenation. In addition, radioactive sources can also effectively treat harmful organic substances such as detergents, organic mercury pesticides, plasticizers, nitrosamines, chlorophenols, etc. Combining the radioactive source irradiation technology with common wastewater treatment technologies (e.g. coagulation, activated carbon adsorption, ozone-activated sludge, etc.) has a synergistic effect and can improve the effectiveness of treatment. When combined with the activated carbon adsorption method, the activated carbon can be regenerated by γ-ray irradiation after the organic matter has been adsorbed by the carbon, so as to realize recycling.

In the former Soviet Union, a pilot plant for radiation source irradiation treatment was built to treat the wastewater from the antibiotic plant, with a daily treatment capacity of 15,000 m^3. All indicators of the treated wastewater are better than those of conventional treatment methods. Similar pilot plants have been built in Hungary, Canada, Japan, and other countries.

2. **Solid waste disposal**

Solid waste refers to solid waste and semi-solid waste materials that pollute the environment during production, construction, daily life, and other activities, including domestic waste, industrial solid waste, and agricultural waste.

(1) **Disposal of domestic and industrial wastes**

Russia has designed a technology to treat domestic and industrial wastes by using fast neutron reactors. This technology is realized by building a waste-burning furnace in the nuclear reactor. The domestic and industrial wastes are regularly loaded into the furnace and fall into a slag tank for oxygen blowing, burning, and vaporizing. To maintain the high temperature in the furnace, a small amount of power coal is continuously added to the furnace. When the furnace temperature reaches about 1500 °C, all the wastes will be vaporized, and the part containing minerals will melt in the slag, while the metal will sink to the bottom after melting. The metal at the bottom will be regularly cast into castings and transported out for processing. The slag removed from the furnace is used for processing construction materials. The gas in the furnace, which reaches 1750 °C, is extracted by an extractor and cooled before being used in chemical production. The furnace and the gas in it are cooled by liquid sodium. This liquid sodium circulates between the double walls of the shell of the waste reactor. At the same time, the liquid sodium with s high temperature of up to 500 °C can also provide heat for the steam generator. The steam formed is used to turn the steam turbine generator, and the condensed hot water flows into the boiler

room. In this way, metals, construction materials, chemical products, electricity, and heat can be obtained from waste treatment. According to the tests, one set of fast neutron reactor devices can process 2×10^4 t of domestic and industrial waste in a year, and the power generation is 5 kW, which is self-sufficient.

(2) **Disposal of waste plastic**

In the treatment and disposal of solid waste, waste plastic has always been a thorny problem due to the difficulties in degradation. For example, polytetrafluoroethylene (PTFE) cannot be decomposed by biochemical method, thus it is difficult to be broken mechanically, and a large amount of toxic fluoride is produced during high-temperature treatment, which makes it difficult to be treated.

In Japan, the wax-like powder of polytetrafluoroethylene with different molecular weights was obtained by the combination of γ-ray irradiation and heating and followed by mechanical crushing, which can be used as an excellent lubricant and additive. Chlorinated polyethylene will release 100 times vinyl chloride when it is used, therefore, it is prohibited in some countries. However, after being irradiated by a certain dose of γ-rays, vinyl chloride will not be produced vinyl chloride, thus expanding the area of usage.

Waste plastics can also be induced to degrade by radiation. The early studies on radiation-induced plastic degradation were completed in the 1950s and 1960s. Like rubber, plastic macromolecules are generally decomposed by the breaking of the C–C bond. Radiation-induced degradation produces gaseous, liquid, and solid small molecule products, which can be used as raw materials for appropriate synthetics. As an example, the irradiation-induced degradation of polytetrafluoroethylene (PTFE) has already been briefly discussed above.

In the global consumption of fluorine resin, about 70% is PTFE. PTFE is expensive, its chemical properties are extremely stable and will not degrade in the environment for decades, which has a negative effect on the environment. Therefore, recycling waste PTFE has important economic value and environmental significance. Both γ-rays ($G = 12.8$) and electron beams ($G = 41.2$) can be used to degrade PTFE. To obtain the product share with the required molecular size, during irradiation, the radiation-induced process can be controlled by the dose, dose rate, and temperature used. All kinds of non-degradable products are widely used. For example, perfluoro olefins can be converted into fluorinated surfactants with special properties after irradiation, and can also be oxidized into perfluoro carboxylic acids for special purposes. Perfluoro alkanes, as by-products, can be used as high-quality insulating materials, solvents, and lubricants. And all these conversions can be used as raw materials for synthesis.

(3) **Treatment of sludge**

Sludge is an unavoidable by-product of the wastewater treatment process. The most common wastewater treatment steps are screen filtration, primary sedimentation, biological treatment, secondary sedimentation, and sterilization. Sewage sludge will

be generated during the sedimentation process before and after biological treatment. Sludge contains a lot of energy and biological value, which is an excellent agricultural fertilizer and soil conditioner. However, it cannot be directly used because it contains a lot of pathogens. In 1979, the U.S. Environmental Protection Agency (EPA) issued the CFR257 regulation, which requires the control of pathogens in sludge. In September 1982, the agency proposed in the supplementary environmental impact report that the sludge in the sewage systems is a useful resource. Conventional methods, such as composting, pasteurization, or chemical treatment, are not very effective in sludge treatment, and it is difficult to realize industrialization. Radiation technology can overcome the shortcomings of commonly used treatment methods and is widely considered a promising method for sludge treatment in the world. Both γ-radioactive sources and electron beam irradiation can be used for sludge treatment.

The advantages of radiation treatment of sludge are: (1) It can kill bacteria and viruses in sludge, and the disinfection effect is more reliable than heat treatment; (2) It does not destroy the organic nitrogen compounds in the sludge, which will not reduce the fertility of sludge and produce unpleasant odor (more nitrogen is lost in the pasteurization treatment, and the fertility of sludge will be reduced); (3) It can prevent the germination of weed seeds in the sludge, but will not affect the germination of normal seeds; (4) The treatment temperature is lower (25–30 °C), reducing corrosion to plant equipment; (5) The irradiated sludge has good dewatering performance, which can save chemical flocculants and some corresponding equipment. After irradiation and sterilization, the sludge can be directly used as fertilizer in farmland.

Many industrial developed countries have made positive progress in the development of sludge radiation treatment technology. The former Federal Republic of Germany built the world's first sludge irradiation treatment experimental plant in Munich in 1973, which applied ^{60}Co as the radioactive source. In 1983, the ^{137}Cs radioactive source was additionally installed. The plant used instantaneous strong γ-radiation to kill bacteria in sludge. The sludge treated by radiation still had the original nutrients, which could be used as fertilizer, whose performance is far better than that of the sludge treated by composting and pasteurization. It is reported that the daily wastewater treatment capacity of the plant was 150 m^3, and the treatment cost was about 4.4 Deutsche marks per cubic meter. Unfortunately, the plant stopped operation in the spring of 1993 due to the need for major repair. At that time, the new German law prohibited the further use of sewage sludge in grassland and feed production areas. This unit was the only full-scale sludge irradiation plant before 1993. After 20 years of operation, about half a million cubic meters of sludge have been treated, which provides valuable experience for research in this field. Sludge irradiation units were also established in the United States, India, Australia, Sandia, and other countries, but most of the units have only operated for 2–4 years, and no further full-scale sludge irradiation units have emerged.

(4) **Others**

Cellulose is the main component of urban waste and agricultural waste. In Japan, wood chips, wastepaper, and rice straw were treated by irradiation to treat to obtain alcohol through saccharification and fermentation. In the United States, this kind of cellulose was irradiated with acid to obtain glucose, with a recovery rate of up to 56%.

Spoiled food can be used as animal feed after irradiation.

7.1.2 Accelerators in the Environment

Various low-energy accelerators are widely used in various fields of the national economy. In industry, it is used for activation analysis, ion implanters of large accelerators, irradiation modification, non-destructive testing, etc. In agriculture, it is used for variety improvement, disease eradication, food preservation, and so on. In medical treatment, it is used for cancer treatment, irradiation disinfection, production of short-lived isotopes, etc. In national defense, high pulse power accelerators can be used as X-ray simulation sources. In terms of environmental protection, the intense beam generated by the accelerator is used for the desulfurization and denitrification of coal-fired flue gas.

High-energy electron accelerators can produce high-energy electrons of 1–10 meV energy, and the high-energy electrons have a certain penetrating power. When the electron beam passes through the thin dispersed fluid, part of it is reflected back into the fluid for irradiation, increasing the dose level of the irradiated body. The accelerator can be turned off immediately when not in use. Irradiation treatment using the electron beam generated by the accelerator is becoming one of the most important means of environmental protection. The electron beam technology is widely applied to the irradiation treatment of waste gas, wastewater, and solid waste.

The irradiation of high-energy electron beams generated by electron accelerators can lead to physical, chemical, and biological effects on some substances and can effectively kill bacteria, viruses, and pests. This technology has been widely used in material modification and new material production in industrial production, environmental protection, processing and production, sterilization and disinfection of medical, and health supplies and food sterilization and preservation. Like cobalt source irradiation, it has the characteristics of normal temperature, no damage, no residual, environmental protection, low energy consumption, simple operation, high degree of automation, and is suitable for large-scale industrial production. Compared with the cobalt source (radiation efficiency of about 20%), the biggest advantage of this technology is that the irradiation beam is concentrated and oriented, the energy is fully utilized, the irradiation efficiency is more than 80%, and no radioactive waste is produced. With the soaring price of cobalt sources and the rising cost of waste source disposal, electron accelerator irradiators have obvious advantages in price and economy. It is a challenging and pioneering work worldwide to build a high-energy

electron irradiation center with a high-power electron accelerator with an energy of 10 meV to carry out research on irradiation technology and new areas of irradiation while developing the irradiation processing industry. It has obvious socio-economic benefits and immeasurable potential value and is one of the most concerned high-tech fields in the world.

1. **Waste gas treatment**

The application of accelerators in waste gas treatment is mainly for the treatment of harmful flue gas. SO_2 and NO_x are the main pollutants in the atmosphere, which mainly come from the flue gas discharged from the chimney. The common flue gas desulphurization and denitrification technologies mainly include the solid phase adsorption and regeneration technique, the wet simultaneous desulphurization and denitrification technique, the absorbent injection method, etc. Most of the technologies encounter difficulties of high costs or complex devices, such as desulphurization by the lime spray, NO_x removal by acid and alkali absorption, or catalytic reduction. The high-energy radiation chemical method is a new type of flue gas desulfurization and denitrification technology, which is mainly divided into electron beam ammonia (EBA) and pulsecorona plasma chemical process (PPCP), of which the electron beam irradiation method is well developed. Electron beam irradiation can remove SO_2 and NO_x from the flue gas, which is helpful to purify the atmosphere and prevent the formation of acid rain. At the same time, nitramine, thiamine, and other by-products can be obtained, which can be used as fertilizer, reduce the difficulty and cost of operation, and produce almost no secondary wastewater.

In the 1990s, accelerators manufactured by the Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences were supplied to Poland and Japan to purify smog. The inferior coal in Poland produced a large amount of toxic oxide of sulfur and nitrogen when burned. When the smoke was irradiated, all the oxides turned into solid precipitates, which can be used as fertilizer. In Japan, Russian-made accelerators have also been used to purify the smoke generated when burning garbage.

(1) Electron beam irradiation for desulfurization and denitrification

① Advantages of electron beam irradiation

Since 1972, Japan has carried out extensive basic research and semi-industrial experiments on the removal of SO_2 and NO_x from flue gas by electron beam irradiation. After more than 30 years of research and development, it has gradually moved towards industrialization from small-scale experiments, pilot-scale experiments, and industrial demonstrations. The basic research, semi-industrial experiment, and industrial experiment that have been started in Japan, Germany, Italy, Poland, the United States, and other countries show that the electron beam irradiation technology has the following advantages: (a) Desulfurization and denitrification can be achieved at the same time, with a desulfurization rate of more than 90% and a denitrification

rate of more than 80%; (b) No wastewater and slag will be produced; (c) No catalyst required; (d) The system is simple, easy to operate, and the process is easy to control; (e) It has good adaptability and load tracking for flue gas with different sulfur content and change of flue gas volume; (f) The by-product of the reaction is a mixture of ammonium sulfate and ammonium nitrate, which can be used as fertilizer; (g) The cost of desulfurization and denitrification is more economical than traditional methods. Disadvantages include high electron beam dose demand, large power demand, high operating costs, and the need to filter aerosol after irradiation.

In addition, electron beam irradiation can effectively purify other industrial waste gases, such as volatile organic compounds (VOCs), automobile exhaust, odorous and toxic gases, and incinerator waste gases. Electron beam treatment of waste gas involves many different physical and chemical mechanisms, such as energy absorption, gas-phase reaction, particle formation, gas–solid interaction, etc.

② Reaction mechanism of electron beam irradiation

The high-energy electron beam of 500–800 keV can be formed by cathode emission and electric field acceleration. When these electron beams irradiate flue gas, the radiation chemical reaction will be generated to produce free radicals such as OH, O, and H_2O, which can react with SO_2 and NO_x and generate H_2SO_4 and HNO_3. Before irradiation, stoichiometric ammonia is added to the flue gas in advance, and the generated atomized H_2SO_4 and HNO_3 interact with NH_3 flowing into the reactor to generate $(NH_4)_2SO_4$, NH_4NO_3, and other by-products. These by-products can be collected by electrostatic precipitation and directly used as fertilizer. After the flue gas is irradiated by the electron beam, the main reaction processes are as follows:

(a) Free radical generation: The coal combustion flue gas generally consists of N_2, O_2, water vapor, CO_2, and other major components, and trace components such as SO_2 and NO_x. When the electron beam is used for irradiation, most of the energy of the electron beam is absorbed by N_2, O_2, and water vapor to generate a large number of highly-reactive free radicals.
(b) Oxidation of SO_2 and NO_x: SO_2 and NO_x are oxidized by active species such as free radicals to produce sulfuric acids and nitric acids.
(c) Generation of ammonium sulfate and ammonium nitrate: Sulfuric acid and nitric acid neutralize with pre-injected ammonia to produce aerosol particles of ammonium sulfate and ammonium nitrate. If there is still unreacted SO_2 and NH_3, the thermochemical reaction will continue on the surface of the particles to produce ammonium sulfate.

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4 \tag{7.1}$$

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \tag{7.2}$$

$$SO_2 + 2NH_3 + H_2O + \frac{1}{2}O_2 \rightarrow (NH_4)_2SO_4 \tag{7.3}$$

③ Treatment process of electron beam irradiation

The experimental device consists of five main parts: flue gas parameter regulation system, accelerator irradiation treatment system, ammonia dosing device, by-product collection device, and monitoring and control system. Figure 7.1 shows the diagram of the technological process of the industrial test device for electron beam irradiation flue gas desulfurization and denitrification. The process consists of flue gas cooling, ammonia adding, electron beam irradiation, and by-product collection. The flue gas of about 130 °C discharged from the boiler enters the cooling tower after electrostatic precipitation. In the cooling tower, the flue gas is reduced to a temperature suitable for desulfurization and denitrification (~ 65 °C) by spraying cooling water. The dew point of flue gas is usually 50 °C, so the cooling water is completely gasified in the tower, and generally no wastewater will be generated. The flue gas after cooling and humidification is sent to the reactor, and then stoichiometric ammonia is injected into the reactor according to the SO_2 and NO_x concentration and the set removal rate. The flue gas is irradiated by the electron beam in the reactor to oxidize the SO_2 and NO_x to generate sulfuric acid and nitric acid and neutralize with the injected ammonia to produce ammonium sulfate and ammonium nitrate. The irradiated flue gas is sent to the by-product collector, and the dry electrostatic precipitator is used to collect and recover ammonium sulfate and ammonium nitrate in the flue gas. The purified flue gas is boosted by an induced draft fan and discharged into the atmosphere from the chimney.

(2) Pulsecorona plasma chemical process

The basic principle of the pulsecorona plasma chemical process (PPCP) is similar to that of the electron beam ammonia (EBA) method. Both of them use high-energy electrons to activate, ionize, or cleave gas molecules such as H_2O and O_2 in the flue

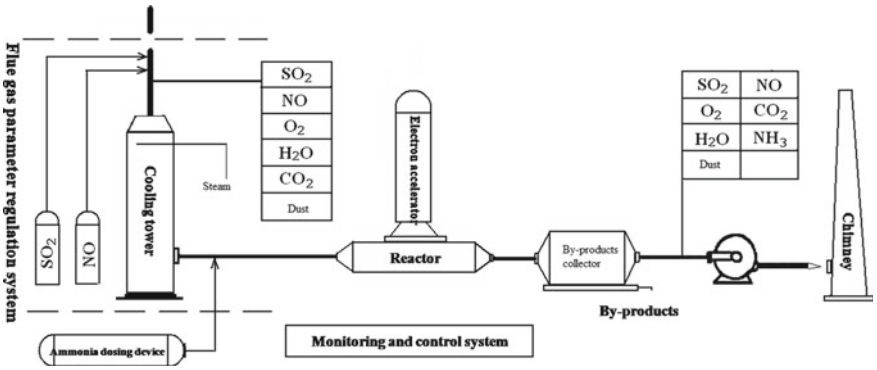


Fig. 7.1 Technological process of the industrial test device for electron beam irradiation flue gas desulfurization and denitrification

gas to produce strong oxidizing free radicals, carry out plasma catalytic oxidation of SO_2 and NO_x, respectively generate SO_3 and NO_x or corresponding acids, and generate corresponding salts and settle down in the presence of additives. The difference between the two lies in the different sources of high-energy electrons. The EBA method is obtained by cathode electron emission and external electric field acceleration, while the PPCP method is generated by the corona discharge itself. It utilizes the combination of a high-voltage power supply (with the rise time of 10–100 ns, the trailing time of 100–500 ns, the peak voltage of 100–200 kV, and the frequency of 20–200 Hz) with a steep rising front and narrow pulse and the load corona electrode system (corona reactor) of the power supply to generate streamer corona plasma between the corona and the air gap of the corona reactor electrode, so as to oxidize and remove SO_2 and NO_x.

The advantage of the PPCP method is that it can remove dust at the same time. Studies have shown that the dust in the flue gas is beneficial to the improvement of the desulfurization and denitrification efficiency of the PPCP method. Therefore, PPCP is the most attractive flue gas treatment method as it integrates the removal of three pollutants and has lower energy consumption and cost than EBA.

2. **Wastewater treatment**

Electron beam irradiation can treat water and wastewater. Irradiation produces active substances in the water, for instance, OH bases can gasify and decompose any organic pollutant in water. The scale of wastewater treatment is decided under certain economic conditions. The appropriate electron beam irradiation device should be selected to ensure that the flow rate of treated wastewater is uniform and that a sufficient dose is received. Factors to be considered include the energy distribution of radiation, the penetration ability in the water, the geometric shape of the volume of radiation-water interaction, etc.

As early as in the former Soviet Union, scientists had purified the groundwater polluted by rubber production wastes in Voronezh. After 10 years of effort, the groundwater of around 30 km was purified.

Irradiation can also effectively kill microorganisms in water. The method of chlorine sterilization for secondary sewage treatment can kill microorganisms, but it will produce toxic chlorinated organic substances such as trichloromethane. Electron beam irradiation can also effectively inactivate bacteriophages. With a smaller dose (e.g. 0.25–1 kGy), ordinary bacteria (such as Escherichia coli, Salmonella, etc.) can be killed by 90%. With a dose of 10 kGy, all bacteria will be eliminated. Using electron beam irradiation instead of chlorine sterilization for secondary wastewater treatment will not produce toxic chlorinated organic substances, and can also carry out effective sterilization. The sterilization effect depends on the thickness of the water layer in the irradiated area, the property of the water, and the effect of different types of bacteria on the sensitivity to radiation. The sterilization efficiency of electron beam irradiation also depends on the penetration ability of electrons in water (see Figs. 7.2 and 7.3). In a flowing system, due to the strong mixing of liquid, the survival curve of irradiated bacteria is more effective than that under stable conditions. While

killing microorganisms, liquid waste can realize discoloration and deodorization, and COD will be greatly reduced.

Due to the continuous expansion of the production of synthetic surfactants and their application in industry and life, the problem of sewage purification is becoming increasingly complex, and the pollution of reservoirs is also increasing accordingly.

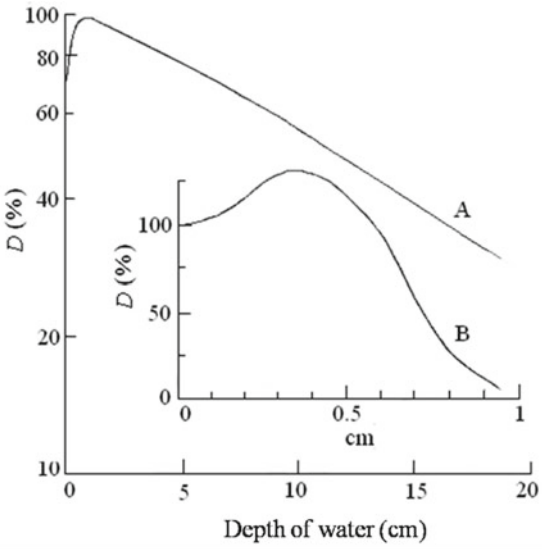


Fig. 7.2 Depth dose D as a function of water depth. **a** γ-rays of 60Co; **b** electron beam of 2 meV

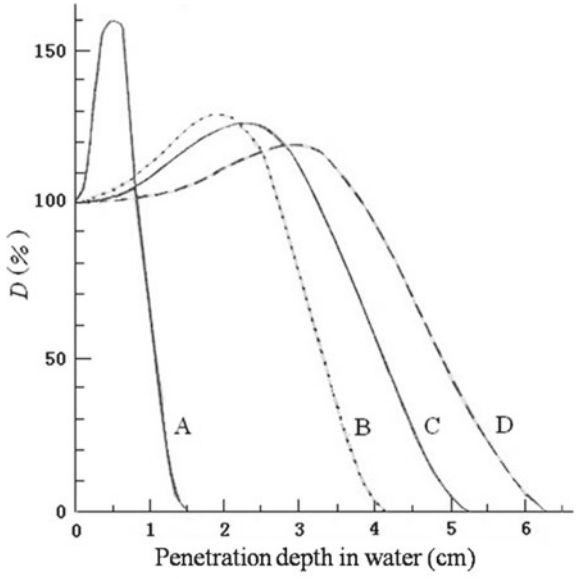


Fig. 7.3 Distribution of depth dose D of different energy beams in water. **a** 3 meV; **b** 8 meV; C: 10 meV; D: 12 meV

These substances are mainly used to produce detergents whose performance is better than that of soaps. In the drainage ditches of industrial enterprises, some substances can also be used in the process of production. Surfactants are characterized by high stability, slow biochemical oxidation, and high foaming performance when chemically reacting with the alkaline solution and salt solution. Although the required effect can be obtained by processing water with activated carbon or ion exchange resin, it is not economical. Radiation causes the surface-active substances to fracture and decompose into lighter substances that can be easily eliminated. Unlike biological purification, radiation purification acts on all compounds and oxidizes them in the presence of oxygen, and the efficiency of purification will be significantly improved under the simultaneous action of radiation and ozone. This can be explained by the conversion of HO_2 free radicals into OH free radicals, which are strong oxidants for most organic compounds.

Sewage and sludge contain usable organic and inorganic substances, which can be used as agricultural fertilizer or added to feed as nutrients. In addition to irradiation degradation of toxic compounds in sewage, special treatment is also required to kill pathogenic microorganisms. The general disinfection method is to heat the sewage at about 70 °C for tens of minutes, and the efficiency of sewage treatment with a 30 kGy radiation dose is also under study. In terms of germicidal efficacy, little difference can be seen between the above two methods. Studies on irradiation-treated sewage sediments have shown that these sediments are actually very similar to the fertilizers obtained by thermal treatment of sewage. The volume of sludge formed during the deposition of the various original water samples is one to two orders of magnitude smaller than the volume of sewage transported to the disinfection plant. Therefore, very low radiation power is required. From the perspective of applications, radiation disinfection of sewage may become a very cheap method, because this method can also remove polymer impurities simultaneously.

Another way of purifying wastewater by electron beam irradiation technology is to regenerate used activated carbon by electron beam irradiation. Due to its strong adsorption capacity, activated carbon can be used to eliminate pollutants from wastewater. However, it is expensive to regenerate used activated carbon by current popular methods. The electron beam irradiation technology can effectively regenerate activated carbon because the surface of used activated carbon is attached with organic matter. Under the nitrogen environment, the recovery rate of adsorption capacity of activated carbon is the highest, and there is almost no loss of activated carbon after irradiation. During irradiation, the higher the temperature of activated carbon, the higher the current of the electron beam, and the higher the recovery rate of adsorption capacity of the activated carbon. By comparing the isothermal adsorption curves of the regenerated activated carbon and the new activated carbon in the aqueous solution of sodium dodecyl sulfate and analyzing the degree of carbon regeneration, it can be found that the isotherm adsorption curves of the two were almost the same.

3. **Solid waste treatment**

Solid wastes treated by electron beam irradiation can be divided into two main categories:

① Wastes requiring irradiation disinfection, such as municipal sewage sludge, biomedical waste, and wastes from international airports and seaports.
② Waste rubber and plastics regenerated after irradiation treatment.

(1) Treatment of sludge

Sludge is a useable resource containing a large number of pathogens, which can be used directly used as fertilizer in farmland after irradiation sterilization. In addition to γ-ray, the sludge can also be irradiated by the electron beam. In Japan, the treatment and disposal of sludge is a thorny problem. About 60% of the sludge in inland and coastal areas needs to be disposed of. The Japan Atomic Energy Research Institute (JAERI) has studied an effective process for sludge treatment—making the compost by electron beam sterilization. Conventional composting must use the heat generated during composting to sterilize the sludge. In this method, compost is produced by microorganisms, but the heat generated by compost can both sterilize and kill microorganisms, and it still takes a long time to produce. In the process developed by the JAERI, sterilization is first followed by composting, and the best composting conditions can be selected to obtain better results. The rate of composting is greatly affected by temperature, and the optimal temperature is 40–50 °C. The optimum pH is 7–8. In order to ferment aerobic bacteria, it is necessary to supplement oxygen in granular sludge with a diameter of about 5 mm. The compost production by the irradiation method only takes 2–3 days, while that by the conventional method will take more than 10 days. To kill pathogenic bacteria, the fermentation temperature should be above 65 °C. In the new process, sterilization and composting are separated, so the best composting conditions can be selected to minimize the composting manufacturing cycle.

(2) Disposal of biomedical waste

Wastes from hospitals, research, diagnostic laboratories, etc. are considered potential pollution sources, which are harmful to public health. It is estimated that about 85% of hospital wastes are non-infectious waste, and the rest are regarded as biomedical waste. But most or all hospitals treat their wastes as biomedical waste.

In North America, the disposal of biomedical waste in landfills without proper treatment (such as burning) is not allowed. However, there may still be about 20% plastic in hospital waste (e.g. polyethylene, polypropylene, PVC, etc.). If burned, toxic gas products will be produced. Thus, these toxic gases must be removed. On the other hand, in order to prevent the risk of infectious diseases when dealing with such wastes, biomedical wastes can be disinfected by irradiation. In this case, to

provide a clean environment, the authorities should adopt and regulate the irradiation procedures.

(3) Disposal of port waste

Wastes from international airports and seaports (such as food scraps, plastics, cellulose, etc.) may contain potential infectious pathogens of animal filterable viruses (e.g., foot and mouth disease, infectious vacciniform disease, African swine fever, etc.). Therefore, in most countries, regulations have been promulgated to deal with these "international wastes". In Canada, these wastes are heated to more than 100 °C for at least 30 min or incinerated for disinfection and sterilization. According to the regulation, containers used for waste storage and transportation should be cleaned and disinfected before reuse.

A possible alternative to international waste disinfection is the use of irradiation (γ-rays or electron beams). The irradiation device can be located in the airport area and can operate automatically and continuously. This conceptual design is reliable and economical and can meet the modern requirements of a clean environment. If the irradiation disinfection of biomedical wastes and wastes from international airports and seaports is appropriate, they can be disposed of by the same irradiation facility.

(4) Treatment of rubber and plastics

Butyl rubber is the raw material for manufacturing automobile inner tubes. To ensure safety, the service life of tires is usually very short, and the number of tires scrapped every year is huge. Recovering rubber from old tires by irradiation is a mature method. The recycled materials obtain valuable processing properties and thus increase the components for manufacturing new tires in order to improve their durability. When the irradiation dose reaches 70 kGy, the plasticity of the original rubber resin and the recycled rubber mixture can be significantly enhanced, while other physical properties such as elongation are only slightly weakened at this dose.

The process of recycling rubber includes cutting the old tire into small pieces and then using the high-energy electron beam or γ-ray irradiation to decompose the macromolecular network structure. At the same time, the crosslinking process will also occur. These processes cause a change in the mechanical properties of the rubber. As a result, less energy is used to grind the raw materials. After the broken fibers are separated, the raw materials can be mixed with other components to produce new tires. The entire recycling process is quite environmentally friendly, with almost no pollution. Some further irradiation effects have also been observed. For example, as the dose increases, the modulus, hardness, and mass of the stent increase, but their corrosion resistance decreases.

The treatment of plastics by electron beam irradiation is similar to the γ-ray irradiation treatment, which has been described in the first section of this chapter.

(5) Other applications

In addition to the above aspects, accelerators have other applications in environmental protection. For example, a high current continuous beam proton accelerator can be used for nuclear waste treatment, nuclear fuel production, and nuclear energy generation in a clean way. By bombarding nuclear waste with a strong beam generated by the accelerator, long-lived radioactive elements can be transformed into useful or short-lived elements. The subcritical nuclear reactor can be driven by the high current proton beam of 1 GeV and tens of milliamperes produced by the accelerator, which can generate electricity safely and cleanly. Using the beam generated by the accelerator and target material for the nuclear reaction is an effective way to produce nuclear fuel.

7.2 Application of Nuclear Analytical Technique in the Environment

Currently, a variety of nuclear analytical techniques and nuclear-related analysis have been widely used in the monitoring of air pollutants, the analysis of water bodies and various environmental samples, and the research on the effects and migration of harmful elements and substances in environmental media. In environmental research, common methods of nuclear technology applied include:

(1) Tracer technique. The tracer method using radionuclides with a short lifetime and similar physical and chemical behavior to the simulation medium as tracers has been widely used in the experimental study of diffusion models in ambient air and water.
(2) Neutron activation technique. It has devolved from total analysis to total chemical state analysis of elements. Neutron activation analysis can not only conduct multi-element analysis but also conduct nuclide analysis, which is not available in other methods and is particularly useful for the determination of pollutants and their traceability.
(3) Proton-excited X-ray analysis and scanning proton microprobe. They have been widely used in the source identification of atmospheric fine particles.
(4) Synchrotron radiation. Synchrotron radiation is electromagnetic radiation emitted by electrons moving at a speed close to the speed of light when they change direction in motion. It is a very pure light source without a bremsstrahlung background. The energy absorbed by the irradiated sample is 103–105 times lower than that by the charged particle (such as electrons, protons, etc.) beam excitation, which greatly reduces the damage (thermal damage) to the sample. Synchrotron X-ray fluorescence analysis has been widely used in

the morphological analysis of environmental samples and is also one of the preferred analytical methods in the study of rare polar environmental samples (e.g., aerosols, bones, snow, and ice).

(5) Mössbauer spectroscopy. It has been successfully applied to the identification of iron particles in the atmosphere, which can not only analyze the amount of pollution but also give the total chemical state of pollutants.

(6) Accelerator mass spectrometry. It is a modern nuclear analysis technology with ultra-high sensitivity, which is mainly used to analyze the isotope abundance ratio of long-lived radionuclides, so as to infer the age of samples or conduct tracing research. Its detection limit can reach 10^{-2}–10^{-15}.

(7) Low temperature plasma technique. It has been widely used in the analysis and identification of pollutants and the treatment of waste gas, waste liquid, and waste residue.

(8) Solid state nuclear track detection. It plays an important role in disaster environments and indoor radon monitoring.

The application of nuclear analytical techniques in the field of radiation environmental monitoring mainly includes:

(1) Monitoring of environmental radiation level: including monitoring of radioactive aerosols in the atmosphere, γ-radiation dose level at ground level, radioactivity in water, soil, and building materials, indoor and outdoor radon concentration, etc.

(2) Monitoring of nuclear facilities: including the monitoring of radioactive effluents from the chimney of nuclear facilities and the monitoring of the level of radiation environment around nuclear facilities.

(3) Using the mobile γ-spectrometer testing technology, the dose distribution of earth radiation and the corresponding nuclide activity can be measured quickly, which allows for rapid investigation of environmental pollution levels and assessment of environmental impact.

The United States, Germany, the former Soviet Union, and China have successively carried out indoor radon concentration studies. Using radon anomaly to predict earthquakes and volcanoes has been continuously studied. In the United States, more than 360 radon-measuring points have been established along the 380 km profile on the San Andress fault in central California, and the nuclear track etching method has been used for the research of earthquake prediction. In addition to direct applications in environmental science, the applications of nuclear monitoring technology in hydrology, geology, meteorology, agriculture, and biology are all closely related to environmental science and environmental engineering.

Among many nuclear analytical techniques, neutron activation analysis and isotope tracer technology are the most widely used, which will be described in more detail below.

7.2.1 Application of Neutron Activation Analysis in the Environment

1. **Application of neutron activation analysis in atmospheric environment**

Atmospheric pollution has become a very important problem endangering human health, and its concentration is generally increasing globally, especially in urban industrial areas. Atmospheric pollution from artificial sources is often difficult to identify because of the long-term addition of natural sources. Therefore, in order to study atmospheric pollution, it is necessary to determine the composition of the chemical element of pollutants. Many analytical methods have been widely used in the study of aerosol components. In addition to the commonly used chemical analytical methods, other methods such as atomic emission spectrometry, atomic absorption spectrometry, X-ray fluorescence analysis, plasma emission spectrometry, electron microscopy scanning X-ray fluorescence analysis, proton-induced X-ray fluorescence analysis, and neutron activation method are widely used. Aerosols have certain characteristics. Their concentration in the atmosphere is very low, and the concentration of the elements it contains is lower, so it is required to select an analytical method with high sensitivity and accuracy. Aerosols contain a large number of elements that are correlated with each other. In order to identify the sources of pollutants and calculate the contribution of each source, multi-element analysis is required, and mathematical models are used to determine the elemental content. Aerosols also contain carbonaceous particles burned at high temperatures, which are difficult to be completely dissolved, and contain some volatile elements (such as Hg, As, Se, etc.). Therefore, it is required to use an analytical method that does not damage the sample in order to accurately determine its total amount. It is difficult for commonly used analytical methods to meet the above requirements. In comparison, neutron activation analysis has become a major means to solve the problem of air pollution because of its high sensitivity, good accuracy, and strong adaptability, which can simultaneously determine the contents of 40–50 trace elements without destroying the sample.

The research methods of aerosol characteristics are as follows:

(1) Sampling and layout

In the field of air pollution monitoring, the collection of representative aerosols from heterogeneous gas systems is the most difficult and critical step in aerosol research. According to the purpose and requirements of the study, the number of sites, sampling time, and frequency differs from one another. The selection of sampling sites and heights, as well as the appropriateness of the sampling technique used, will affect the results of the study. Thus, a more appropriate approach must be selected based

on certain conditions. For example, when collecting aerosols in the airflow with a certain flow rate, sampling should be carried out according to the requirements of dynamic conditions (sampling from emission chimney of pollution source, aircraft, etc.), otherwise, the results obtained will have a large deviation. So far, there is no existing method that can meet various purposes and requirements.

Eight main methods are used to collect aerosols, including gravity settling, centrifugal separation, inertial collection, dry impact, filtration, electrostatic precipitation, thermal precipitation, and ultrasonic agglomeration. Currently, the most commonly used methods are filtration (collecting total aerosol particles) and impact (collecting aerosol particles of different sizes).

(2) Selection of filter membrane

① Collection efficiency of filter membrane

Organic membranes or nucleopore membranes have high collection efficiency for small particles, but the airflow velocity is relatively low. Although polystyrene fiber membrane can pass through high gas volume, it is difficult to ash and is not suitable for the application in radiochemical separation neutron activation analysis. The Whatman 41 filter membrane has a collection efficiency of 85–90% for submicron particles. The Zefluor filter membrane has a collection efficiency of 99% for 0.3 μm particles at a flow rate of 32 L/min. The efficiency of the filter membrane decreases with the decrease of particle size, the increase of filter membrane aperture, and the increase in surface velocity of particles on the filter membrane. The general organic filter membrane is applicable to collect particles $\geq$ 0.3 μm. Glass fiber is suitable for large volume samplers due to its ability to allow airflow to pass through quickly and with less resistance, although its collection efficiency is relatively low.

② Purity of filter membrane

When using neutron activation analysis to determine the elementary composition of aerosol, the purity of the sampling filter membrane is the decisive factor to determine the detection limit of the element to be measured. Therefore, it is crucial to select the filter membrane with low impurity content. Several commonly used filter membranes with good purity include the Zefluor filter membrane, Fluoropore filter membrane, Nclepore filter membrane, Whatman 41 filter membrane, etc.

(3) Analytical procedures for the determination of aerosols

① Preparation of samples and standards

During the sampling process, because the filter membrane is easily susceptible to moisture, the filter membranes must be weighed before and after sampling under the condition of constant temperature and humidity to obtain the mass of collected aerosol particles. The weighed filter membrane samples are pressed into 3–8 mm thin sheets by a nylon stamping die for irradiation.

② Sample irradiation

The radioactivity produced by neutron irradiated samples depends on the following factors: (a) The content of the element in the sample, strictly speaking, is the content of a certain isotope of the element that produces nuclear reaction; (b) Fluence of irradiated neutrons; (c) Activation cross-section of the element to be measured or one of its isotopes to neutrons; (d) Irradiation time, etc.

When using neutron activation analysis for atmospheric aerosols or any other environmental substances, the first factor to be considered is the neutron fluence at the location of the nuclear reactor pipeline available for irradiation. Because this will affect the types of elements in the measurable aerosols and their detection limits. According to the nuclear properties of the elements to be measured, the radioactivity of each radionuclide can be measured using different irradiation and decay times, and the concentration of each element in the aerosol can be calculated.

The following are the workflows of short-term irradiation and long-term irradiation.

Short-term irradiation (determined by short-lived nuclides): It is carried out on a microreactor. Put the sample into the polyethylene irradiation cylinder, put the cylinder into the "rabbit", then send the "rabbit" into the central pipe of the microreactor with a pneumatic conveyor (neutron fluence rate is 9×10^{11} m/s). After 10 min of irradiation, send the "rabbit" back into the sub-packing box, remove the "rabbit" and the irradiation cylinder, transfer the sample into the small measuring box, and then transfer the small box to the detector of the measuring device for measurement.

Long-term irradiation (determined by medium- and long-lived nuclides): Cool the sample after a short irradiation measurement for one week and wrap it with ultrapure aluminum foil. Put the sample into the irradiated aluminum cylinder together with the standard and the standard reference for quality control, and send it to the heavy water nuclear reactor pipeline (neutron fluence rate is 6×10^{13} m^{-2} s^{-1}) for irradiation for 20–40 h. After irradiation, transfer the sample to a plastic measuring box. After cooling for 5–6 days, carry out the first measurement with a counting time of 2000 s. After cooling for 15–16 days, conduct the second measurement with a counting time of 4000 s. Figure 7.4 illustrates the irradiation and technical procedures.

④ Radioactivity measurement and data processing

According to the nature of each radionuclide, the γ-spectrum of each sample is measured with different irradiation times and decay times. Data processing is carried out by computer, after peak searching, calculation of net peak area, and isotope identification and analysis, the net peak area of characteristic peaks of each nuclide can be obtained. After the deduction and correction of each interference contribution, the content of elements to be measured in the sample can be calculated by comparing it with the standard.

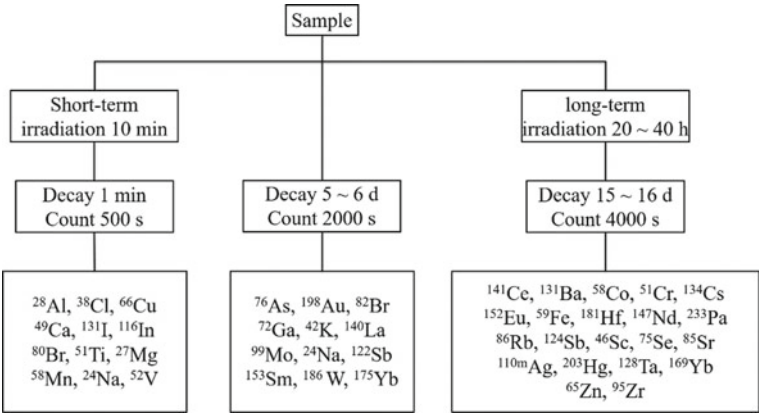


Fig. 7.4 Illustration of irradiation and technical procedures

2. **Application of neutron activation analysis in water environment**

Water is an active medium in the environment, and it is also the link of material exchange in the environment. With the large-scale exploitation and utilization of natural resources, human factors have been included in the geological environment, changing the composition of the hydrosphere. The development of modern industry has caused a large amount of industrial wastewater to be discharged into rivers, lakes, and seas, polluting water bodies and seriously threatening people's health, which has attracted the attention of the world. In order to determine the pollution situation of natural waters, it is necessary to analyze the harmful elements As, Hg, Cd, Pd, etc. in the water, and compare the results with the natural background values of the elements under the unpolluted condition, so as to provide a scientific basis for the prevention and treatment of pollution. Because the content of pollution elements in water is extremely small and many kinds of elements can be found, advanced analytical methods are required.

Neutron activation analysis has the characteristics of high sensitivity and simultaneous determination of multiple elements, which has been widely used in the analysis of various freshwater (including rivers, lakes, rain, marsh water, seawater, and groundwater). For elements with very low content (0.001–0.1 μg/L), preconcentration is required before analysis, which can be carried out by ion exchange, solvent extraction, electrodeposition, low-temperature evaporation, activated carbon adsorption, co-precipitation, freeze-drying, etc. The pre-concentrated water sample and the standard are packaged together for neutron irradiation at a certain fluence rate. After appropriate irradiation time and decay time, the sample will be transferred out and placed on the detector to measure the radioactivity, and then the element content can be calculated.

The detection limit of the analytical method depends on the matrix composition of the sample and the measurement conditions. In 1980, the Neutron Activation Analysis Laboratory of the Institute of High Energy Physics, Chinese Academy of

Sciences preconcentrated natural water by the freeze-drying method and analyzed various elements in water by the neutron activation method. The detection limits are listed in Table 7.1. Due to the high neutron fluence rate of the reactor used to irradiate the sample and the high detection efficiency of the Ge (Li) detector, the analytical sensitivity of rare elements and rare earth elements is higher than other analytical methods.

3. **Application of neutron activation analysis in soil environment**

At present, activation analysis has become one of the most effective methods in trace element analysis. The matrix composition of soil samples is extremely complex, with large sample size and many elements to be measured, and the variation range of element content is large. Neutron activation analysis is an ideal method to study trace elements in the soil. In 1978, the Neutron Activation Analysis Laboratory of the Institute of High Energy Physics, Chinese Academy of Sciences established an instrumental neutron activation analysis method that does not damage samples for the determination of trace elements in soil, rocks, and river sediments. This method has been used to study the trace elements in soil, the composition of trace elements in lunar rock samples, the archaeological samples, and the determination of various reference materials.

The analysis method of soil samples is to simultaneously send the prepared soil samples and the standard into the reactor and irradiate them for a certain time under a certain amount of fluence. Analyze the irradiated samples and standards by γ-ray spectrometer under the same geometric conditions after different cooling times. For example, send the prepared soil samples together with the standards to the heavy water reactor (neutron fluence rate is about 6×10^{13} m^{-2} s^{-1}) or the swimming reactor (neutron fluence rate is about 1×10^{13} m^{-2} s^{-1}) for irradiation for about 10–15 h. After different cooling times, the irradiated samples and standards are analyzed for γ-nuclide activity with a high-resolution HPGe detector under the same geometrical conditions. The γ-ray spectrum analysis, correction of various interferences, and

Table 7.1 Detection limits

Element	Detection limit (μg/L)	Element	Detection limit (μg/L)	Element	Detection limit (μg/L)
Ag	0.04	Cs	0.005	Sb	0.007
As	0.002	Eu	0.001	Sc	0.0002
Au	0.00004	Fe	5	Se	0.05
Ba	2	Hf	0.004	Sr	6
Zn	0.5	La	0.01	Sm	0.0003
Ca	2	Lu	0.001	Tb	0.004
Ce	0.05	Mo	0.1	Th	0.005
Co	0.01	Nd	0.2	U	0.005
Cr	0.07	Rb	0.2	Yb	0.004

Table 7.2 Irradiation time, cooling time of samples and measured elements

Neutron fluence rate	Irradiation time	Cooling time	Elements determined
1×10^{13}–6×10^{13} m^{-2} s^{-1}	10–15 h	5 d	As, (Au), K, La, Na, Sm, U, W, Yb
		15 d	Ba, Lu, Nd, Rb
		30 d	Ce, Co, Cr, Cs, Eu, Fe, Hf, Ni, Sb, Sc, Sr, Ta, Tb, Th, Yb, Zr

calculation of elemental content are all completed by a microcomputer programmed γ-ray spectrometer system. Table 7.2 lists the irradiation time, cooling time, and elements determined in the work.

In order to check the reliability of the analytical method and realize the quality control of the analysis, various reference materials and reference samples developed and issued by the National Bureau of Standards (NBS) and the United States Geological Survey (USGS) can be determined at the same time as the samples are analyzed, and several samples can be analyzed in parallel. The results show that the values of most elements are in good agreement with the NBS identification and literature values, with the accuracy and precision ± 10%.

Water sample analysis can only represent the water quality at the moment of sampling. The bottom sediment is the comprehensive reflection of the contribution of various pollution sources in the catchment area to the environmental quality of the region. The National Institute for Environmental Studies (NIES) of Japan has realized the quantitative determination of more than 50 elements in marine sediments by instrumental neutron activation analysis (INAA). Chengdu University of Science and Technology in China also used neutron activation analysis to determine more than 30 elements in the sediment samples of the urban river and used the Clark value of river sediment (i.e. the average content of the element in river sediment) as the comparison standard to obtain the basic data for evaluating river pollution.

7.2.2 Application of Isotopic Tracer Technology in the Environment

A class of elements with the same proton number but different neutron numbers in the atomic nucleus are called isotopes, which can be divided into stable isotopes and radioactive isotopes. Those that can spontaneously emit particles and decay into another isotope are called radioactive isotopes or unstable isotopes. At present, there are about 1700 known isotopes, of which about 260 are stable isotopes.

The isotopic tracer method is a microanalytical method that uses radionuclides (or stable nuclides) as tracers to label the object of study. The radionuclides (or stable nuclides) used for isotopic tracing and their compounds have the same chemical and biological properties as the corresponding ordinary elements and their compounds

existing in nature but have different nuclear physical properties. Therefore, isotopes can be used as a label to make labeled compounds containing isotopes (such as labeled food, drugs, and metabolic substances) to replace corresponding non-labeled compounds. By using the nuclear physical properties of radioisotopes that continuously emit characteristic rays, nuclear detectors can be used to track the location, quantity, and transformation at any time. Although the stable isotope does not emit rays, it can be determined by mass analysis instruments such as mass spectrometers, gas chromatographs, and nuclear magnetic resonance using its mass difference with the ordinary corresponding isotope. Both radioisotopes and stable isotopes can be used as tracers. However, as tracers, stable isotopes have low sensitivity and few kinds available and are more expensive, which is limited in applications. Using radioisotopes as tracers not only has high sensitivity but also has the characteristics of the simple measurement method, accurate quantification, and accurate positioning.

For environmental engineering, agricultural environmental protection, and environmental chemistry, the isotopic tracer technique shows outstanding advantages. By adding labeled compounds or tracers to the studied system and by means of isotope determination technology, the laws of movement and change of the substance with similar substances can be found. Due to the special radiation properties of isotopes, when using isotopic tracer techniques to measure samples, high sensitivity and accuracy can be achieved without separation. This method has been widely used to study the migration behavior of pollutants in soil, surface water, and groundwater. In addition, in the research on the transfer law of pollutants in biological bonds and the mechanism of pollutant treatment, tracer techniques are often applied in the study of the migration and transformation of key nuclides, which has played an extremely important role in the treatment and disposal of nuclear waste.

By determining the content difference of the tracer isotope in the sample under different conditions, the environmental matrix that occurred in nature can be inferred. For example, using isotopes as an accurate time scale, a series of changes in the marine environment can be inferred and predicted through the study of uranium series disequilibrium in seawater. In the field of environmental hydrogeology, systematic experience has been accumulated in the study of surface water and groundwater using ^{14}C, tritium, and several stable isotopic tracer techniques. The application of radionuclide tracer technology in agricultural environmental protection also has a long history. A typical example is that the application, absorption, degradation, transfer, and accumulation of pesticides and chemical pollutants in the ecosystem can be tracked comprehensively using labeling technology. Tracer technology also plays an important role in the high-tech fields because it can reveal the laws of atomic and molecular motion and other phenomena that are difficult to find by other methods. In the field of environmental chemistry, it can be used to identify intermediate products of reactions. When studying the metabolic processes of biological organisms, the tracer method can not only quantitatively determine the laws of transfer and change of metabolic substances but also determine the quantitative distribution of metabolic substances in various organs, making it an extremely powerful tool for ecological research. In addition, since the tracer with very high specific radioactivity can be obtained manually, the sensitivity and accuracy of radioactivity determination can

be greatly improved. This feature makes the tracer technology continue to expand its application scope in the environmental field.

Isotopic tracer techniques include the radioisotope tracer method and the stable isotope tracer method.

1. **Radioisotope tracer method**

Radioactive isotopes have three characteristics.

(1) They can emit various rays. Some emit α-rays, some emit β-rays, some emit γ-rays, or two of them are emitted at the same time. Among them, α-ray is an α-particle beam with a positive charge, and β-ray is an electron beam with continuous energy, usually with a negative charge.
(2) The rays emitted are determined by the different nuclei themselves. For example, each time a ^{60}Co nucleus decays, it emits three particles, that is, one β-particle and two photons, and eventually decay into stable ^{60}Ni.
(3) It has a certain lifetime. The time required to reduce the number of nuclei of the radioisotope that began to exist to half is called the half-life. For example, the half-life of ^{60}Co is 5.26 a.

The radioisotope tracer method is commonly used in radiochemistry to replace the non-radioactive atoms in compounds with radioactive atoms of the same element, such as replacing ^{12}C atoms in an organic matter with ^{14}C atoms. Thus, the movement of these radionuclides can be tracked in the chemical reaction, biological reaction, or migration process. Additionally, the radioactive tracer technique is unique in studying the flow direction of groundwater, monitoring the cracks of reservoirs and dams, and studying the movement speed and migration of sediment in river water.

The isotope dating techniques in macro-environmental studies are irreplaceable by other methods. Since the radioactive intensity of ^{14}C is a function of time, people can simply use the half-life of ^{14}C as the only basis for the age of groundwater. For example, people can obtain the time required for the transformation of the snow water from the source mountains to the groundwater of an area by measuring the ^{14}C content of the groundwater in a certain area and the snow water from the source mountains. This provides an important basis for effective control and management of estimating the limit of groundwater availability in the region and predicting the consequences of excessive groundwater use. Similarly, the application of isotopic analytical techniques to study the origin of a lake can tell whether the lake will dry up in a period of time. The conclusion will undoubtedly play a very important role in the development of the lake area. For certain areas where nuclear energy is applied or areas near nuclear facilities, the concentration of some radionuclides in the environment directly reflects the quality of the environment. For instance, the migration of radon in the environment has been paid attention to by environmentalists all over the world.

Radionuclide tracer techniques have been widely used in various disciplines because of their high sensitivity, simplicity, and independence from environmental and chemical factors. Radionuclides existing in nature are usually used in the tracing studies of geoscience and environmental science. For example, ^{14}C is used to study

the circulation patterns of global ocean currents, ^{10}Be is used to trace the source of volcanic magma to verify the theory of plate subduction, and ^{36}Cl is used to trace the permeability of groundwater. The use of ^{129}I to trace nuclear leakage has become an important means of nuclear verification. Tracer studies in chemistry, biology, and medicine mostly adopt the method of labeling compounds with radionuclides. The most commonly used compounds are ^{3}H, ^{14}C, ^{32}P, ^{125}I, ^{131}I, etc. Tracer techniques can also be used to study the distribution, migration, and transformation of trace elements in crops, the loss of chemical fertilizers and pesticides and their residues in soil, as well as agricultural ecological environment problems such as soil and water loss and grassland degradation. For example, applying ^{15}N tracing to study fertilization techniques can improve the utilization rate of nitrogen fertilizer by 10–20%.

2. **Stable isotope tracer method**

Since the 1980s, mathematical models that can truly reflect the objective situation are often required due to the development of environmental management, environmental quality assessment, environmental impact assessment, and pollution trend prediction. After the models are put forward, their reliability is also required to be verified. The improvement in accuracy and precision of tritium, ^{14}C, ^{18}O, and other environmental isotope measurement techniques provides great convenience for model verification. Stable isotope measurement techniques have further expanded the application scope of nuclear measurement technology in environmental science.

Hydrogen and oxygen isotopes can be used to study the water cycle. Water on the earth forms a water cycle through evaporation, condensation, precipitation, infiltration, and runoff. Some thermodynamic properties of water molecules are related to the mass of hydrogen and oxygen atoms, thus isotope fractionation will occur during the water cycle. Since there are three stable oxygen isotopes and two stable hydrogen isotopes, nine different isotopic combinations exist for ordinary water molecules, namely $H_2{}^{16}O$ (molecular weight is 18), $H_2{}^{17}O$ (molecular weight is 19), $H_2{}^{18}O$ (molecular weight is 20), $HD^{16}O$ (molecular weight is 19), $HD^{17}O$ (molecular weight is 20), $HD^{18}O$ (molecular weight is 21), $D_2{}^{16}O$ (molecular weight is 20), $D_2{}^{17}O$ (molecular weight is 21), and $D_2{}^{18}O$ (molecular weight is 22). Since the vapor pressure of various isotopes of water molecules are inversely proportional to the mass of the molecule, thus $H_2{}^{16}O$ has a much higher vapor pressure than $D_2{}^{18}O$. The water vapor generated by the evaporated liquid water thus enriched H and ^{16}O, and the residual water enriched D and ^{18}O. The fractionation of stable isotopes of hydrogen and oxygen is caused by the process of water circulation. Therefore, the hydrogen and oxygen isotope contents in water can be used to study the water cycle.

Stable isotopes are non-radioactive isotopes that naturally exist in organisms. Carbon and nitrogen have two stable isotopes with different neutron numbers, namely ^{13}C and ^{12}C and ^{14}N and ^{15}N, respectively, in which the content of heavy isotopes (such as ^{13}C and ^{15}N) in organisms is very low. For example, according to the difference in the ^{15}N isotope ratio in nitrate from different sources, it can be effectively determined whether the pollutant is from fertilizers, or from urban sewage or minerals in the soil. Similarly, since the isotopic abundance of ^{18}O in deep water differs from that in surface water, the determination of ^{18}O in water can determine the age and

recharge relationship between the two. In general, it is of little significance to determine the absolute content of stable isotopes, but to compare them with international standards for comparative study, that is, to compare the abundance of stable isotopes (enrichment). The stable isotope abundance is expressed as the ratio between the ratio of the two most abundant isotopes in the sample and the response ratio in the international standard, expressed with the symbol δ. Since the ratio difference between the sample and the standard reference is small, the stable isotope abundance is expressed as thousandths of the deviation between the sample and the standard. The abundance of the two stable isotopes, carbon and nitrogen, in the substance is generally expressed by $\delta^{13}C$ and $\delta^{15}N$ respectively. The international reference material of carbon element is Pee Dee Belemnite, which is a carbonate material with a universally recognized isotope absolute ratio of $^{13}C/^{12}C = 0.0112372$. The international standard substance of nitrogen element is the atmosphere, and $^{15}N/^{14}N$ in atmospheric nitrogen is 0.003676. Taking carbon as an example, the calculation method of stable isotope abundance is introduced, and the calculation of $\delta^{13}C$ is shown in Eq. 7.4.

$$\delta^{13}C_{\text{sample}}(‰) = \left[\left(^{13}C/^{12}C\right)_{\text{sample}}/\left(^{13}C/^{12}C\right)_{\text{standard}} - 1\right] \times 1000 \tag{7.4}$$

Small differences in the mass of isotopes cause small differences in their physical and chemical properties (e.g., conduction rates in the gas phase, bond energy strength, etc.), thus differences in the isotopic composition before and after the reaction of substances can be found. This property was successfully introduced into many biological research fields in the early 1970s, such as research on photosynthetic pathways, light energy utilization, environmental pollution, plant water utilization, mineral metabolism, climate effects, and biomass changes.

The molecular isotope technique developed in recent years, also known as compound specific isotopic analysis (CSIA), is increasingly becoming an important and effective "environmental indicator" due to its characteristic feature and stability. Stable isotope tracing can be used to trace the source of petroleum pollution and its evolution in the environment. There are some differences in the chemical composition of different crude oils and products. The so-called "chemical fingerprint" technology is used to distinguish oil pollution in the environment by chemical composition and biomarker characteristics. Normal alkanes, polycyclic aromatic hydrocarbons, and isoprenoids are commonly used chemical fingerprints. However, the chemical composition is easily changed by environmental processes such as volatilization, leaching, and biodegradation, so the application of "chemical fingerprints" has certain limitations. By comparison, isotope fingerprints are widely used in environmental tracing research because of their characteristic feature and relative stability.

7.3 Application Prospect of Nuclear Technology in Environmental Science

Nuclear science and technology applied in environmental research have made remarkable achievements in the atmospheric environment, water environment, soil environment, agricultural environment, internal environment, catastrophic environment, marine environment, sediment erosion environment, and so on. These achievements not only have important scientific significance but also provide a scientific basis for global environmental governance, which provides huge social and economic benefits.

Judging from the current progress of nuclear technology research in various countries, nuclear technology will be applied in both developed and developing countries more widely in the future. Since nuclear technology plays an important role in environmental research, many countries have carried out basic research and industrial practice on radiation treatment of water, wastewater, sludge, industrial solid waste, etc.

The technology of using radiation to treat sludge, wastewater, and other biological wastes can replace the traditional landfill, oceanic jettison, incineration, and other methods, ensuring that the environment is not subject to secondary pollution.

The application of some nuclear techniques involves the operation of open radioactive substances, which raises the requirements for laboratory specifications and experimental equipment, as well as the quality of researchers and analysts. The neutron activation analysis requires the use of nuclear reactors, accelerators, or neutron sources as radiation sources, but in the current situation, it is difficult to be widely used. In recent years, a large number of studies on the determination of environmental samples using activation methods have been published, and a considerable part of them are completed by using neutron sources and small accelerators, which may be the result of efforts to improve the popularity of the application of activation analysis.

Given the current situation, developing the application of nuclear technology in the environmental field can solve many technical difficulties in environmental studies. In addition, the introduction of nuclear testing technology will also lead to the combination of environmental protection equipment and nuclear testing instruments, thus further promoting the development of the environmental protection industry. It is believed that the "nuclear environmental protection instrument" industry will emerge in the near future. The combination of nuclear and environmental protection will also further play the role of the former nuclear technicians so that environmental protection can be more fully developed.

Exercise

1. Evaluate the characteristics of electron beam irradiation.
2. What are the main nuclear technology methods used in environmental research?
3. What characteristics do radionuclides need to have when using radioactive tracer methods?

Bibliography

Dempster, H. S., Sherwood Lollar, B., & Feenstra, S. (1997). Tracing organic contaminants in groundwater: A new methodology using compound-specific isotopic analysis. *Environmental Science & Technology, 31*(11), 3193–3197. https://doi.org/10.1021/es9701873

El-Nemr, K. F., & Khalil, A. M. (2011). Gamma irradiation of treated waste rubber powder and its composites with waste polyethylene. *Journal of Vinyl and Additive Technology, 17*(1), 58–63. https://doi.org/10.1002/vnl.20245

Elsner, M., & Imfeld, G. (2016). Compound-specific isotope analysis (CSIA) of micropollutants in the environment—current developments and future challenges. *Current Opinion in Biotechnology, 41*, 60–72. https://doi.org/10.1016/j.copbio.2016.04.014

Kim, T.-H., Nam, Y.-K., Park, C., & Lee, M. (2009). Carbon source recovery from waste activated sludge by alkaline hydrolysis and gamma-ray irradiation for biological denitrification. *Bioresource Technology, 100*(23), 5694–5699. https://doi.org/10.1016/j.biortech.2009.06.049

Kolesov, G. M. (1995). Neutron activation analysis of environmental materials. *The Analyst, 120*(5), 1457–1460. https://doi.org/10.1039/AN9952001457

Landsberger, S., & Kapsimalis, R. (2013). Comparison of neutron activation analysis techniques for the determination of uranium concentrations in geological and environmental materials. *Journal of Environmental Radioactivity, 117*, 41–44. https://doi.org/10.1016/j.jenvrad.2011.08.014

Nichipor, H. V., Dashouk, E. M., & Yatsko, S. N. (1995). Investigation of SO_2, NO and H_2S oxidation in humid air by electron beam. *Radiation Physics and Chemistry, 46*(4, Part 2), 1111–1114. https://doi.org/10.1016/0969-806X(95)00333-S

Pikaev, A. K. (2000a). Current status of the application of ionizing radiation to environmental protection: I. Ionizing radiation sources, natural and drinking water purification (A Review). *High Energy Chemistry, 34*(1), 1–12. https://doi.org/10.1007/BF02761780

Pikaev, A. K. (2000b). Current status of the application of ionizing radiation to environmental protection: II. Wastewater and other liquid wastes (A review). *High Energy Chemistry, 34*(2), 55–73. https://doi.org/10.1007/BF02761832

Pikaev, A. K. (2000c). Current status of the application of ionizing radiation to environmental protection: III. Sewage sludge, gaseous and solid systems (A review). *High Energy Chemistry, 34*(3), 129–140. https://doi.org/10.1007/BF02762421

Ponomarev, A. V. (2020). Radiolysis as a powerful tool for polymer waste recycling. *High Energy Chemistry, 54*(3), 194–204. https://doi.org/10.1134/S0018143920030121

Rooney, M. A., Vuletich, A. K., & Griffith, C. E. (1998). Compound-specific isotope analysis as a tool for characterizing mixed oils: An example from the West of Shetlands area. *Organic Geochemistry, 29*(1), 241–254. https://doi.org/10.1016/S0146-6380(98)00136-3

Wang, J., & Chu, L. (2016). Irradiation treatment of pharmaceutical and personal care products (PPCPs) in water and wastewater: An overview. *Radiation Physics and Chemistry, 125*, 56–64. https://doi.org/10.1016/j.radphyschem.2016.03.012

Wang, J., & Wang, J. (2007). Application of radiation technology to sewage sludge processing: A review. *Journal of Hazardous Materials, 143*(1), 2–7. https://doi.org/10.1016/j.jhazmat.2007.01.027

Wasserman, J. C., Figueiredo, A. M. G., Pellegatti, F., & Silva-Filho, E. V. (2001). Elemental composition of sediment cores from a mangrove environment using neutron activation analysis. *Journal of Geochemical Exploration, 72*(2), 129–146. https://doi.org/10.1016/S0375-6742(01)00158-3

Witkowska, E., Szczepaniak, K., & Biziuk, M. (2005). Some applications of neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry, 265*(1), 141–150. https://doi.org/10.1007/s10967-005-0799-1

Yin, Y., & Wang, J. (2015). Biohydrogen production using waste activated sludge disintegrated by gamma irradiation. *Applied Energy, 155*, 434–439. https://doi.org/10.1016/j.apenergy.2015.05.105

Chapter 8
Applications of Nuclear Technology in Agriculture



As early as the 1940s, the interpenetration and integration of nuclear technology and agricultural science and technology had begun. It was not until the 1970s that the concepts of "radio agronomy" and "nuclear agricultural science" were formally put forward. It mainly studies the application and mechanism of nuclides and radiation and related nuclear technologies in agricultural science and agricultural production, which can be divided into nuclear radiation technology and its application in agriculture and nuclide tracer technology and its application in agriculture.

Nuclear technology is one of the most effective technologies to increase agricultural output and improve the quality of agricultural products. It can provide high-quality seeds for agriculture, control diseases and pests, evaluate fertilizer efficiency, control pesticide residues, maintain nutritional quality, prolong the storage time of harvested products, and identify grain quality. Nuclear agronomy is an interdisciplinary subject formed by the application of nuclear technology in agriculture, mainly involving radiation-induced breeding, insect radiation sterility, tracing of fertilizers, pesticides, and water, radiation preservation, nuclear instrumentation for agriculture, etc. Solving the problem of food, improving food quality, and ensuring human nutrition are the core of agricultural science and technology development. Nuclear agriculture can provide strong scientific support to solve the above problems. The breeding of new varieties, the management of soil and fertilizer, and the preservation of agricultural products are all inseparable from nuclear technology.

Radiation breeding is an important part of nuclear agriculture. China, the United States, Japan, and other countries lead the world in this application. In the future, the development trend of radiation breeding is to expand the application field, strengthen directional induction mutation, improve the mutation rate, and basic theoretical research on radiation breeding.

Irradiation preservation technology has the characteristics of saving energy, sanitation and safety, maintaining the original color, aroma and taste of food, and improving quality, etc., which is more and more widely used and the technology is increasingly mature. The sterile insect technique is a new technology for modern

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6_8

biological pest control and is currently an effective means of exterminating certain insect species. The isotope tracer technique can reflect the metabolic process of an element (or compound) in the organism or the physical and chemical behavior of the agricultural environment more realistically, and it has advantages that cannot be replaced by other methods at present. The application of this technology in agriculture has solved the key technical problems in the fields of soil, fertilizer, plant protection, and nutrient metabolism of animals and plants in agricultural production. It plays an important role in revealing the production laws of agricultural, livestock, and fishery production and improving traditional cultivation and breeding techniques. The radiographic detection technology developed in recent decades is of great significance in agricultural applications because of its simple methods and rapid detection, especially the possibility of continuous monitoring without destroying the sample to be tested.

Nuclear agronomy, as a specialized discipline, covers a wide range of topics. This chapter will focus on the introduction of the three areas of radiation breeding, irradiation preservation, and sterile insect technique. For other content, readers can refer to relevant textbooks or materials.

8.1 Radiation Breeding

The species, form, and characteristics of organisms are controlled by their own genetic information. Radiation breeding uses rays to treat animals, plants, and microorganisms to cause gene mutation or chromosome aberration of the main genetic material of the organism—DNA, resulting in the variation of the relevant characteristics of the organism. Then, through artificial selection and breeding, the favorable variation is inherited, so as to improve the crop (or other organism) varieties and cultivate new varieties. This technology of using radiation to induce the change of biological heredity and cultivate new and excellent varieties through artificial selection is called radiation breeding.

8.1.1 History of Radiation Breeding

Since Muller of the United States found that X-rays can induce drosophila to produce a large number of various types of mutations in 1927, and Fresjeben and Lein of Germany used mutagens to obtain beneficial mutants in plants in the early 1940s, until the 1960s, the research on radiation-induced mutation did not make rapid progress, but it was still in continuous practice. By the end of the 1960s, the Food and Agriculture Organization of the United Nations (FAO) and the International Atomic Energy Agency (IAEA) jointly held a training course on plant mutation breeding

and published the *Manual of Mutation Breeding*. Since then, plant radiation mutation breeding has completed the transition from initial basic research to practical application. In the 1970s, the attention of mutagenesis breeding gradually turned to disease resistance breeding, quality breeding, and hybridization of mutants. After the 1980s, the wide application of molecular genetics and molecular biology injected new vitality into mutation breeding, especially the application of molecular marker methods in the 1990s, which made it possible to carry out directional mutation of actual varieties.

Since the application of radiation technology in agricultural breeding, enormous social and economic benefits have been produced. It has undergone a process of rapid development in the twentieth century. In 1934, Indonesian scientists used X-rays to irradiate tobacco to breed new varieties, ushering in a new era of crop radiation breeding. In 1958, the United States carried out research on large-scale field radiation breeding. Japan used radiation to irradiate rice in the field and obtained 545 mutants, which increased the protein content. In 1964, the United States used thermal neutron radiation to breed "Lewis" soft-grain wheat with lodging resistance, early maturity, and high yield. In 1986, Italy used thermal neutron radiation to breed lodging-resistant and high-yield durum wheat. In addition, the "Novosibirsk 67" wheat variety bred by the former Soviet Union has the characteristics of cold resistance, early maturity, and high quality; the improved variety of dwarf lodging resistant rice bred in Japan has an annual income of more than 1 billion yen; the improved varieties of pepper and peppermint with resistance to fusarium wilt developed in the United States have an annual output value of 20 million dollars; the French rice variety "Delta" was of great economic value.

8.1.2 Basic Principles of Radiation Breeding

Radiation breeding is the use of artificial creation of new types of mutations, which has the characteristics of breaking the linkage of character, realizing genetic recombination, high mutation frequency, multiple mutation types, stable and fast mutation characters, simple method, and short breeding period. While constantly creating new varieties, radiation breeding has also made great progress in the study of mutagenic effects and mechanisms, exploring the variation of genetic material under radiation and the laws of breeding favorable mutant varieties, so as to guide the practice of mutation breeding, solve the food crisis facing mankind, and improve the nutrition level.

1. **Possible mechanism of mutation caused by ionizing radiation**

In general, the average energy loss of each ionizing event during ionizing radiation is about 33 eV, which is sufficient to break very strong chemical bonds. Therefore, after the organism is exposed to ionizing radiation, many biologically active substances can be damaged, in which the damage to biological macromolecules is

the material basis of most biological effects of radiation. There are two main ways to damage biological macromolecules by ionizing radiation: direct effect and indirect effect. Direct action refers to the direct interaction of incident particles or rays with biological macromolecules (such as DNA and RNA) to ionize or excite these macromolecules, causing ionization or excitation of these macromolecules. Indirect action refers to the interaction of incident particles or rays with water molecules around biological macromolecules, which can ionize or excite water molecules. In fact, in any case, both direct and indirect effects exist simultaneously, and their respective contributions to the occurrence of ionization or excitation depend on many factors including the nature of the radiation, the size and state of the target, the water content of the tissue, the temperature at the time of irradiation, the presence or absence of oxygen, and the presence or absence of radioprotectors or radiosensitizers.

(1) **Changes in the structure of DNA molecules**

Deoxyribonucleic acid (DNA) is the most fundamental class of macromolecules in organisms, serving as a carrier of genetic information, directing the biosynthesis of proteins and enzymes, and dominating various functions of cells. The basic structure of DNA is dynamic and constantly changing, so it is natural for errors to occur, especially during DNA replication and recombination, both external environmental factors and internal factors of organisms often lead to damage or change of DNA molecules. The change of DNA is the material basis of all breeding. The genetic effect of radiation-induced mutations is due to the ability of radiation to ionize and excite various molecules in the organism, resulting in changes in the structure of DNA molecules, causing gene mutation and chromosome aberration, which lead to changes in genetic factors and passing them on to future generations with new genetic factors.

a. **Types of DNA damage caused by ionizing radiation**

Ionizing radiation can cause various types of damage to biological DNA. Under the action of ionizing radiation, a proton can be struck directly on the base and ionize the base. Hydrogen atoms and free radicals interact and can undergo addition reactions and dehydrogenation reactions. Due to proton transfer, the amino-keto-type hydrogen bond between the base pairs is transformed into an imino-enol type, resulting in the damage of the base structure, which can ultimately lead to a change in the state of the advanced structure of DNA (DNA supercoiled structure), thus causing a series of changes such as DNA replication and expression. The types of DNA damage mainly include base change, strand break, and cross-linking.

(a) **DNA base change**: There are following types: base ring destruction, base shedding and loss, base substitution (i.e. purine base is replaced by another purine base, or purine base is replaced by pyrimidine base), formation of pyrimidine dimer, etc.
(b) **DNA strand breakage**: It is the main form of radiation damage. The cleavage of the phosphate diester bond, the destruction of the deoxyribose molecule, and the destruction or shedding of the base can all cause nucleotide chain breakage.

The breakage of one strand in a double-strand is called single-strand breaks (SSBs), and the breakage of both strands at the same or adjacent place is called double-strand breaks (DSBs). Double-strand breaks are often accompanied by the breaking of hydrogen bonds. Although a single-strand break occurs 10–20 times more frequently than a double-strand break, it is relatively easy to repair. For most haploid cells (such as bacteria), one single double-strand break will be a fatal event.

(c) **DNA cross-linking**: After DNA molecules are damaged, covalent bonds will be formed between bases or between bases and proteins, resulting in DNA-DNA cross-linking and DNA-protein cross-linking. These crosslinks are the molecular basis of chromosomal aberrations seen under the microscope after cells are exposed to ionizing radiation, which will affect cell function and DNA replication.

The above damage will eventually lead to changes in the structure of the DNA molecules, resulting in gene mutation and chromosome aberration at the molecular level of DNA, which underlie the overall genetic mutations.

b. **Gene Mutation**

The change of gene structure caused by the addition, deletion, or change of base pairs in DNA molecules is called gene mutation. Gene mutations mainly include the following types:

(a) **Point mutation**: Refers to the variation of a single base on DNA. According to the interstrand distance of the Watson-Crick model and the characteristics of the chemical structure of the base, under normal conditions, A-T complementary pairings and G-C complementary pairings formed, thus the foundation of relatively stable genetic traits was laid. Under the influence of nuclear radiation, if the structure of the base changes, abnormal pairings may occur. As long as this abnormal pairing is not repaired, mutations at the molecular level will occur. This abnormal pairing is usually divided into transition and transversion. The substitution of purine for purine (such as the substitution between A and G) and pyrimidine for pyrimidine (such as the substitution between C and T) is called transition, and purine to pyrimidine or pyrimidine to purine is called transversion.

(b) **Deletion**: Refers to the loss of one or a fragment of nucleotide on a DNA strand.

(c) **Insertion**: Refers to the insertion of one or a fragment of a nucleotide into the DNA strand. In the sequence encoded for protein, if the number of missing and inserted nucleotides is not an integral multiple of 3, the reading frame shift will occur, which will cause all the amino acid sequences translated later to be confused, which is called a frame-shift mutation.

Genetic mutations can usually cause certain phenotypic changes, which may have four consequences for the organisms: (a) lethality; (b) loss of certain functions; (c) change the genotype without changing the phenotype; and (d) the occurrence of a result that is conducive to the survival of species and lead to an evolution, which is the basis of mutation breeding.

c. Chromosome aberration

Chromosome aberration refers to the increase or decrease in the number of chromosomes or the change in their structure. It includes the multiplied increase of the entire chromosome complement, the increase or decrease of the number of paired chromosomes, the increase or decrease of a single fragment of a chromosome, and the change of the position of individual fragments of a chromosome. Like gene mutation, the variation of chromosome structure is also one of the important sources of biological genetic variation. Compared with gene mutation, chromosome structural variation usually involves larger fragments, even to the extent that it can be recognized by a light microscope.

Chromosome structural variation involves the process of breaking and rejoining of chromatin fibers—the breakage and reunion hypothesis. Chromatin fibers can be broken in some way before and after replication and rejoined through repair mechanisms, including wrong splicing. Especially when several different breaks occur simultaneously and are very close in space, rearrangement is not difficult to occur (reconstructive healing and non-reconstructive healing). Now that it is known that the unreplicated chromosome or chromatid contains only one DNA double helix molecule, and the chromosome break is actually the break of the DNA strand, it is speculated that the reason why the chromosome can be rejoined after the break may be due to the sticky ends extending from the broken end of DNA in the form of a single strand. Chromosome aberration is divided into numerical aberration and structural aberration.

(a) Chromosome numerical aberration

The entire chromosomes of a normal sperm or egg are called the chromosome group (abbreviated as n), also known as haploid. In a normal human body, half of the chromosomes are from the father and the other half are from the mother. There are 46 chromosomes or 23 pairs, that is, two chromosomes are 2n, so it is called diploid. The increase or decrease in ploidy or change in the number of a pair of chromosomes based on diploid is collectively referred to as chromosome aberration. The former type of change produces polyploidy, and the latter type is called aneuploid aberration.

Polyploid: If the number of chromosomes in a cell is three times that of a haploid, it is called a triploid (human: $3n = 69$). If it is four times that of a haploid, it is called tetraploid (human: $4n = 92$). Those with more than triploid are generally called polyploids. In humans, polyploid is relatively rare, occasionally seen in spontaneous abortion fetuses and some hydatidiform moles.

Aneuploid: Aneuploid aberration is an irregular increase or decrease of the chromosome number in a cell compared with the normal diploid. Those with more chromosomes are called polysomic. The number of chromosomes increased by one, namely $2n + 1$, is called trisomic. And the number of homologous chromosomes increased by two, namely $2n + 2$, is called tetrasomy. By analogy, those that reduce one chromosome, namely $2n-1$, are called monomers.

(b) **Chromosome structural aberration**

It refers to chromosome breakage and rejoining in abnormal combinations. The types of aberration are:

Deficiency or Deletion: Refers to a phenomenon that a certain fragment of a chromosome and the genes it carries are lost together, thus causing a mutation. It occurs in the middle or at both ends of the chromosome.

The genetic effects of deletion are as follows: First, the vitality of organisms will be reduced, affecting growth and development. Second, pseudodominance. In heterozygotes, some recessive genes can appear due to the influence of deletion, but this dominance is pseudodominance. Third, change the linkage strength between genes. The missing chromosome formed by radiation forms the missing homozygote in the genetic process. The deletion will shorten the chromosome strand, strengthen the linkage strength of distant genes, and reduce the exchange rate. Fourth, serious genetic diseases may occur, leading to a decline in the viability and yield of crops.

Duplication: The phenomenon that a certain fragment of the same chromosome is added to cause variation. According to the sequence and position of repeat fragments, duplication can be divided into three types: tandem duplication, reverse duplication, and translocation duplication.

Duplication and deletion occur simultaneously, and the duplicated chromosome fragment comes from another chromosome deletion fragment. Duplication disturbs the inherent balance of genes. As the number of genes increases, the phenotypic effect also changes, that is, the number of genes in the repeat fragment is 3 in the cell of the repeat heterozygote and 4 in the cell of the repeat homozygote, which changes the gene pairwise balance of the organism and leads to the variation of the organism.

Inversion: A chromosome that is broken in two places, forming three fragments, with its middle fragment rotated 180° and rejoined. It includes paracentric inversion and pericentric inversion.

Paracentric inversion refers to that the inversion fragment is in one arm of the chromosome, while pericentric inversion refers to that the inversion fragment has centromeres or the inversion section is related to two arms. The genetic effect caused by inversion can in turn inhibit or reduce the recombination or exchange of genes within the inversion loop, change the exchange rate or recombination value of genes, and affect the regulation mode among genes.

Translocation: The attachment of a fragment broken from one chromosome to another. Each of the two chromosomes breaks and exchanges their acentric fragments to respectively form new derivative chromosomes and reciprocal translocation. In reciprocal translocations, it is called an unbalanced translocation if there is a loss of chromosome fragments. If there is no loss of chromosome fragment and the phenotype is normal, it is called a balanced translocation. There are two types of translocations, one is reciprocal translocation, and the other is simple translocation. Reciprocal translocation is the most common translocation. It refers to that two non-homologous chromosomes break after being irradiated, and the breaking chromosomes and fragments exchange and recombine. Simple translocation means

that a fragment of a chromosome is embedded in an arm of a non-homologous chromosome.

Translocation also produces genetic effects, including semi-sterility, reduction of recombination rate of some genes near the translocation site, and occurrence of pseudolinkage and chromosomal fusion. The probability of alternate segregation and adjacent segregation produced by translocation is equal. Alternate segregation allows for normal breeding, while adjacent segregation leads to sterility. The translocation causes chromosome fragments near the translocation site not tight enough at synapsis, resulting in a reduction in the probability of exchange, thus leading to a decline in the recombination rate.

Chromosome aberration is a typical manifestation of radiation damage in plants. Chromosome aberration (aberration type, aberration behavior, and genetic effect) has been observed in mitotic and meiotic cells of radiation-treated materials. After radiation, plants such as snapdragons and Oenothera can induce haploid generation, chromosome breakage, and structural rearrangement. In addition, radiation to Commelina communis will also cause variations in chromosome behavior, such as the appearance of chromosome bridge, chromosome backwardness, etc.

(2) **Repair of radiation damage by cells**

The repair of the system is an important and decisive process in the process of mutation, which is of great significance to studying the repair of organisms for radiation breeding. Ionizing radiation acts on DNA, causing damage to its structure and function, thus causing biological mutation and even death. However, under certain conditions, the organism can repair the damage to its DNA. This ability is a protective function acquired by organisms in the process of long-term evolution. DNA repair is a reaction of cells to DNA damage, which may restore the DNA structure to its original state and perform its original function again. However, sometimes it does not completely eliminate DNA damage, but merely enables cells to tolerate this DNA damage and continue to survive. Perhaps the damage that has not been completely repaired will be shown under suitable conditions (such as the canceration of cells), but if the cells do not have such repair function, they cannot cope with the frequently occurring DNA damage events and cannot survive. At present, it is known that the repair systems of DNA damage by cells include mismatch repair, direct repair, excision repair, recombination repair, error-prone repair, etc.

a. **Reverse repair**

This is a relatively simple form of repair, which can generally restore DNA to its original state. It mainly includes photorepair, rejoint of single-strand breaks, direct insertion of base, transfer of alkyl, etc.

(a) **Photorepair**: This is the earliest discovered DNA repair method. The repair is completed by DNA photolyase in bacteria. This enzyme can specifically recognize the dimer of adjacent pyrimidine covalently bound on the nucleic acid strand and bind to it. This step does not require light. After binding, if exposed to 300–600 nm light, the enzyme will be activated to decompose the dimer into

two normal pyrimidine monomers, and then the enzyme will be released from the DNA strand, and the DNA will return to its normal structure. Similar repair enzymes were later found to be widely present in plants and animals, and have also been found in human cells.

(b) **Rejoint of single-strand breaks**: DNA single-strand breaks are common damages. Some of them can be completely repaired by the involvement of DNA ligase alone. This enzyme is commonly found in all kinds of biological cells, and the repair reaction is easily carried out. However, double-strand breaks are almost impossible to be repaired.

(c) **Direct insertion of base**: The shedding of purines from the DNA strand results in purine-free sites which can be recognized and bound to DNA purine insertion enzymes. In the presence of K^+, free purine or deoxypurine nucleoside can be catalyzed to form glycosidic bonds at the insertion point. The inserted base is highly specific and strictly pairs with the base on the other strand, so that the DNA strand can be completely restored.

(d) **Alkyl transfer**: An ^{6}O-methyl guanine methyltransferase is found in cells that can repair damaged DNA by directly transferring methyl from the guanine O^6 site of the DNA strand to the cysteine residue of the protein. The repair capacity of this enzyme is not very strong, but the repair activity of this enzyme can be induced under the action of low-dose alkylating agents.

b. **Excision repair**

Excision repair is the most common way to repair DNA damage. It can repair a variety of DNA damage, including base-free sites formed by base shedding, pyrimidine dimers, base alkylation, single-strand breaks, etc. This kind of repair method exists in all kinds of biological cells. The repair process requires a series of actions by various enzymes, the basic steps are as follows: First, nuclease recognizes the damaged site of DNA and cleaves the phosphodiester bond. Different DNA damage requires different specific endonucleases to recognize and cleave. Second, the nucleic acid exonuclease will remove the damaged DNA fragments. Third, under the catalysis of DNA polymerase, the complete complementary strand can be used as a template to fill the gap that has been cleaved. Finally, join the newly synthesized DNA fragment to the original broken DNA strand by the DNA ligase. In this way, the original structure of DNA can be restored.

c. **Recombination repair**

The above excision repair is achieved by combining the original correct complementary strand as a template to synthesize a new fragment after the removal of the damaged fragment, but in some cases, there is no complementary strand that can be directly used. Using the other daughter-strand DNA as a template, a new DNA fragment is synthesized to fill the gap in the parent-strand DNA, catalyzed by DNA polymerase, and finally ligated by DNA ligase to complete the repair.

The damage cannot be completely removed by recombination and repair. The damaged DNA fragment remains on the parental DNA strand, but the DNA molecule

synthesized after recombination and repair do not have damage. After repeated replication, the damage is "diluted", and only one cell in the offspring cells has damaged DNA.

d. **SOS repair**

"SOS" is an international emergency call signal. SOS repair is a kind of DNA repair method induced when DNA is severely damaged and the cell is in a critical state. The result of the repair can only maintain the integrity of the genome and improve the survival rate of the cell, but with many errors left. Thus, it is also called error-prone repair, which makes the cell have a high mutation rate.

When the damage of two strands of DNA is adjacent, the damage cannot be repaired by excision or recombination. At this time, under the action of endonuclease and exonuclease, the DNA strand gap at the damaged site is caused. Then a whole set of special DNA polymerase—SOS repair enzymes produced by damage induction catalyze the synthesis of DNA at the vacant site. The added nucleotides are almost random, and the integrity of the DNA double strand is still maintained, enabling the cell to survive.

At present, there is not much understanding about the types of reactions, enzymes involved in repair, and repair mechanisms of DNA repair in eukaryotic cells, but it is clear that DNA damage repair is closely related to cell mutation, lifespan, aging, tumorigenesis, radiation effects, and the role of some toxic agents.

Higher plants have repair systems and are more capable of repair. It is reported that 50% of the single-strand breaks can be repaired when protoplasts of carrot were irradiated with 2×10^2 Gy γ-rays and placed for 5 min after irradiation, and all the breaks were repaired after 1 h. The embryos of barley seeds treated with 3×10^8 Bq-kg^{-1} of γ-rays (^{137}Cs) were found to have 65% of the single-strand breaks repaired after 2 h of immersion in water.

Inhibition or activation of the repair system in plants greatly affects the mutation rate. There are many ways to inhibit or activate. For example, can be used as both a radiation protection agent and a radiation sensitizer. Under certain conditions, treating seeds or crops with caffeine can improve the mutation rate. Further studies have shown that caffeine is an inhibitor of dark repair, which can preferentially block error-free excision repair, thus increasing the mutation rate. Bleomycin (BLM) can inhibit polynucleotide ligase, reduce DNA repair and significantly increase mutation rate. Enzyme-catalyzed photoreactivation can reduce the mutation rate of microorganisms. In crop radiation breeding, inhibitors of repair are often used to improve the mutation rate. For example, irradiated barley seeds (within 5 h after germination) were prepared with Na_2EDTA with a concentration of 1 mol/L and Tris–HCl buffer solution with a concentration of 0.1 mol/L and a pH of 7 to prepare inhibitors, and washed with water after treatment at 25 °C for 5 h. After being treated with 5 mmol/L caffeine and 1 mmol/L bromodeoxyuridine nucleoside (5-bromo-2-deoxyuridine, BUDR), the chlorophyll mutation rate of M_1 generation caused by EDTA was higher than that caused by caffeine, while the effect of mutation rate caused by BUDR was not obvious. However, in M_2 generation (the second generation of mutant plants), both EDTA and BUDR increased the dwarf mutation rate.

The above examples show that studying the repair process is very important for radiation breeding.

(3) **Radiosensitivity and mutation dose**

Selecting the appropriate mutation dose based on the characteristics of the mutagen and the sensitivity to the mutagen is the key to the effectiveness of mutation breeding. The appropriate mutagen dose is the dose that can most effectively induce beneficial mutations in crops. Within a certain range, the increase of irradiation dose is beneficial to the improvement of mutation rate and mutation spectrum. However, when the dose exceeds a certain range, increasing the dose will lead to some undesirable consequences such as reduced survival rate, increased sterility, and increased adverse mutation rate. Since there is a certain relationship between the damage indexes such as seedling height, sterility, survival rate, and mutation rate of the M_1 generation individuals, the degree of damage of M_1 generation plants is commonly used as a parameter to determine the mutagen dose, that is, the radiosensitivity of irradiated materials is used to determine the mutagen dose.

Radiosensitivity refers to the degree of corresponding changes in the morphology and function of individuals, tissues, cells, or cell inclusions under different doses of radiation. Under the condition of identical irradiation factors, different body factors lead to different natures of response to radiation.

The radiosensitivity of the organism is related to the following factors:

(a) Biological species: the higher the evolution of the species, the more complex the organizational structure of the organism, and the higher the sensitivity.
(b) Biological individuals: generally speaking, with the development of individuals, the sensitivity gradually decreases, but the elderly are more sensitive than adults.
(c) Tissue and cell: the radiosensitivity of tissue and cell is in direct proportion to its division ability and inverse proportion to its degree of differentiation, but with exceptions.
(d) The internal environment of tissues and cells: the increase of oxygen content or temperature in local tissues can increase radiosensitivity, while hypoxia and low temperature can reduce radiosensitivity. Some hormones and chemicals can also change the radiosensitivity of the body.

In practical applications, the dose required to produce quantitative biological effects is often used to reflect radiosensitivity. Low dose required means high sensitivity, and vice versa. In mutation breeding, it is often necessary to determine the radiosensitivity of the material used.

a. **Method for determination of radiosensitivity of crops**

The measurement of radiosensitivity is generally carried out at the individual, cell, or metabolic levels, and the common indicators are:

(a) Seedling height and root length: the dose of inhibiting a certain seedling height or root length is used to measure the sensitivity.
(b) Plant survival rate: the plant survival rate after irradiation is used to identify the radiation sensitivity of various crops.

(c) Plant sterility: the plant sterility after radiation treatment is a good indicator to test the sensitivity of radiation sensitivity. Within a certain dose range, the damage to plant height, leaf size, and other vegetative organs of crops may be small, but the reproductive organs have a strong response in the later stage.
(d) Leaf spot and area of soybean primary leaves: because of the high correlation between primary seedling height, leaf area, and leaf spot, the leaf area and leaf spot number can be used to replace the height of seedlings to determine the radiosensitivity of legumes.
(e) Peroxidase activity and catechol content: the activity of radiation toxin and corresponding enzyme system can be used as the indicator of crop radiosensitivity.
(f) The size of interphase nucleus volume (INV) and interphase chromosome volume (ICV): measuring the size of INV and ICV is a classical method for identifying the radiosensitivity of various crops.
(g) Determination of micronucleus cell rate: Micronucleus is an abnormal structure of eukaryotic cells, which is often produced by the action of radiation or chemical drugs. It is a determination method with chromosome damage and spindle toxicity as the endpoints.

b. **Mutation dose of crops**

The radiation dose of crops is calculated based on the absorbed dose, and the standard dose unit is Gy.

The absorption of energy by the genetic material of crops can cause structural damage. The structural damage is only regarded as a pre-mutation, that is, a mutation at the molecular level has occurred, but only when the energy absorbed by the organism (radiation reaches a certain dose level) is sufficient to destroy the chemical bonds in the organism can it cause the biological mutation in the organism and display the mutant character. In radiation breeding, the commonly used expression methods of mutation dose are (a) median lethal dose (LD_{50}): the dose required when 50% of the crops die after irradiation; (b) median dwarf dose (D_{50}): the dose when the plant height of the crop is reduced to 50% of the control group after irradiation; (c) critical dose: when the growth of crops has been significantly inhibited, but 20–30% of the plants still have the acceptable dose for the ability to form seeds during the reproductive process (Table 8.1).

Therefore, it is necessary to select appropriate irradiation dose for radiation breeding to ensure high mutation rate and excellent rate of varieties.

Table 8.1 Resonance energies of biologically important purines and pyrimidines ($\beta = 8.37 \times 10^4$ J/mol)

Compound	Resonance energy	Number of π electron	Resonance energy of each πelectron (β)
Adenine	3.894	12	0.32
Guanine	3.838	14	0.27
Hypoxanthine	3.385	12	0.28
Xanthine	3.484	14	0.25
Uric acid	3.374	16	0.21
Cylosine	2.280	10	0.23
Uracil	1.918	10	0.19
Thymine	2.050	12	0.17
5-Methylcytosine	2.412	12	0.20
Oratic acid	2.35	14	0.17
Barbituric acid	1.743	12	0.15

8.1.3 Radiation Breeding Method

1. **Common sources of mutation and treatment methods in radiation breeding**

(1) **Proton**

In the work of artificial radiation mutation, it can be observed that proton beams can cause changes such as aberration, fragmentation, and bridge on the cell chromosome. It is estimated that the value of relative biological effectiveness (RBE) is between 1.0 and 1.9. However, due to the different biological indicators used, the RBE values are also different. Protons can be obtained by accelerating H^* in cyclotrons or by electrostatic accelerators. The common method of irradiation is to place the seeds on a stainless steel mesh, seal the seeds with the mixture of dichloroethane and polyvinyl formal, and then fix the mesh on the bracket at a certain angle for irradiation.

(2) **π^- meson**

π^- meson can be produced by bombarding carbon atoms in graphite with high-energy protons of 380 meV. π^- meson has the characteristics of charged heavy particles, which penetrates almost along a straight line in the medium. When the π^- meson gradually slows down in the process of ionization and excitation, it will be captured by the atomic nucleus in biological tissue. The atoms that capture π^- mesons emit characteristic X-rays due to excitation. After the π^- meson is absorbed, in addition to a small part of the energy used to overcome the nuclear binding energy, the rest of the energy appears in the form of nuclear burst fragments, which are absorbed by local tissues, called "starbursts". Studies have shown that about 73% of the π^- mesons are captured by oxygen atoms, 20% by carbon atoms, 3% by nitrogen atoms, and 4% by heavier atoms after entering the tissue. In the case of the reaction between oxygen

and π^- meson, π^- meson capture generates a single charged particle, an α-particle, a heavy particle (mass number can be ≥ 3), and three neutrons. Because these particles are produced in the reaction process, the biological effect becomes more obvious, thus π^- meson can play a more unique role in artificial mutation breeding.

(3) **Gamma-ray**

The gamma-ray is an electromagnetic wave with a very short wavelength (10^{-8} cm–10^{-11} cm), which has a strong penetrating ability to tissues. Gamma rays transfer energy through the interaction with matter, causing changes in genetic material.

The gamma-ray source is the main mutagenic irradiation source for radiation breeding, and ^{60}Co devices, ^{137}Cs devices, and other irradiation devices are often used to treat tissues, seeds, or plants. A strict control of irradiation dose in the treatment process is the key to radiation breeding. For this reason, strict requirements are set for the accuracy of the irradiation methods and dosimetry instruments used. During the irradiation process, the distance between the radiation source and the processing material, the material and size of the container for storing the irradiated object, the location of the radiation source, and the uniformity of the dose distribution of the irradiation field should be strictly controlled.

(4) **Neutron**

Compared with γ-rays, the radiobiological effect of neutrons is far greater. Due to the wide energy range of neutrons (10^{-3} eV–10^{7} eV), the neutrons commonly used in radiation breeding are fast and thermal neutrons, which are obtained from isotope neutron sources (such as ^{252}Cf), accelerators, or reactors.

When using neutrons to treat mutagenic materials such as seeds, it is necessary to accurately measure the neutron fluence or absorbed energy in the mutagenic materials. The activation foil method can be used to measure the neutron fluence rate in crop seeds at different depths. Due to the scattering and collision of neutrons, changes in both neutron fluence and energy can be seen. In order to prevent thermal neutron interference, some activation foils need to be coated with cadmium before irradiation to ensure the accuracy of the injection dose.

Accelerator neutron source has the advantages of low construction and operation cost, stable neutron beam, narrow neutron energy distribution range, and convenient use, making it a main neutron source of radiation breeding.

(5) **Beta-ray**

Due to the small mass, beta-rays will continuously change the direction of motion within the range of Coulomb force after being injected into the medium. Therefore, when using beta-irradiation, the range of beta-rays within the seed should be measured for each energy. In radiation breeding, the range of beta-particles in soft tissue (in cm) is often estimated by 50% of the maximum energy (in MeV). For example, the maximum energy of the beta-ray of ^{32}P is 1.71 meV, and its maximum range in soft tissue can be estimated as approximately 0.86 cm.

When applying beta-rays for external irradiation, the following methods are generally used:

a. Add beta-decay nuclides to the polymeric material melt to make films of various shapes to irradiate ovaries, pollen grains, seeds, etc.
b. Dissolve beta-decay nuclides evenly into volatile solvents (such as acetone, ether, etc.), and inject them into a box with hard film on the bottom, and place them in a fume hood. When the solvent volatilizes, radioactive material substances will be evenly adsorbed on the film. Then, spray a very thin layer of polymer solution to form a protective film. Such a simple sealed radioactive source can be used for irradiation of pollen grains, germ, etc.
c. Inject radioactive solution into the interlayer of a double-layer lead cylinder or plastic cylinder with a thin inner wall (which is easy to be penetrated by beta-rays), and the branches, germs, growing points, inflorescences, etc. that need to be irradiated can be put into the cylinder for irradiation.

Commonly used beta-ray internal irradiation methods include:

a. **Seed soaking**: Soaking seeds with a solution of certain radioactive concentration can induce mutation when radioactive substances are immersed in seeds. Radionuclides commonly used for internal irradiation include ^{32}P, ^{35}S, ^{3}H, ^{131}I, etc. Take ^{32}P as an example, the radioactive concentration of barley and wheat dry seeds is 7.4×10^4–4.63×10^6 Bq·mL^{-1}. Even if the radioactive solution with very low radioactive concentration (7.4×10^2 Bq·mL^{-1}), the formation of chromosome bridges and fragments can still be observed. The amount of soaking solution for each seed is 0.1– 1 mL, and the treatment time ranged from 1 to 15 d.
b. **Plant treatment**: Add ^{32}P compound and a certain amount of carrier into the culture soil so that the plants can absorb radioactive ^{32}P through the root system, or inject ^{32}P compound solution into the leaf sheath before the formation of the plant's pollen mother cell so that the gametophyte (i.e., the plant body that produces gametes and has haploid chromosomes during the alternation of plant generations) can receive internal irradiation. Soak the leaves under cotton buds with ^{32}P solution (concentration = 7.4×10^6 Bq/mL) for one week one day before cotton flowering. In order to ensure that 32P is delivered to the flower bud, the main stem of the leaf is peeled in a circular manner. The mutation effect obtained by this method is 10 times higher than that obtained by neutron irradiation of dry seeds o soaking dry seeds with ^{32}P solution, but the selection of soaking time of leaves has a great impact on the mutation rate.
c. **Inflorescence treatment:** Inflorescence treatment is used to obtain pollen irradiated by beta-rays. This method is to cut the inflorescence and insert it into a certain concentration of a radioactive solution or inject the radioactive solution into the plant with inflorescence to allow the radionuclides to enter the pollen. For example, when the inflorescence is impregnated with ^{32}P, the commonly used radioactive concentration is 3.7×10^3–7.4×10^5 Bq·mL^{-1}, and the concentration of the carrier ^{31}P is 0.02–0.2 mg·mL^{-1}. Due to the different metabolic pathways of different radionuclides in plants, the depth of radionuclides into the microspore is closely related to the time after injection.

d. **Internal irradiation treatment of woody plants**: There are three commonly used methods for artificial mutation of woody plants by internal irradiation: (a) soak the ear in radioactive solution for a certain time before grafting; (b) inject a radioactive solution of certain activity directly into the trunk; and (c) inject the radioactive solution into the base of flower buds, adventitious buds, and twigs of fruit trees. For example, pear trees can be injected with 7.4×10^4–1.11×10^6 Bq of the radioactive solution, and the volume of injection is 0.001– 0.01 mL.

The following points should be noted when adopting internal irradiation methods:

a. Select the appropriate pH value of the radioactive solution. For example, when the leaves are soaked with phosphate (containing 32P), if the pH value is 3, the leaves can absorb phosphorus well, but if pH $\geq$ 4, the absorption rate of phosphorus by the leaves will be greatly reduced.
b. Use an appropriate amount of carrier. If the number of carriers is too large, the absorption of radionuclides by crops will be reduced, and the expected mutagenic purpose will not be achieved.
c. Understand the transport and distribution of the nuclides used in crops. It is necessary to have a general understanding of the transport and accumulation of each radionuclide in the crop, so as to increase the amount of radionuclide entering the target part of the crop and achieve effective irradiation.
d. Understand the best time for radionuclide injection into crops. The best mutagenic effect can be obtained only by knowing when the mutated crops introduce radionuclides.

^{32}P is a radiation source with a very important application value in radiation breeding by internal irradiation. Phosphorus is an important component of the genetic material DNA of animals and plants. When "feeding" crops with ^{32}P, as long as the "feeding" time is appropriate (the physical half-life and biological half-life of ^{32}P should be fully considered), ^{32}P can enter the DNA molecular structure through the metabolic pathway. After the decay of ^{32}P located on the main strand of the DNA molecule, the phosphorus atom at the position of ^{32}P will change into the sulfur atom, thus damaging the phosphate ribose ester bond on the DNA molecule. At the same time, the recoil nucleus-sulfur atom and the 1.71 meV beta-particle produced by ^{32}P decay will also cause various damages to the DNA strand structure.

(6) **Ion beam**

Ion implantation is a high technology that emerged in the early 1980s, mainly used for the surface modification of metallic materials. It has been gradually used in crop breeding since 1986 and has been gradually introduced into microbial breeding in recent years. Ion implantation mutagenesis uses ion implantation equipment to generate high-energy ion beams (40–60 keV) and inject them into organisms to cause permanent changes in genetic material, and then select excellent strains from the mutant strains. The ion beam has the dual effects of energy deposition and mass deposition on organisms, resulting in various biological effects such as death, indirect damage of free radicals, chromosome duplication, translocation, inversion or DNA

molecular breakage, base deletion, etc. Therefore, ion implantation mutagenesis can obtain a high mutation rate with a wide mutation spectrum, low mortality, high positive mutation rate, and stable traits.

2. **Oxygen, temperature, water content, and storage method**

In addition to the selection of mutagenic factors and the appropriate irradiation dose, the environmental conditions before and after treatment are also important factors affecting radiation breeding. The change in irradiation conditions not only greatly affects the irradiation sensitivity of crops, but also affects the mutation rate and mutation direction. Therefore, mutation rate, mutagenic effect (mutation rate/irradiation dose), and mutagenic efficiency (mutation rate/biological damage) can be improved by adjusting the environmental conditions. The environmental conditions affecting mutation are various, and the main environmental factors considered in radiation breeding are oxygen, temperature, and water content. The impact of these factors on biological effects is very complex and should be given full attention.

(1) **Oxygen**

Among various conditions affecting radiation damage, oxygen is the main influencing factor, and other factors such as moisture and humidity are more or less related to the role of oxygen. When an organism is exposed to oxygen (or air), its radiation sensitivity is generally higher than that in a vacuum or inert gas, which is caused by the synergism of oxygen. Oxygen has a synergistic effect because it is a scavenger of hot electrons ($O_2 + e^- \rightarrow O_2^-$), and hot electrons can recover the radiation damage. In addition, peroxyl radicals have a long lifetime, which aggravates radiation damage. Different crops have different oxygen enhancement efficiencies (OER). Among the eight crops shown in Table 8.2, onion has the lowest OER, while rice has the highest OER. Only when seeds are soaked in the absence of oxygen, the radiosensitivity of crops is related to nucleus volume (NV) and intercellular chromosome volume (ICV).

(2) **Temperature**

Temperature effect refers to the phenomenon that the radiosensitivity of biological system decreases with the decrease of temperature during irradiation. However, in radiation mutatoin breeding, since the interaction of other factors cannot be completely ruled out, the biological reaction caused by temperature change seems to be more complex. The reason why temperature can cause changes in radiation damage is mainly because it affects the structure of macromolecules such as DNA (e.g. loose hydrogen bonds, and higher temperature leads to changes in the three-dimensional structure of molecules. At the same time, the change of temperature will also affect the ability of free radicals to attack macromolecules.

Radiation breeding often uses “heat shock” to reduce the radiation damage when dealing with crops without reducing the mutation rate. The so-called “heat shock” refers to irradiating the seeds at a low temperature (such as −78 °C) and then treating

Table 8.2 Relationship between the response of extremely dry seeds to radiation and nucleus elements

Species	NV ($\mu_3 \pm$ S.E.)	ICV ($\mu_3 \pm$ S.E.)	D_{50}, seed soaking with O_2	D_{50}, seed soaking without O_2	OER
Onion	901 ± 21.0	56.31 ± 1.31	13.0	17.5	1.3
Radish	57 ± 1.9	3.17 ± 0.11	59.0	137.0	2.3
Fescue	435 ± 7.1	10.36 ± 0.17	8.1	28.5	3.5
Alfalfa	293 ± 23.0	9.16 ± 0.72	21.5	78.5	3.6
Lettuce	193 ± 0.3	10.72 ± 0.02	10.5	42.5	4.0
Cucumber	117 ± 2.2	8.36 ± 0.16	6.3	45.5	7.2
Barley	308 ± 7.4	22.00 ± 0.53	5.0	47.0	9.4
Rice	83 ± 4.1	3.46 ± 0.17	4.5	75.0	16.7

them with high-temperature water (such as 60 °C). This "heat shock" breeding method can improve the survival rate and seed-setting rate of the M_1 generation without reducing the mutation rate of the M_2 generation. Irradiating seeds at a very low temperature (such as liquid nitrogen atmosphere) is conducive to limiting the activity of free radicals to reduce radiation damage, and is conducive to further increasing the radiation dose to improve the mutation rate. Research has shown that "heat shock" can reduce the double-strand breaks of DNA and the rate of chromosomal aberration, but it increases the rate of DNA base damage (i.e., the rate of a gene mutation). Therefore, if a large irradiation dose is combined with low-temperature treatment, a more ideal radiation breeding effect will be obtained.

(3) **Water content**

In radiation breeding, seeds are usually selected as the object of treatment. Regulating the water content of seeds is a major step, and the water content in the environment plays a role in regulating the water content of seeds. At the same time, the water content in the seeds is not only a part of the body structure but also regulates the gas content of the organism. Therefore, like other factors, water does not exist alone, but forms part of a complex system. When a high chromosome aberration rate is needed, the water content of seeds can be adjusted to a low level (<6%) and irradiated under aerobic conditions.

When γ-rays are used to irradiate seeds with different water content, the radiation effect changes sharply with the change of seed water content. However, when the water content reaches a certain range (such as 14–18% for wheat), the relationship between biological effects and the change in water content is very small. Because of this characteristic, it is suggested that the water content of seeds should be adjusted to 13–14% (irradiation under aerobic conditions) in advance when X-rays and γ-rays are used for the mutagenesis test.

During seed storage, the water content of seeds also varies greatly due to the change in environmental humidity.

In the research of radiation breeding, the method of adjusting the seed water content is to use different proportions of glycerol and distilled water mixture in order to adjust the vapor pressure (relative humidity) in a closed container, and then store the seeds in the closed container for a period of time. As the relative humidity in the container is easy to adjust, the seeds can reach the expected water content. When adjusting the water content of seeds by this method, attention should be paid to the concentration and volume of glycerol and aqueous solution, the storage time of seeds in closed containers, the type of seeds, the original water content of seeds (when the glycerol-aqueous solution is 500 ml, it can be used for 2000–6000 barley seeds), etc. In addition, P_2O_5 or KOH solution desiccator with silica gel can also be used to balance the water content of seeds. If dry seeds are needed, seeds can be stored in a calcium oxide vacuum dryer, and the moisture content of the seeds obtained will be 2–8%.

(4) **Storage**

The biological effect of seeds during storage after irradiation is called the storage effect. Studies have shown that the biological effects of seeds during storage are related to the indirect effects of radiation and the repair effects of the organism. Storage effect has certain practical significance for radiation breeding. Generally speaking, seeds need to be stored for some time before breeding after irradiation, which is because the irradiated seeds need to go through a certain period to repair the biological damage caused by radiation.

The storage effect is closely related to the storage conditions (such as temperature, humidity, atmosphere, etc.). For example, irradiate wheat seeds with γ-rays (12–13% water content), and store them at low temperatures (0–2 °C), high temperature (40 °C), and room temperature for 1–120 days, the radiation damage increased, but the degree of damage varied with the temperature during storage. Another example is that if barley seeds are stored in an environment with higher humidity than when they are irradiated, the damage will be repaired. If stored in the same or low humidity, the damage will be strengthened. The water content of irradiated seeds is also related to the storage effect. When the water content of seeds is less than 6%, its biological effect decreases with the increase of the humidity of the storage environment during storage. When the water content is 7.6–12.6%, the biological effect will be independent of environment humidity. The damage of extremely dry seeds stored under non-vacuum conditions increased with the storage time, but not under vacuum conditions.

3. **Selection of induction material**

The inducing material is closely related to mutation. The main factor limiting the generation and discovery of mutation is the gene structure of the inducing material organism, rather than a specific factor. In different growth and development stages, the possibility of plant mutation is different, especially in the early stage of organ growth and development, the mutation rate after irradiation is the highest. With the development of the growth process, the mutation rate gradually decreased, and the terminal mutation rate decreased to the lowest. Research has shown that there is a correlation between the growth and decline of mutation rate and the amount of nucleic

acid and auxin in the growth point. Therefore, the mutagenic effect of radiation on crops at different growth stages is different.

Using seeds as the most common inducting material in radiation breeding is due to the advantages of easy handling of convenient mass processing, use, and transportation of seeds.

(1) **Selection of mutagenic material**

When dealing with vegetative propagation materials, every individual somatic cell may have mutations, but whether the mutant cells can be expressed depends on two aspects. Firstly, the mutation must occur in a dividing cell, and the mutant cell must have the ability to compete with normal cells. Otherwise, although the mutation has occurred, it is only surrounded by normal cells and cannot be expressed. Secondly, the mutant cell must exist in the cell layer that can express the phenotype. Otherwise, although the mutant cell can divide and reproduce, its mutant character cannot be expressed.

Materials commonly used in asexually propagated crops include dormant buds, various adventitious buds and flower buds in meiosis, dormant branches, cuttings, and leaves before and after rooting, tubers, stolons, plants, etc.

For fruit trees, the leaf buds of dormant branches are usually selected as irradiation materials. In the dormant leaf buds of deciduous fruit trees such as apples, pears, peaches, and cherries, each leaf bud generally contains 7–10 nutrient leaves, as well as leaf primordia. There are axillary bud primordia at the leaf primordia at P3 stage or P4 stage. The number of bud primordia of different tree species varies greatly. Species with fewer bud primordia cells and strong splitting ability are ideal materials.

The apical meristem is an independent histogen layer, and mutations occurring in a certain layer are generally limited in that layer. Therefore, the meristem is selected for treatment at the early stage of ontogenesis in order to obtain a higher mutation rate. For example, the early accessory buds on sweet cherry trees are ideal meristems. The irradiated accessory bud can be developed by removing the main buds or treating the accessory buds with lanolin auxin (cytokinin and indoleacetic acid promote the development of accessory buds, while gibberellin inhibits the development). In addition, the dormant winter buds of fruit trees that have been induced in the spring are also ideal materials for treatment, because they can produce higher mutation frequency than summer buds.

The irradiation treatment of bulbs and tubers is best carried out in the growth stage because there are fewer primordial cells during this period. However, some studies have shown that larger bulbs and tubers have more scaly buds and can tolerate higher doses. Thus, it is better to choose larger bulbs as treatment materials than small bulbs, but the key is to choose the appropriate treatment time.

Adventitious buds originate from a single cell on the surface. If the treated material is induced to produce adventitious buds, it is expected that the non-chimeric mutant can be obtained. Therefore, leaves that can produce adventitious buds and root cuttings of fruit trees that propagate from the roots are more desirable treatment materials. Like sexually propagated crops, varieties should be carefully chosen when selecting mutagenic materials. The mutation spectrum of different genotypes is

different. When inducing other colors of chrysanthemum, the pink variety is the best starting material. The same is true for the pink variety of tulips, the yellow variety is difficult to mutagenize into other colors.

(2) **Asexual reproduction crop treatment method**

In terms of treatment methods, asexual reproduction crops are similar to sexual propagation. During the mutation of fruit trees, the mutation dose varies greatly due to different gene types and physiological conditions. For example, before irradiation treatment of deciduous fruit trees, a small amount of test material (such as scions, cuttings, etc.) selected by different dose treatments can be used to find 30–40% lethal dose as the mutagenic dose, so as to obtain a large favorable mutation rate.

4. **Tissue and cell culture technology in radiation breeding**

Radiation mutagenesis has the characteristics of a single cell, and the chimerism caused by it has a great interference with the appearance and selection of mutation and mutant. Thus, tissue and cell culture techniques are very important in both experimental mutagenesis and breeding. It is easier to treat cells or tissues at different stages by tissue culture. This is because the replication of chromosomes at different stages is asynchronous, and the replication period at each stage is particularly sensitive to mutation treatment. If a specific stage is selected for treatment, specific variations can be caused. The degree of gene activation is also different in different tissues of higher plants and the same tissues at different growth stages. Therefore, the type of tissue treated or the reproductive stage can be selected as needed.

(1) **Radiosensitivity and mutation dose of cells and tissues in vitro**

Like plants, the radiosensitivity of cells or tissues in vitro is also subject to a variety of factors. Callus is a commonly used treatment material in radiation breeding, and almost all plant tissues (commonly used are leaves, stem segments, endosperm of seeds, anthers of floral organs, etc.) can be induced to produce callus. Among them, another culture can form the haploid callus, and haploid plants can be directly induced from the callus. Haploid cells can also be produced by suspension culture of haploid callus, which can be further irradiated to induce homozygous diploid mutants, which is of great significance for radiation breeding.

The radiosensitivity of callus is different from that of plant tissue or seed. For example, comparing the sensitivity difference of dry tobacco seeds and tobacco callus to γ-rays, the result is that the seeds can still germinate and grow after being irradiated at a dose of 3.78×10^{11} Bq·kg^{-1}, but the growth of callus gradually stops and tends to die. Therefore, it is generally believed that callus is more sensitive to γ-rays than seeds. Another example is that the radiosensitivity of callus clones induced by maize anthers treated with γ-rays and neutrons is far greater than that of dry seeds, but the test results when using kidney beans as inducing materials are the opposite (seedlings are more sensitive to radiation than seeds, and seeds are more sensitive to radiation than callus). Radiosensitivity is a relative index, and the results are related to crop types, experimental conditions, and observation time. For example, the callus induced by rice anthers treated with 3.78×10^{11} Bq/kg of γ-rays can continue to

grow within one month, but the function of inducing organs has been lost. When the callus induced by sorghum seedling cuttings is treated with γ-rays, the lethal rate will be more than 80% at the dose of 1.90×10^{11}–4.77×10^{11} Bq/kg, and the ability to grow into green seedlings will be lost at the dose of more than 9.55×10^{10} Bq/kg.

Different protoplasts have different responses to the same dose. At the same time, the type of radiation, the composition of the culture medium, and the culture conditions also affect the radiosensitivity of protoplasts to a certain extent. Even in a protoplast culture community, there may be several components with different sensitivities. The cell survival rate can be expressed by an exponential relationship, and its radiosensitivity can be identified by the mean lethal dose D_0.

(2) **Radiation effects in cell culture**

a. **Dose effect**: After the cells cultured in vitro are treated with ionizing radiation, the lethal effect of cells is strictly related to the induced mutation effect. Within a certain dose range, the mutation frequency of cells gradually increased with the increase of dose, while the survival rate decreased.
b. **Dispersed dose effect and short time interval effect**: When carrying out split ionizing radiation, if the time interval between each time is relatively long, the cells can be repaired to a certain extent, and this effect is called the dispersed dose effect. If the time interval is short, the short time interval effect will occur, that is, the radiosensitivity of cells will increase instantaneously. For example, within 10 min after radiation to carrots, the degree of damage will be great, but after 30 min, 90% of the damage will be repaired.
c. **The influence of indirect effect**: The indirect effect refers to the irradiated sample itself forming damage, and the energy deposited in the sample continues to transfer, causing damage to other normal macromolecules. If the irradiated callus is inoculated with the non-irradiated callus, the non-irradiated callus will also be damaged.
d. **Repair effect of delayed plate culture**: For example, use the suspension culture cell of haplopappns gracilis as the material to induce resistance mutation to cycloheximide. If the irradiated suspension is stored on the shaking table under dark conditions, the cell survival rate will be improved after the plate culture is delayed for a certain period. Under this condition, the potentially lethal damage (PLD) can be significantly repaired. However, a longer delay will not improve the cell survival rate.

(3) **Isolation and selection technology of mutant cells or mutants**

There are two methods for the isolation and selection of mutant cells or mutants. One is through cell or tissue culture. After radiation treatment, induce and culture the mutants according to conventional methods, and then select the mutants according to the needs of breeding. It is possible to cultivate homozygous plants through haploid culture, then treat the protoplasm of mesophyll cells with radiation, induce mutant plants through plate culture and other technologies, and then select according to agronomic traits. Another possibility is to treat the anther or the callus of pure line

plants, and then select them after inducing them into plantlets. Mutants can be selected in the M_1 generation using this method, and the mutation rate and mutation spectrum can be greatly improved.

For example, tobacco anthers treated with γ-rays can be selected by haploid culture technology in the M_1 generation, and the mutation rate is significantly increased. The specific method is as follows:

(i) Culture the tobacco anthers for testing into seedlings, double them with colchicine and let them self-pollinate to produce a pedigree for mutagenesis.
(ii) Treat the microspores with different doses of ^{60}Co γ-rays and develop the survival curve. The LD_{50} can be calculated as 15 Gy (dose rate = 300 Gy·h^{-1}).
(iii) Collect anthers when the corolla and sepals of tobacco flower organs were equal in length (p = s).
(iv) Treat the cultured anthers. The observation results showed that the callus induction rate was higher when treated within 7 days of the culture time. After 7 days, the longer the culture time, the higher the mortality rate. The induced callus would also stay in the callus stage for a long time and could not form organs.
(v) Gradually transplant the induced plants to the field.
(vi) For obvious mutants, cut off the petioles and culture them to obtain mutants from the callus.

The second method refers to the microorganisms selection method during cell culture. The principle is that when dealing with cell colonies, only a part of the cells become mutants. If these mutant cells cannot grow (cannot replicate DNA) on the minimal medium, but can still be in the survival state, then some treatment can be given so that some cells that can grow normally die, and the mutant cells can be isolated and retain to cultivate into some defective mutants.

During cell culture, cell suspensions can be obtained in many ways. For example, it can be obtained by oscillating callus. It can also be obtained by subculture after crushing materials such as seedlings without bacteria and seeds with hygroscopic expansion through a homogenizer. In addition, cell suspension can also be obtained from different plant tissues with cellulase and pectinase. However, it should be noted that there are not only free single cells in the suspension, but also cell clusters formed by plant aggregation. Due to different methods of planting and different materials for testing, sometimes there are a large number of cell clusters in the culture medium, but only a few free cells. Sometimes a large number of highly dispersed free-cell cultures are obtained because radiation events have the characteristics of single-cell events. Therefore, the individuals added by the cell cluster are obviously unfavorable for radiation breeding.

8.1.4 Application and Prospect of Radiation Breeding

The American Müller is not only the founder of artificial mutation but also the first successful mutation breeder. The CIB drosophila strain cultivated by him is a

very useful new variety of drosophila. In the 1930s, Swedish scientists Gustafsson, Nybom, and Hagbery began to work on mutation breeding and made great achievements. By the 1950s, Sweden had become the center of radiation mutation breeding research in the world. In the 1970s, mutation breeding has become a prairie fire, and the number of new varieties obtained by mutation has been countless.

The genetic effect of radiation-induced mutation is that radiation can ionize and excite various molecules in the organism, causing changes in DNA molecular structure, and resulting in gene mutation and chromosome aberration. Under the action of ionizing radiation, the normal metabolism of biological organisms is disturbed, and the growth and development of organisms are seriously inhibited, which causes genetic factors to change and pass on to the offspring with new genetic factors.

In early radiation breeding, X-ray was the main source of mutation. After the 1960s, γ-rays and neutron beams were widely used. Since the 1980s, helium, neon lasers, and ion beams have also been used in radiation breeding, but ^{60}Co γ-rays are still the most commonly used radiation mutation source for flowers and crops. The number of γ-ray breeding products accounts for more than 56% of the total. Treatment materials include plant seeds, pollen, asexual reproductive organs, tissue culture (callus), and living plants, and animal materials include poultry eggs, fish eggs, and microorganisms. Through this method, a large number of early-maturing, dwarf, disease-resistant, stress-resistant, high-quality, and other special mutants with utilization value were obtained, providing a large number of genetic seed resources for breeding. For example, the fast neutron irradiation mutation breeding of chestnuts is to irradiate chestnut branches with fast neutrons to select and breed excellent mutant plants, so as to achieve high quality and high yield of chestnuts.

There are two types of radiation treatments: external irradiation and internal irradiation. External irradiation treatment is to send seeds or plants into the irradiation room for irradiation or plant them in the cobalt garden for long-term chronic irradiation during the whole growth period. Internal irradiation treatment is to introduce radioactive elements such as ^{32}P and ^{35}S into the irradiated seeds or some organs of plants through seed soaking and injection. In order to improve the effect of radiation mutation, multiple mutagenic factors can be used. Using the hybrid progeny as radiation material can obtain favorable variants and then cross with conventional materials. The combination of radiation mutation and in vitro culture technology, and the use of living irradiation and other technologies can improve varieties or create new mutation types.

1. **Development of radiation mutagenesis methods and technologies**

At present, in the research and practice of radiation breeding, focusing on improving the frequency of induced mutation and selection efficiency, the methods and technologies of radiation breeding such as mutagenic factors, mutagenic objects, mutagenic conditions, and screening methods have been constantly improved.

The selection of irradiation materials is one of the important links in radiation breeding. The genetic background of the original materials plays an important role in the performance of mutant characters and the efficiency of mutation. In the early stage of radiation mutation, seeds are generally treated. In recent years, almost all

plant organs and propagules have been used for mutagenesis, such as dormant seeds, germinating seeds, heterozygous seeds, seed embryos, pollen, polyploids, adventitious buds, root buds, branches, bulbs, callus, etc. As for the flowers that are often cultivated by asexual reproduction technology, radiation mutation often induces somatic variation in plants, and then transmits the variation to the offspring through asexual reproduction to form asexual propagation lines, so the application prospect of radiation mutation in flowers is very broad.

The key to the success of radiation mutation breeding is to take the appropriate radiation dose, that is, to achieve more variation without causing too much damage to the plant. According to long-term practice, half lethal dose or critical dose is usually used for the selection of general dose.

The limitation of mutation breeding lies in how to identify and select excellent mutants by effective means. Before the 1970s, it was only judged by conventional agronomic shape. In the 1970s and 1980s, the variation at the cellular level and the detection of isozymes at the sub-molecular level were observed by chromosome compression. Since the 1990s, molecular marker technology has been developing continuously. Caetano-Anolles and others have used molecular markers on crops to analyze some mutants, distinguish true and false mutants, and label mutant genes using a continuous relationship with molecular markers.

2. **Prospect of radiation breeding**

Although radiation mutation has made some progress in breeding varieties, the mutation rate of favorable characters is not high enough, the mutation spectrum is not wide enough, and the mutation has no directionality. Broadening mutation spectrum, increasing mutation rate, directional mutation, and shortening breeding cycle are the development direction of radiation mutation breeding in the future. The following aspects should be paid attention to on the premise of adapting to resistance breeding (disease resistance, cold resistance, low light resistance, heat resistance, etc.) and quality breeding (including plant color, plant shape and smell, plant height control, etc.) in the world seed industry.

Select appropriate mutagenic sources and develop new mutagenic sources. Different mutagenic sources are suitable for different plant breeding objectives, and the application of X-rays to γ-rays has greatly improved the mutation rate. The mutagenic source is an effective material basis to ensure plant breeding. At present, the radiation used to deal with mutagenic materials is generally a single mutagenic source. In the future, space-carrying technology should be used to carry out comprehensive mutagenic research on multiple radiation sources.

Selection of mutagenic materials. As the radiosensitivity of crop materials varies greatly in different tissues, organs, and developmental stages, the selection of appropriate materials is beneficial to the improvement of the mutation rate and the broadening of the mutation spectrum. For example, with the development of modern tissue culture technology, callus, or other materials from tissue culture are used as mutagenic materials. Broertjes and some other scholars have made progress in the applications of flowers such as chrysanthemums, tulips, canna, etc.

Directed mutagenesis is the continuous goal of radiation breeding. Based on the mutants provided by mutation, molecular markers were used to screen molecular markers linked with target genes. Build a genetic map, carry out target gene mapping and trait linkage analysis, and carry out directional breeding of new varieties. On the contrary, control various mutagenic factors, analyze the changes of known genes, mutate the materials to make the breeding objectives tend to be favorable, and improve the relative frequency of target variation traits in the total variation.

Tissue culture is also called rapid propagation. The combination of tissue culture technology and radiation breeding has opened up a broad prospect for showing somatic mutations, which overcomes the randomness, chimerism, and single-cell mutation defects of radiation-induced mutations, resulting in high breeding efficiency and short cycle. However, this method lacks directionality. If it can be combined with molecular markers, it can increase directionality based on high breeding efficiency, short cycle, and high mutation rate. Therefore, this chapter proposes a new compound breeding idea combining mutation, tissue culture, and molecular markers, which will create a new situation in both flower breeding practice and mutation mechanism research.

8.1.5 Compound Mutation

After long-term use of mutagens for a certain strain, in addition to the "fatigue effect" of the mutagen, it will also cause adverse consequences such as prolonging the growth cycle of the strain, reducing the spore quantity, and slowing down metabolism, which is unfavorable to the control of fermentation process. In actual production, several mutagens are often used to treat the strains in combination and cross-use.

Compound mutation includes the successive use of two or more mutagens, the repeated action of the same mutagen, and the simultaneous use of two or more mutagens. It is generally believed that compound mutation has a synergistic effect. If two or more kinds of mutagens are properly combined, the effect of compound mutation is better than that of the single mutation, but there are also examples of reduced effect after compound mutation. Compared with a single factor, the mutagenic effect of compound factor has great advantages. However, because the genetic background of most microorganisms, especially antibiotic-producing bacteria is still unknown at present, the selection and use of mutagens, especially compound mutagens are often with great blindness.

The purpose of mutation is to obtain new mutations. In the Morgan era, the richness of genetic research was closely related to the discovery of new mutations. At present, the content and means of genetic research are far different from those in the past, but obtaining new mutations and selecting the mutants beneficial to human beings is still one of the hot spots. There are many new methods to cultivate new varieties such as using molecular biological technology to cultivate transgenic animals and plants, but mutation breeding is still a simple, easy, and common method.

8.2 Radiation Preservation

Radiation preservation of food is a new technology that uses ionizing radiation to extend the preservation time and improve the quality of food. Its basic principle is to use the particle beam of the ray or accelerator product to irradiate the food and cause a series of physical, chemical or biochemical reactions to achieve the purpose of killing insects, sterilizing, inhibiting germination, inhibiting ripening, etc., thus reducing the consumption of food due to corruption in storage and transportation, increasing the supply, extending the shelf life, improving the hygienic quality of food, etc.

8.2.1 Introduction to Radiation Preservation

Radiation preservation is a kind of "cold processing" technology without adding additives, which can maintain the original flavor and improve the technological quality of food. There is no pesticide residue in irradiated food, which will not pollute the environment and will not induce radioactivity. Among them, γ-ray has strong penetration ability, it can uniformly and thoroughly treat prepackaged or cooked food, which is convenient to operate and saves time. Irradiation can completely kill insects and sterilize, and can be used as an effective quarantine measure. Irradiation processing consumes less energy, most of the processing does not need refrigeration, which is an ideal method to save energy. Besides, the irradiation operation is easy to control and suitable for large-scale and continuous processing.

1. **Irradiation condition**

Radiation sources and radiation devices are the basic conditions for radiation preservation. Three kinds of radiation sources are used for fresh-keeping or preservation: γ-rays generated by ^{60}Co and ^{137}Cs, β-rays generated by electron linear accelerators, and X-rays generated by X-ray tubes.

Two kinds of devices can be used in the laboratory test stage, namely ^{60}Co or ^{137}Cs radiation device and electron accelerator. For small and thin-packaged items, a linear accelerator is easier to manage.

In order to meet the special process requirements, such as improving the uniformity, ensuring temperature control during irradiation, reducing the oxygen content during irradiation, reducing the mechanical damage (bruise) of food during transmission, irradiation and storage, and improving the utilization rate of radiation sources in the plant from an economic point of view, the design of the irradiation plant should be very perfect. In addition to specify the appropriate irradiation type and dose range, the influence of other conditions and factors should also be considered. Take the irradiation of potatoes as an example, the factors to be considered include whether to irradiate immediately after harvest or after several weeks of storage, whether to irradiate in bulk or package, the packaging materials and containers used, and whether to store at room temperature or 10°C after irradiation.

The irradiation conditions of food for health and safety experiments should be consistent with those of food for human consumption as far as possible. For food used for animal experiments, the dose should be at least the maximum dose used for commercial promotion. In addition, during irradiation processing, certain physical properties, such as water content, oxygen potency, temperature, and storage conditions after irradiation, are required to be as close as possible to the conditions for commercial promotion.

The effect of radiation disinfection depends on the product nature, microbial species, irradiation dose, and storage conditions after radiation, which should be treated differently according to needs.

2. **Dose and dose rate for various products and samples**

The absorbed dose of food under the action of radiation is different, and the changes are also different. The size of the absorbed dose has a direct impact on insect killing, sterilization, changes in nutrient composition, inhibition of growth, and metabolism, and is related to the effect of radiation preservation. Therefore, the absorbed dose of food after irradiation must be measured as accurately as possible.

Different kinds of food and different preservation purposes have their own optimal radiation dose. The FAO/IAEA/WHO Joint Expert Committee believes that the key to achieving the ideal quarantine requirements for eliminating pathogenic microorganisms or plant pests is to determine a minimum critical dose threshold. At the same time, to meet the technological requirements, the minimum irradiation dose must also be specified. In order to avoid the use of excessive radiation doses which may produce some harmful compounds for human health, a maximum radiation dose threshold needs to be determined (in Table 8.3, the D_{10} value is the irradiation dose required to kill 90% of the microorganisms).

Generally speaking, low-dose irradiation (less than 10 kGy) is used to reduce microbial microorganisms, reduce the number of non-spore pathogenic microorganisms, and improve the technical quality of food, while high-dose irradiation (10–50 kGy) is used for sterilization and virus elimination for commercial purposes. Under appropriate physical conditions, the use of uniform irradiation disinfection (radappertization) with a dose of 10–70 kGy does not seem to affect the safety of food for human consumption. The accepted dose limit is 15 kGy, and the average dose value is generally 10 kGy when uniformity is considered (Table 8.4).

It must be pointed out that good technology requires mastering radiation dose measurement and quality control. In food irradiation, a high dose rate is usually used, and the uniformity of dose distribution should be fully considered in the design of irradiation devices.

3. **Comprehensive treatment technology**

Food irradiation is a technology that can save more energy than the traditional physical storage method. If radiation can be combined with other physical or chemical treatment methods, it can reduce the total dose of one or two treatments or the amount of chemical reagent, so as to reduce costs, save energy and improve the irradiation effect.

Table 8.3 D_{10} value for important food pathogenic bacteria or microorganisms

Pathogenic bacteria	D_{10} value/Gy	Suspending medium	Irradiation temperature/°C
A. hydrophia	0.14–0.19	Beef	2
C. jejuni	0.18	Beef	2–4
E. coli O157: H7	0.24	Beef	2–4
I. monocytogenes	0.45	Chicken	2–4
Samoneliaspp	0.38–0.77	Chicken	2
S. aureus	0.36	Chicken	0
Y. enterocolitica	0.11	Beef	25
C. botulinum (sports)	3.56	Chicken	−30
C. botulinum A	4	Food	–
C. botulinum B	3.3	Buffer solution	–
B. pumilus	3	Buffer solution (anaerobic)	–
C. perfringens	2.1–2.4	Meet	–
B. subtilis	2–2.5	Buffer solution	–
S. cerevisiae	2–2.5	Buffer solution	–
B. stearothermophilus	1	Buffer solution (with Oxygen)	–
S. typhimurium	0.7	Buffer solution	–
P. chysogenum	0.4	Frozen egg	–
E. coli	0.2	Meet solution	–

Table 8.4 Dose range required for various effective treatments

Purpose	Dose range/Gy
Inhibition of potato and onion germination	30–100
Sterility of insects and parasites	30–200
Kill insects and parasites	50–500
Reduce the number of nutritive bacteria, molds and fungi by 10^6	10^2–10^3
Reduce the number of dried or lyophilized nutritive bacteria, molds and fungi by 10^6	2×10^2–2×10^3
Number of viruse decreased by 10^6	10^3–4×10^3
Food sterilization	2×10^3–4.5×10^3
Improve the rehydration rate of dehydrated vegetables	10^3–82×10^3

Low-dose radiation treatment and medium-degree heating treatment are effective and economic means to prevent food spoilage. High-dose radiation disinfection and heat treatment of enzyme inactivation enables meat, poultry, and aquatic products to be stored for several years without freezing. Experiments have confirmed that the bacteria remaining in food products after irradiation are generally more resistant to environmental conditions (e.g., temperature, pH, inhibitor) than the bacteria

in untreated food products, which is the same as the bacteria after heating sterilization. Therefore, a comprehensive treatment combining radiation treatment with other methods plays an important role in improving sterilization ability, reducing energy consumption, and improving food quality.

(1) **Preservative and ionizing radiation**

Salt is the oldest preservative used by human beings, which can increase the sensitivity of irradiation sterilization. Sodium chloride can sensitize conidia during irradiation, and iodized salt can even enhances the sensitivity of spores. The combined treatment of radiation and salicylic acid has a synergistic effect on inhibiting the germination of potatoes and onions in general storage. The germination can be completely inhibited with the lowest dose.

(2) **Heating and ionizing radiation**

The combination of heating and radiation treatment can improve the antiseptic effect of radiation treatment (especially for protein food) while having no side effects on the quality of normal cell tissue. For various tropical and subtropical fruits, slight heating and low-dose irradiation can effectively prevent fruit decay caused by fungal pathogens. Heat and radiation treatment of peanuts (65 °C, 500 Gy) can inactivate some toxic fungi such as aflatoxin. The shrimp can be stored for 35 days after being washed with seawater and treated with 2000 Gy irradiation, while the storage time after being heated for 5 min after washing and treated with the same dose of irradiation is 35 days to 42 days.

Irradiation treatment can be combined with microwave, infrared, and low-dose chemicals to control the pest. It is not effective to use one method alone, but combined use of multiple methods can reduce radiation dose and save costs.

(3) **Repeated irradiation**

Repeated irradiation of food should be avoided. Repeated irradiation can cause the accumulation of radiation decomposition products, but due to its low concentration, the toxicological hazard is small. Repeated irradiation can also lead to a decline in the sensory properties and nutritional value of food. Avoidance of repeated irradiation is based on the following reasons: (a) the concentration of radiation decomposition products is a linear function of dose; (b) the concentration of some radiation decomposition products decreased obviously and rapidly after irradiation; and (c) the overall average dose required based on toxicology and other factors to be considered has been established.

Therefore, repeated irradiation is only allowed in two cases: the irradiated food is a kind of processed food that has been irradiated at a low dose (for example, the dried onion processed from the onion with radiation inhibition), and the food containing a small amount of irradiated ingredient (such as meat products and concentrates containing irradiated spices). In both cases, the radiation products formed in the final product are insignificant.

Dividing the total dose to be irradiated into multiple irradiations should not be regarded as repeated irradiation.

(4) **Packaging material**

During irradiation processing, food packaging materials have a certain impact on the radiation effect. After years of experiments, it has been shown that there are two types of packaging materials and containers available: reliable metal containers, and light multi-layer film packaging materials.

There are several requirements for metal containers:

a. Properly control the can-making equipment to ensure that there is no gap.
b. Use the cool process if possible.
c. Use non-polluting cooling water.
d. Master the minimum physical damage.

For light multilayer film packaging materials, the radiation dose level of polymer materials should be fully considered. Under the action of radiation, polymer materials will undergo a series of reactions, including cross-linking, degradation, formation of double bonds, gas emission, and oxidation. The order of radiation resistance of polymer materials commonly used in food packaging from high to low is polystyrene > polyethylene terephthalate > cellulose acetate > polyethylene > cellophane. Halogen-containing materials such as polyvinyl chloride and polyvinylidene chloride will release free halogen during irradiation, which will affect the texture and flavor of food. Therefore, halogen-containing polymers are generally not used as food packaging materials.

Radiation preservation of food has been proven to be a safe and effective technology through more than 40 years of worldwide research. At present, about half of the countries in the world are conducting developmental research on it.

8.2.2 Research and Application Status of Irradiation Worldwide

The world witnessed a food irradiation boom from the late 1960s to the early 1970s. The United States, Japan, and other developed countries built several food irradiation devices with ^{60}Co as the radiation source to test their technical and economic feasibility.

In the late 1970s, with the progress of accelerator technology and its advantages of safety and efficiency, some countries began to use electronic accelerators to process food. The former Soviet Union scientists used the Van de Graaff accelerator (electrostatic accelerator) as the radiation source and found that the same dose of γ-radiation had the same effect on killing the main pests in the grain. From 1976 to 1977, the former Soviet Union developed a semi-productive device for radiation disinfestation of grain, which was designed by the Food Research Institute and produced by the Institute of Nuclear Physics, Siberian Branch of the former Soviet Academy of Sciences. At that time, the manufacturing cost of the two accelerators was 440,000 USD. In 1980, the former Soviet Union built a production system for treating grain

by electron beam irradiation in the Odessa Port Depot of Ukraine, which is mainly intended to replace chemical agents to treat imported grain when it is infected with pests, with a treatment of approximately 2×10^5–3×10^5 t per year. As it was only used to kill grain insects, its installed power was small and the irradiation dose was only 0.3 kGy. Since 1950, more than 50 countries around the world have carried out or are carrying out research on radiation treatment of up to thousands of food. As of 2000, 38 countries have officially approved the hygienic standards of 223 kinds of irradiated food.

The electron beam irradiation technology has been proven to be a mature technology with broad prospects and has been widely used in developed countries such as Russia, the United States, and Japan. According to a joint announcement issued by FAO, IAEA, and WHO in 1980, it was confirmed that when the total average absorbed dose of any food does not exceed 10 kGy, no toxicological risk is found, and it is also safe in nutrition and microbiology. This conclusion was recognized by the Codex Alimentarius Commission (CAC). By 1999, the three organizations issued a joint announcement again, which proved that there was no safety problem in irradiated food with a dose of more than 10 kGy. The high-energy electron beam sterilization method produced by electron accelerators is becoming the development trend. As long as the radiation device is constructed and operated in strict accordance with the isolation design and control requirements, its safety management will not have any problems. In order to ensure the effectiveness of sterilization, WHO has formulated a unified standard that can completely kill bacteria as long as the absorbed dose is controlled within a certain range. No radioactivity will remain in the items irradiated by the electron beam, thus this method is not only an important means of disinfection and sterilization of disposable medical supplies but also a reliable and effective option to kill anthrax to resist international terrorism.

8.2.3 Prospect

With the development of the economy and technology, people are more and more aware of the importance of protecting the environment. It has become the consensus of all countries in the world to reduce environmental pollution and leave enough development space for future generations. In recent years, the variety of food treated by irradiation has increased continuously, mainly including aquatic products, meat, dried and fresh fruits, dried and fresh vegetables, spices, cooked food, grain, feed and medicinal materials, various packaging materials, various medical supplies, and so on, which has achieved satisfactory results and obvious economic and social benefits. In the control of stored grain pests and microorganisms, the comprehensive control technology based on green and pollution-free irradiation technology will replace the method based on chemical agents, which will become the development trend of stored grain pest control in the future with broad market prospects.

8.3 Radiation Disinfestation

Radiation disinfestation is the technology that uses ionizing radiation to control insect pests. The irradiation effect is related to the amount of dose, and its biological effect results in chromosome translocation of insect germ cells and damage at the appropriate dose, which makes some of the irradiated insects lose the ability to continue their offspring (heredity sterility) and can be passed on to the next generation, making the next generation more sterile than the current generation. This dose is called the semi-sterile dose. The amount of dose, higher than which will lead to the complete sterile of insects, is called the sterile dose. When the irradiation dose is further increased, the pest will not be able to complete the generation alternation and slowly die, which can achieve the purpose of prevention and control. This dose is called the delayed lethal dose. When the irradiation dose is further higher, the pest will be directly killed in a short time, which is called the lethal dose.

8.3.1 Introduction to Radiation Disinfestation Method

Radiation control of pests, especially the sterile insect technique (SIT), is a biological control method of "controlling insects with insects", which has no negative impact on the human ecological environment. It is different from the traditional biological control method, which does not rely on natural enemies or inhibitors (such as bacteria, bacteria, viruses, antibiotics, etc.), but uses the characteristics of the insect instinct to continue the race to achieve the effect of killing pests. This section will focus on the relevant knowledge of SIT. Table 8.5 lists several examples of the application of radiation sterile technique to control pest populations.

1. **General principles and characteristics**

Without considering the effect of pest population density on the reproduction rate and ignoring the impact of environmental conditions on the survival rate of pests, it is assumed that a pest population is 1 million, and each generation propagates at a ratio of 5 times. If the control measure that kills 90% per generation is adopted, the residual rate will be 10%. As shown in Table 8.6, only 62,500 animals can be killed by the fifth generation. When the population size decreases, only a small amount of pesticides can kill the pests and reduce the amount of pesticide.

If the male sterility technique is used, the release of the sterile male is 9 times that of the normal male, and the probability of mating between a normal male and a normal female is 1/10 are released after the first generation, the proportion of sterile males and normal females will increase sharply, that is, the mating probability of normal males and normal females will decrease sharply.

Table 8.5 Applications of SIT to control pest populations

Order	Insect name	Test site
Diptera insects	Corkscrew fly	Southeastern United States
	Mediterranean trypetid	Hawaii, California (United States); Tanerife (Spain)
	Citrus fruit trypetid	Guam (United States)
	Melon fruit trypetid	Guam (United States)
	Mexico trypetid	Tijuana (Mexico); California Border (USA)
	Inslan fruit trypetid	Warren (Australia)
	Glossina morsitans	Lake Kariba (Zambia)
	Onion fly	Wageningen (Netherlands)
	Culex pipiens	New Delhi (India)
	Anopheles	Lake Apastepeque (El Salvador)
	Blood fly	Kervill (Texas, USA)
	Horsefly	The Hague (Florida, USA)
	European housefly	Lazio (Italy)
	South American trypetid	Small-scale experiments in coastal valleys of Peru
	Anopheles quadrimaculatus	Florida (United States)
Coleoptera insects	*Boll weevil*	Southeastern United States
	Gill horn golden beetle	Vendlintcourt (Switzerland)
	Red cotton bug	Small-scale experiments in coastal valleys of Peru
Lepidoptera insects	*Cydia pomonella*	Canada, United States
	Tobacco bud noctuid	Virgin Islands, United States
	Corn noctuid	Virgin Islands, United States
	Tobacco green worm	Virgin Islands, United States
	Pink bollworm	Virgin Islands, United States

Table 8.6 The change of population size when spraying insecticide on the population with fivefold reproduction per generation

Generation	Untreated group	Prevention and control area
1	1,000,000	1,000,000
2	5,000,000	500,000
3	25,000,000	250,000
4	125,000,000	125,000
5	625,000,000	62,500

The natural pest population (Y) that survived after releasing the sterile male can be expressed by the following formula.

$$Y = \frac{N}{S+N} \times V \tag{8.1}$$

where

N number of natural insect population;
S number of sterile males;
V survival probability of egg to adult under natural conditions.

It can be seen that the radiation male sterility method has a significant effect on controlling pests when the population density is low. The key to the success of the control of radiation sterility is the ability of the natural population to recover its quantity. That is to say, the growth ability of the number of viable individuals, that is, the reproduction rate, is closely related to insect physiology, ecology, environment, and other factors. The actual reproduction rate is calculated by the following formula.

$$R = \frac{V P^j bf}{1 - bP^k} \tag{8.2}$$

where

V survival rate from egg to adult eclosion;
P daily survival probability of female adults;
j mediant of the female adult from eclosion to the first spawning;
b average number of eggs per spawning;
f the proportion of female eggs in the average number of eggs;
k the number of days between the first spawning and the next spawning.

When the reproduction rate is 1, that is, when the population is in equilibrium, the probability of survival from egg to adult eclosion V_{eq} is given by the following formula:

$$V_{eq} = \frac{1 - P^k}{bfp^j} \tag{8.3}$$

If the maximum value of V (Vmax) is known, the actual reproduction rate (R) can be calculated by the following formula.

$$R = \frac{V_{\max}}{V_{eq}} \tag{8.4}$$

2. **Sterile insect technique**

The factors considered in the sterile insect technique include the selection of control objects, appropriate dose and irradiation method, artificial breeding, packaging and

transportation, and field release, as well as the population dynamics, migration capacity, and control effect of pests.

(1) **Selection of control objects**

The control object must meet the following five conditions:

a. It can establish a large-scale feeding method, which is economical and reasonable.
b. The released sterile males can be fully dispersed in nature.
c. Sterile treatment should not adversely affect the mating behavior of sterile males. Sterile males should have the same vitality and mating competitiveness as the males from wild populations, and no adverse effects should occur on their foraging and longevity.
d. The female should be monogamous. Even if it is polygamous, the sperm of a sterile male is as competitive as that of a wild male.
e. Species with low population densities or the natural population of pests are significantly reduced in a certain period.

In addition, the pest distribution area must be geographically isolated with a natural barrier to prevent pests from migrating from neighboring areas. The released sterile insects must be harmless to humans, animals, and plants. The ecology and biology of the species must be detailed. The sterile insect technique requires more sterile males than natural males, the more the better, so the cost of cultivating sterile males is also an important consideration. When male sterile pests are released into nature, they should have strong vitality, high dispersion, and a strong ability to pursue females. If the above requirements cannot be met, the sterile insect technique is not an appropriate method to be adopted.

(2) **Appropriate dose and irradiation method**

The radiation of α-rays, β-rays, γ-rays, and fast neutrons can all lead to the sterility of insects. The dose of radiation sterility is the absorbed dose of insect sterility, which refers to the radiation dose absorbed by the unit mass of the insect body when the irradiation causes complete sterility. Generally speaking, the sterilization dose of Diptera is 20–90 Gy, that of Coleoptera is 24–120 Gy, and that of Lepidoptera is 250–500 Gy. The sterilization dose varies greatly among different families in the same order. For example, in dipteran insects, the sterilization dose of mosquitoes is much higher than that of flies. The dose of Anopheles to sterilize is 1.15×10^{11} Bq/kg, while that for screwworm flies is only 2.39×10^{10} Bq/kg.

In order to restrain the reproductive period of the irradiated pests and avoid the injury caused by the collision of pupae eclosion adults during the irradiation, a low temperature of 0–2 °C is generally used for inhibition, followed by the irradiation. Different insects, different insect states, different developmental stages, and different sexes have different radiosensitivity to various rays and are generally more sensitive at the early stage of development. On the premise of determining the type of radiation used and the appropriate dose of irradiation, select the period when it is most sensitive to germ cells and least damage to somatic cells, as well as having no effective effect

for mating competitiveness, irradiate with the best dose rate and better results can be achieved.

(3) **Semi-sterility pest control**

Some insects need very high doses to cause sterility, for example, the sterilization dose of lepidopteran pests is 3.82×10^{11}–4.77×10^{11} Bq/kg. If insects are irradiated with this amount of radiation, although it may cause sterility, it will also cause great damage to somatic cells, which will seriously affect the living ability and mating ability of pests. This requires a reduction in irradiation. Using a semi-sterile irradiation dose to irradiate insects, only 50–70% of the eggs of their offspring cannot be hatched, but the hatched adults are still highly sterile, just like male sterility, which can also achieve the purpose of controlling insect species.

The conditions for using the semi-sterility method of pest control should consider:

a. The maximum semi-sterile irradiation dose does not affect the life span of the pest nor reduce its vitality and mating ability.
b. The semi-sterile irradiation dose is sterile for most male insects, while for female insects, it must be sterile or near sterile. The offspring of the treated female and the normal male can still be hatched, but their vitality is weak and the degree of harm is low. In this way, the mixed pupae can be released after irradiation, so as to avoid the difficulty of distinguishing male and female pupae in the artificial breeding process, and releasing semi-sterile males and sterile females into nature at the same time to control the pest population.
c. For pests, the F_1 generation is more sterile than the parent generation. The ideal result is that the parent generation is semi-sterile and the F_1 generation is sterile.

(4) **Effects of radiation on insect cytogenetics and reproductive physiology**

The sensitivity of various cells to radiation is different. The growing and dividing cell tissue is more sensitive to radiation than the stopped-growing cell tissue, the germ cell is more sensitive than the somatic cell, and the germ cell is more sensitive at the early stage of development than at the mature stage. The sensitivity of each part of the cell to radiation is also different, and the nucleus is more sensitive than the cytoplasm. Radiation effects mainly occur in the nucleus. Under the radiation effect, the chromosome is damaged, mitosis, meiosis, and cell differentiation are inhibited or stopped, and nucleus pyknosis occurs.

Radiation mutation can be divided into two types: one is a gene mutation, and the other is chromosome aberration. Under low-dose irradiation, the mutation is usually caused by a single hit, while under high-dose irradiation, the mutation is caused by multiple hits. The mutation frequency of germ cells increases with the increase of irradiation dose within a certain range, beyond which cell death will occur. The dominant lethal mutation is a type of radiation mutation, and the amount of radiation that causes such mutations varies among different species of insects.

Radiation also has certain effects on the gonads of female insects. At low doses, the development of the ovary is inhibited, the egg laying does not decrease, but the egg hatching rate will be decreased. Under the action of a high dose, the ovarian function

stops and gradually degenerates, the oocyte and trophoblast nucleus is destroyed, and the amount of eggs laid is reduced, or even no eggs are laid. Oogonia is highly sensitive to radiation at the early stage of egg formation. When exposed to large doses of radiation, the formation of eggs will stop completely. If the trophoblast is damaged by radiation, the normal development of eggs will be affected. At the end of egg formation, the resistance to radiation is enhanced, and the egg can mature even after being exposed to high doses of radiation.

Radiation also has effects on the gonads of male insects. Generally speaking, the reproductive cells of male insects at different stages of development are also different in sensitivity to radiation. For example, the spermatogonia of the sperm of the corn borer and peach borer are the most sensitive to radiation, followed by spermatocytes and sperm cells, and the mature sperm has the strongest resistance to radiation.

In the larval stage of insects, the male gonad is in the early stage of sperm formation, that is, the spermatogonia stage. After being irradiated by a certain amount of radiation, the germ cells are completely destroyed, thus the adult insects have no sperm. However, the somatic cells are also in the stage of differentiation and growth at this time and are also damaged by radiation, therefore, most insects die before eclosion. In the pupae stage of insects, sperm is in the process of formation. After being exposed to a certain amount of radiation, sperm loses its activity, that is, its ability to move and fertilize. After mating, the male will not fertilize even if the inactive sperm is sent to the female. Before eclosion, even if the insect sperm is irradiated at the mature stage, the dominant lethal mutation can occur in the sperm. In this case, although the sperm has the ability to fertilize, the fertilized egg cannot divide and develop normally, it will die in the process of embryonic development, or after hatching, which is the technical basis of radiation infertility.

The genetic basis of radiation semi-sterility is that radiation causes the break of the chromosome. For dipteran and hymenopteran insects with a monocentric structure of chromosomes, after the male insect is been irradiated, the deletion and bridge caused by chromosome breakage will be brought into the fertilized egg, resulting in the imbalance of zygote chromosomes, and the first and second mitosis of zygote will be stopped, resulting in early embryo death. However, for lepidopteran insects with a full centromere structure, after the male is been irradiated, the broken part of the chromosome cannot form a deletion or a chromosome bridge, but all enter into the fertilized egg, and during cell division, the broken chromosome is recombined in the form of translocation, and thus some chromosomes are repaired. The dominant lethal mutation of chromosome occurs in the early embryo of insects with monocentric structure, but in the late embryo of insects with full centromere structure. In addition, due to the full centromeric structure, most of the chromosomes are connected with the spindle, so a lot of energy is required to break the chromosomes. Therefore, the radiation sterile dose and lethal radiation dose of Lepidopteran insects are higher than those of Dipteran and Hymenopteran insects, especially after the chromosome break of the whole centromere structure, it can still be rearranged in the way of translocation. This kind of translocation can make the offspring highly sterile, which is the basis for reducing the exposure and applying semi-sterile technology to eliminate lepidopteran pests. That's to say, the treatment of pests with semi-sterile irradiation can lead

to more than 95% of F_1 generation pests losing fertility by transferring the cell chromosome translocation caused by radiation to the next generation.

8.3.2 Characteristics of Sterile Insect Technique

(a) No environmental pollution, conducive to ecological balance. Radiation sterility is a biological control method, without chemical residue, with no impact on crops and the ecological environment, and does not harm human, humans, animals, or natural enemies of pests and beneficial insects, which is a very safe and sanitary control method.
(b) Strong specificity and clear objectives. Only one specific kind of insect can be controlled without harm to other insects.
(c) The control is lasting and thorough. Radiation sterility can exterminate a pest over a large area. If this pest is no longer migrated from other areas, crops (as well as livestock and forests) can be protected from damage for a long time.
(d) Special effects. Special results can be achieved by using the sterile insect technique on pests with strong natural concealment (borer habit), or those that have developed drug resistance, or those that are difficult to control in general.
(e) Significant economic benefits. Because the control effect is lasting and it is possible to achieve the goal of extermination and eradication of pests, the benefits will be long-term. For example, the ratio of technical benefit to costs of control and rooting out of the screw-worm can reach 50:1.
(f) High one-time investment. The sterile insect technique requires a large number of insects to be raised artificially and released to nature. The cost of manpower, materials, and equipment (feed, radiation source, etc.), as well as the released transportation equipment and personnel investment in the feeding process, are very large. However, the large investment of the start-up fund is worthwhile when weighed against the results achieved in the long term.

In principle, the sterile insect technology requires that the number of sterile males is larger than that of natural males. The higher the proportion of sterile males released and wild normal males, the better the effect. For this reason, large-scale insect breeding plants should be established to obtain a large number of artificially raised, qualified, and irradiated sterile insects at a low cost, which is the primary issue related to the success of this technology. Therefore, this method is not suitable for insects that cannot be raised in large numbers or can be raised in large numbers but are expensive.

8.3.3 Lethal Dose

In addition to radiation sterility, the high energy of rays can also be used to directly kill pests. According to a large number of scientific experiments, a series of radiation lethal doses of pests have been obtained, as shown in Tables 8.7, 8.8, and 8.9 (the dose units are 10^{10} Bq/kg, except for those marked with Gy).

The γ-rays generated from ^{60}Co or ^{137}Cs sources are generally used to kill pests. Through experiments or consulting references, different dose rates and irradiation doses can be selected to directly kill pests. This technology is mainly used in the fields of killing pests in the process of grain storage, food pests, field pests, pests in the archives library, plant quarantine, etc.

Table 8.7 Lethal dose of some pest larvae

Insect species	Temperature (°C)	Age/day	Dose (10^{10} Bq/kg)	Mortality rate (%/day)
Sitophilus zeamais	26	5–20	3.81	100/21
Callosobruchus maculatus	27	14	60 Gy	LD_{100} (Total lethal dose)
Sitophilus granaries L	26	7–11	3.81	99.9/60
Tribaolium confusum Duval	30	14–15	52 Gy	99.9/28
Tribolium castaneum Herbst	30	14–15	105 Gy	99.9/28
Callosobruchus chinensis (Linnaeus)	28	–	11.47	LD_{100}
Oryzaephilus surinamensis Linne	30	10–11	86 Gy	99.9/21
Lasioderma serricorne	28	–	11.47	LD_{100}
Dermestes Maculatus Degeer	–	Early period	7.62	100/15
Trogoderma granarium Everts	–	–	5.74	LD_{100}
Tephritidae	–	–	7.62	LD_{100}
Bactrocera dorsalis Hendel	–	Old age	15.28	LD_{100}
Bactroceracucuribitae (Coquillett)	–	–	14.87	LD_{100}
Large white	22	–	7.62	LD_{100}
Scirpophaga incertulas	28	Mature	15.76	100/13
Sitotroga cerealella	28	–	34.37	–
Helicoverpa armigera (Hübner)	–	Old age	23.87	100/11
Ephestia cautella	22	–	28.64	22.4/7

Table 8.8 Lethal dose of some pest pupae

Insect species	Temperature (°C)	Age/day	Dose (10^{10} Bq/kg)	Mortality rate (%/day)
Callosobruchus maculatus	27	27	200 Gy	LD_{100}
Sitophilum granarius L	26	26–32	10.69	100/28
Tribaolium confusum Duval	30	20–31	145 Gy	99.9/28
Tribolium castaneum Herbst	30	26–27	250 Gy	99.5/21
Oryzaephilus surinamensis Linne	30	Early pupae	145 Gy	99.5/28
Oryzaephilus surinamensis Linne	30	Late pupa	308 Gy	85/15
Broad bean weevil	28	–	22.87	99.9/63
Rhizopertha dominica	30	–	23.87	LD_{100}
Dermestes Maculatus Degeer	28	–	95.46	LD_{100}
Three kinds of green flies *(Lucilia illustris, Lucilia cuprina, Lucilia sericata)*	–	2–3	2.86	LD_{100}
Musca domestica L	–	0.2–0.8	1.91	LD_{100}
Anastrapha Ludens (Loew)	–	–	23.87	LD_{100}
Plutella xylostella (Linnaeus)	22	1 day before eclosion	33.41	LD_{100}
Scirpophaga incertulas	–	Pre-pupa	15.76	91.3/10
Pectinophora gassypiella	26	Overwintering pupae	57.35	41.3/12
Helicoverpa armigera (Hübner)	–	Early pupae	238.65	LD_{100}

8.4 Prospects of Nuclear Technology Applications in Agriculture

8.4.1 Water Content Measurement in Large Areas by Cosmic-Ray Neutron Sensor

Moisture is important for a country or region to achieve sustainable development. Soil moisture content and groundwater resources determine the industrial, agricultural, and population arrangement that a country or region carries. The moisture of a point or a small area of land can be measured by conventional methods, which cannot detect the moisture of a region. For soil moisture detection, the cosmic-ray neutron sensor (CRNS) can measure the moisture content of a circular area with a diameter of 250 m. The method can generate neutrons from the reaction of heavy ions in the universe with the air, so as to react with the soil on the ground surface (mainly with H). By measuring the number of neutrons entering the air and soil per unit of time, the relationship curve between neutron number and regional soil water

Table 8.9 Lethal doses of some adult pest

Insect species	Temperature (°C)	Age/day	Dose (10^{10} Bq/kg)	Mortality rate (%/day)
Sitophilus zeamais	28	26–28	11.47	100/16
Callosobruchus maculatus	27	0–1	1700 Gy	100/2
Sitophilum granarius L	24–25	21	160 Gy	100/21
Tribaolium confusum Duval	30	4–11	222 Gy	99.4/24
Tribolium castaneum Herbst	26	4–11	340 Gy	99.9/21
Oryzaephilus surinamensis Linne	30	–	206 Gy	99.9/21
Rhizopertha dominica	30	–	250 Gy	100/63
Cryptolestes pusillus Oliver	28	–	120 Gy	100/15
Dermestes Maculatus Degeer	28	–	95.46	100/10
Cryptolestes ferrugineus (Stephens)	28	–	14.32	100/23
Cryptolestes turcicus (Grouville)	28	–	14.32	100/13
Aleurobius farinae	–	–	257.74	100/7
Coptotermes formosanus Shiraki	–	–	28.64	100/3
Blattodea	–	–	28.64	100/10
Silverfish	–	–	28.64	100/20
Louse	–	–	66.82	100/26
Anobiidae	–	–	152.74	100/29

content can be obtained. The CRNS method is calibrated for the soil water content (SWC), removing the signal of other SWCs in the environment, and obtaining the water content to provide a scientific basis for the carrying capacity. These provide a scientific basis for the industrial and agricultural, population carrying capacity, and sustainable development of a certain region.

8.4.2 Treatment of Radioactively Contaminated Soil

After the Fukushima nuclear accident, the International Atomic Energy Agency (IAEA) and the Food and Agriculture Organization (FAO) jointly developed the DSS4NAFA software, which is used for contamination data collection, data analysis, decision-making, and advice-giving for agricultural products following a nuclear accident. The software enhances the response to nuclear emergencies in agriculture.

8.4.3 Soil Erosion Assessment and Ocean Acidification Monitoring

^{239}Pu, ^{240}Pu, ^{137}Cs, ^{7}Be, and ^{210}Pb are tracers for soil erosion assessment, especially for long-term soil erosion and degradation using ^{239}Pu and ^{240}Pu with longer half-lives, which is conducive to the scientific management of cultivated land and the control of desertification. If CO_2 is not absorbed by seawater and controlled, the concentration of CO_2 in the atmosphere will reach 700 ppm, leading to the extinction of a large number of organisms on earth. At present, The CO_2 concentration in the atmosphere is maintained at 400 ppm after CO_2 is absorbed by seawater. A large amount of CO_2 entering the ocean will lead to acidification of the seawater. Ocean acidification leads to the death of a large number of algae, the loss of food for marine organisms relying on algae, and irreversible damage to marine ecology. The effects of seaweed photosynthesis and ocean acidification on marine ecology can be studied by ^{32}Si and ^{67}Cu tracing. In addition, radioisotope tracing is also used to study the erosion of acidified seawater on the coast. These technologies provide a scientific basis for the governance of sustainable human development.

8.4.4 Other Prospects on Nuclear Agronomy

In order to improve the yield of saline land and desert crops, effective water and fertilizer management is needed. Products that retain water in the soil are the key, of which the main technology is the synthesis of hydrogels using radiation.

The combination of nanotechnology and radiation technology can be explored to develop nanomaterials for food packaging, which can be biodegradable, reflect the freshness of food during storage, and inhibit spoilage bacteria, etc. Chitosan can be widely used as plant growth promoter after radiation degradation. The products of radiation degradation of natural substances (chitosan, seaweed, kala algae, crab and shrimp shells, etc.) can replace pesticides and chemical fertilizers, inhibit viruses and bacteria, and be used as natural antioxidants for food, drug, and cosmetics to

achieve freshness. These technologies are the development direction of technology R&D and industrialization that nuclear agronomy will focus on in the future.

Exercise

1. What are the types of DNA damage? Please describe them in detail.
2. What factors are related to the radiosensitivity of the body?
3. The determination of radiosensitivity is generally performed at three levels: individual, cell, or metabolism. What are the common indicators?
4. What is the basic principle of radiation preservation?
5. In radiation pest control technology, what conditions must be met by the control object?

Bibilography

Almeida, A. C., Dutta, R., Franz, T. E., Terhorst, A., Smethurst, P. J., Baillie, C., & Worledge, D. (2014). Combining cosmic-ray neutron and capacitance sensors and fuzzy inference to spatially quantify soil moisture distribution. *IEEE Sensors Journal, 14*(10), 3465–3472. https://doi.org/10.1109/JSEN.2014.2345376

Evett, S. R., & Steiner, J. L. (1995). Precision of neutron scattering and capacitance type soil water content gauges from field calibration. *Soil Science Society of America Journal, 59*(4), 961–968. https://doi.org/10.2136/sssaj1995.03615995005900040001x

Fan, K., & Zhang, M. (2019, August 6). Recent developments in the food quality detected by non-invasive nuclear magnetic resonance technology. In *Critical reviews in food science and nutrition.* Taylor and Francis Inc. https://doi.org/10.1080/10408398.2018.1441124

Feliciano, C. P. (2018, March 1). High-dose irradiated food: Current progress, applications, and prospects. In *Radiation physics and chemistry.* Elsevier Ltd. https://doi.org/10.1016/j.radphyschem.2017.11.010

Ferreira, I., Antonio, A. L., & Verde, S. C. (2018). *Food irradiation technologies: Concepts, applications and outcomes.* The Royal Society of Chemistry.

Franz, T. E., Zreda, M., Rosolem, R., Hornbuckle, B. K., Irvin, S. L., Adams, H., Kolb, T. E., Zweck, C., & Shuttleworth, W. J. (2013). Ecosystem-scale measurements of biomass water using cosmic ray neutrons. *Geophysical Research Letters, 40*(15), 3929–3933. https://doi.org/10.1002/grl.50791

International Atomic Energy Agency. (2016). *Nuclear technology review 2016*.

International Atomic Energy Agency. (2017). *Nuclear technology review 2017*.

International Atomic Energy Agency. (2018). *Nuclear technology review 2018*.

International Atomic Energy Agency. (2019). *Nuclear technology review 2019*.

International Atomic Energy Agency. (2020). *Nuclear technology review 2020*.

Klenke, J. M., & Flint, A. L. (1991). Collimated neutron probe for soil water content measurements. *Soil Science Society of America Journal, 55*(4), 916–923. https://doi.org/10.2136/sssaj1991.03615995005500040003x

Kume, T., & Todoriki, S. (2019). Current status of food irradiation in the world. *RADIOISOTOPES, 68*(7), 469–478. https://doi.org/10.3769/radioisotopes.68.469

Nishihira, J. (2020). Safety of irradiated food. In *Genetically modified and irradiated food: Controversial issues: Facts versus perceptions* (pp. 259–267). Elsevier Inc. https://doi.org/10.1016/B978-0-12-817240-7.00016-4

Phogat, V. K., Aylmore, L. A. G., & Schuller, R. D. (1991). Simultaneous measurement of the spatial distribution of soil water content and bulk density. *Soil Science Society of America Journal, 55*(4), 908–915. https://doi.org/10.2136/sssaj1991.03615995005500040002x

Ravindran, R., & Jaiswal, A. K. (2019, July 1). Wholesomeness and safety aspects of irradiated foods. In *Food chemistry*. Elsevier Ltd. https://doi.org/10.1016/j.foodchem.2019.02.002

Smolko, E., Cerchietti, L., Clozza, M., Giardina, E. B., Villela, F., & Divo, M. D. (2014). Radiation processed materials in products from polymers for agricultural applications. In *Radiation processing of marine algal polysaccharides as plant growth promoters* (pp. 18–25).

Wang, J., & Yu, Y. (2011). Effect of gamma irradiation pretreatment on embryo structure and long-term germinating characteristics of rice seed. *International Agrophysics, 25*(4), 383–388.

Zheng, L. L., Wang, R. Y., & Sun, J. J. (2012). Fuzhao Baocang Jishu Zai Shiping Zhongde Yingyong Jinzhan [Application progress of radiation preservation technology in food]. *ShiPing Yanjiu Yu Kaifa, 33*(03), 239–240.

Zhu, X., Shao, M., Jia, X., Huang, L., Zhu, J., & Zhang, Y. (2017). Application of temporal stability analysis in depth-scaling estimated soil water content by cosmic-ray neutron probe on the northern Tibetan Plateau. *Journal of Hydrology, 546*, 299–308. https://doi.org/10.1016/j.jhydrol.2017.01.019.

Chapter 9
Peaceful Use of Nuclear Energy



The twentieth century was an important stage in the rapid development of human civilization. However, this development mainly depends on the uncontrolled development and utilization of natural resources such as coal, oil, natural gas, and other fossil fuels. These limited and non-renewable natural resources cannot meet the growing world energy demand for long. The American Petroleum Institute estimates that the crude oil reserves on the earth that have not yet been exploited are less than 2 trillion barrels, and the time available for human exploitation is not more than 100 years. Oil and natural gas will be exhausted by the end of the twenty-first century. According to the World Energy Congress, although the coal resources are relatively rich, the proven recoverable reserves of coal in the world are about 9.842×10^{11} t, which can only be exploited by humans for more than 200 years. By about 2500, fossil resources will be exhausted. During the process of consuming these fossil resources, a large amount of waste is produced. For example, the global emission of carbon dioxide alone is up to 2.10×10^{11} t per year, accompanied by other toxic substances such as SO_2 and NO_x. With the rapid development of global industry, the amount of waste emissions has shown an obvious upward trend, which has caused serious damage to the ecological environment on the earth and posed a great threat to the living space of humans.

With the rapid development of the world economy, the contradiction between energy production and consumption, energy demand, and environmental protection has become increasingly serious. The limited energy reserves have been unable to meet the increasing demand of mankind, and the energy situation is becoming more and more severe. In order to cope with the shortage of energy supply and alleviate the deterioration of the ecological environment caused by energy consumption, the existing traditional energy sources should be fully utilized, new energy-saving technologies should be researched, new energy sources should be actively developed, and research on the relationship between energy and environment should be carried out.

New energy is relative to traditional energy. It usually refers to nuclear energy (fission energy and fusion energy), wind energy, solar energy, geothermal energy,

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6_9

tidal energy, biomass energy, ocean thermal energy conversion, etc. In addition, technologies that can improve the efficiency of energy utilization and change its use modes, such as magnetic fluid power generation, coal gasification, and liquefaction, are new energy conversion technologies that also belong to the category of new energy technology. Nowadays, the rise of oil prices and the progress of science and technology have promoted the development and utilization of new energy.

Although the above green energy has attracted more and more attention from scientists, it is difficult to realize large-scale industrial production and application in a short time due to geographical location, climate conditions, and other factors. At present, only nuclear energy is safe and economical energy that can be used on a large scale. There are two main types of nuclear energy, namely nuclear fission energy and nuclear fusion energy. The available resources of these two kinds of energy are very rich, among which the exploitable nuclear fission fuel resources (including thorium) can be used for thousands of years, and the nuclear fusion resources can be used for hundreds of millions of years. Fission nuclear energy has been greatly developed so far. However, the production of nuclear fuel for nuclear fission power generation and the process of power generation produce a large amount of nuclear waste, which is more hazardous. Compared with nuclear fission energy, nuclear fusion energy can be exploited in a cleaner way. Therefore, scientists are generally optimistic about using the huge energy released from controllable nuclear fusion reactions to generate electric energy. Nuclear fusion power generation is still under research and development. At present, many countries and regions are vigorously developing nuclear fission power generation and actively carrying out international cooperation to promote the realization of nuclear fusion power generation.

This chapter will briefly describe the principles, types, and non-military applications of nuclear energy.

9.1 Principles of Nuclear Energy and Characteristics of Nuclear Power Generation

It is well known that the nucleus is composed of neutrons and protons. The mass of an atom should be equal to the sum of the masses of the elementary particles that make it up. However, in reality, it is not that simple. Through precise experimental measurements, it has been found that the mass of an atomic nucleus is always less than the sum of the masses of its protons and neutrons. For example, a helium atom is composed of two protons and two neutrons, with two electrons outside. The mass of the helium atom should be:

$$\begin{aligned} m_{He} &= 2m_p + 2m_n + 2m_e = 2 \times 1.00728u + 2 \times 1.00867u \\ &\quad + 2 \times 0.00055u = 4.033u \end{aligned}$$

where m_p is the proton mass, m_n is the neutron mass, and m_e is the electron mass; u is the mass unit, $1u = 1.66 \times 10^{-24}$ g.

However, the measured mass of helium atom $m_{He} = 4.00260u$, which is 0.0304u less than the total mass of its basic particles. Another example is the ^{238}U atom, whose nucleus consists of 92 protons and 146 neutrons, and has 92 electrons outside the nucleus. The total mass of these particles should be 239.986u, but the atomic mass of ^{238}U measured directly is 238.051u, which is 1.935u less.

The mass reduction phenomenon described above also exists in other nuclei. This phenomenon is called "mass defect".

According to Einstein's mass-energy relationship $E = mc^2$, the reduction of mass during the nuclear reaction must be accompanied by the release of energy, that is, $\Delta E = \Delta mc^2$. This energy released when a number of protons and neutrons are combined to form a nucleus is called the binding energy of the nucleus, namely nuclear energy.

The general chemical reaction is only the change of the bonding relationship between atoms, that is, the change of the binding state of electrons outside the nucleus, and the nuclear structure will not change. Since the binding force between nucleons is much greater than that between atoms, the energy change of a nuclear reaction is several million times greater than that of a chemical reaction. For example, the heat released when 4 g of hydrogen is completely burned can boil about 1 kg of water, while the heat released in the nuclear reaction of synthesizing 4 g of hydrogen atoms can boil 5.0×10^3 t of water. The difference between the heat released by the two manners is up to 5 million times. Another example is that 1 kg ^{235}U fission can release energy equivalent to 2.7×10^3 t of standard coal. The fusion reaction of 1 kg tritium releases more energy, which is equivalent to the heat of 1.1×10^4 t of standard coal or 8.6×10^3 t of gasoline after combustion.

Nuclear energy includes nuclear fission energy, nuclear fusion energy, nuclide decay energy, etc. The main forms of nuclear energy are nuclear fission energy and nuclear fusion energy. Nuclear fission energy is the energy released by the nuclear fission reaction of heavy elements (uranium or thorium, etc.) under the bombardment of neutrons. Nuclear fusion energy is the energy released by the nuclear fusion reaction of light elements (deuterium and tritium). The following section focuses on the generation of these two forms of nuclear energy.

9.1.1 Nuclear Fission Energy

Some heavy nuclear atoms, such as ^{235}U, undergo a nuclear fission reaction under the bombardment of thermal neutrons, producing two nuclides and several neutrons of different mass, and releasing a large amount of energy. Take ^{235}U as an example:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{137}_{56}\mathrm{Ba} + {}^{97}_{36}\mathrm{Kr} + 2{}^{1}_{0}\mathrm{n} + 200\ \mathrm{MeV} \tag{9.1}$$

It is estimated that the energy released from the complete fission of 1 kg ^{235}U is equivalent to the chemical energy released from the complete combustion of 2.7×10^3 t of standard coal. In an uncontrolled chain reaction, it takes only one nanosecond (10^{-9} s) to start the fission of an atomic nucleus and release neutrons until the neutrons trigger the fission of the next generation of atomic nuclei. In a very short time and a limited space, the huge energy released by nuclear fission will inevitably cause a violent explosion. The atomic bomb is made according to the principle of this uncontrolled chain reaction. By controlling the chain reaction, nuclear fission energy can be slowly released, which can be used for direct heating or power generation. Nuclear fission power plants use controllable nuclear fusion to generate electricity.

The nuclear materials used to generate nuclear fission energy are mainly ^{235}U and ^{239}Pu. The abundance of ^{235}U in natural uranium is only about 0.7%. Although ^{232}Th and ^{238}U have high abundance and large storage in nature, they cannot be directly used for the generation of nuclear fission energy. However, these proliferative materials can be converted into high-quality fissile nuclear fuels such as ^{233}U and ^{239}Pu through nuclear reaction under the action of fast neutrons, thus greatly improving the utilization rate of resources. Just the proven uranium reserves are sufficient to be used from now to the era when nuclear fusion energy and solar energy replace nuclear fission energy.

9.1.2 Nuclear Fusion Energy

Nuclear fusion is a process in which the nuclei of two or more light elements, such as the nucleus of hydrogen isotope deuterium (^2_1H or D) or tritium (^3_1H or T), polymerize into a heavier nucleus. In this process, because the mass loss of some light elements such as deuterium in fusion is larger than that in nuclear fission reaction, according to $E = mc^2$, more energy will be released.

There are many kinds of fusion reactions, in which the followings are easier to achieve, and the phenomenon of energy release has been observed in the laboratory.

$$\begin{aligned}
&D + D \rightarrow {}^3He + n + 3.25\ MeV \\
&D + D \rightarrow T + p + 4.00\ MeV \\
&T + D \rightarrow {}^4He + n + 17.6\ MeV \\
&{}^3He + D \rightarrow {}^4He + p + 18.3\ MeV \\
&{}^6Li + D \rightarrow 2^4He + 22.4\ MeV \\
&{}^7Li + p \rightarrow 2^4He + 17.3\ MeV
\end{aligned} \tag{9.2}$$

As with the atomic bomb, if the fusion reaction is not controlled, the hydrogen isotopes deuterium (D) and tritium (T) will release a large amount of heat immediately when the nuclear fusion reaction occurs, and will also produce a huge explosion. The hydrogen bomb is made using this principle. The explosion of a hydrogen bomb is

an uncontrollable process of energy release, and the duration of the whole process is very short, only a few millionths of a second. As an energy source, fusion reactions are expected to occur slowly and continuously under artificial control and to convert the energy released into electrical energy output. This process of nuclear fusion under artificial control is called controllable nuclear fusion.

9.1.3 Characteristics of Nuclear Power Generation

Nuclear power generation is currently the most important way of using nuclear energy for peaceful purposes in the world. Nuclear power generation has many obvious advantages in terms of economy and environmental protection.

1. **Rich nuclear energy resources and high energy density**

Uranium, thorium, deuterium, and other resources needed to produce nuclear energy are abundant on the earth. The proven nuclear fission fuel on the earth, namely uranium and thorium resources, is equivalent to 20 times of organic fuel in terms of its energy content. In nature, each ton of seawater or river water contains an average of 30 g of deuterium. It is estimated that global seawater contains about 2.34×10^{14} t of deuterium, which can be extracted in large quantities. The unit capacity of these nuclear resources is very huge. For example, the energy generated by 1 t of pure uranium fission is equivalent to the energy generated by 2.7×10^6 t of standard coal, while the energy generated by 1 t of deuterium fusion is equivalent to 1.1×10^7 t of standard coal. It can be seen that 1 t of seawater can replace 33 t of standard coal. Therefore, the space for the use of nuclear energy is very large, especially after the completion of the nuclear fusion power station, due to the existence of a large amount of available deuterium resources on the earth, mankind will no longer be troubled by the energy problem.

2. **Nuclear power is clean energy, which is conducive to environmental protection**

After the combustion of fossil fuels such as oil and coal, a large amount of coal cinder, soot, and oxides such as sulfur, nitrogen, and carbon, as well as carcinogens such as mercury and cadmium are released into the external environment. These substances not only directly endanger human health and crop growth but also lead to acid rain and the greenhouse effect, which greatly damage the global ecological balance. The site selection, construction, and operation of the nuclear fission power plants must comply with the nuclear safety regulations (rules) and relevant laws confirmed internationally or approved by the national government departments. Solid and liquid radioactive wastes shall be recovered and temporarily stored (re-sent for treatment and disposal), and gaseous radioactive effluents shall be filtered by special facilities and released after meeting the standards. Therefore, the nuclear power plant discharges only a small amount of residual tail gas and wastewater that have been treated and meet

the corresponding emission standards to the environment. Decades of experience in operating nuclear power plants shows that the total dose of radioactive emissions from nuclear power plants is 1.2 Sv on average for each 1.0×10^{11} kW h (equivalent to 3.6×10^{14} J) power generation, while the total dose of radioactive substances in the ash of coal-fired power plants is 3.5 Sv. This shows that even from the perspective of radioactive emissions only, the harmfulness of nuclear fission power is smaller than that of thermal power. Nuclear fusion power plants, in some sense, produce almost no radioactive waste.

3. **In terms of cost performance, nuclear power is superior to thermal power**

The cost of thermal power generation mainly includes the construction and depreciation of the power plant and the cost of fossil fuels such as oil and coal. The fuel cost of thermal power plants accounts for 40–60% of the power generation cost. Since nuclear fission power plants pay special attention to safety and quality, their construction cost is generally 30–50% higher than that of thermal power plants, but their fuel cost only accounts for 20–30% of the power generation cost, which is lower than that of thermal power plants. Experience has proved that the power generation cost of nuclear fission power plants is 15–50% lower than that of thermal power plants on the whole. Coal and oil are valuable raw materials for the chemical industry and textile industries, they can be used to manufacture various kinds of fiber, synthetic rubber, synthetic fertilizer, plastics, dyes, pharmaceuticals, etc. Their reserves on the earth are limited, and their value as raw materials is much higher than that only as fuel. Therefore, replacing coal and oil with nuclear fuel is conducive to the rational utilization of existing resources.

9.1.4 Application Field of Nuclear Energy

Nuclear energy can be used to directly heat plants or homes, generate electricity, desalinate seawater, prepare hydrogen fuel, produce isotope heat sources and light sources and batteries for spacecraft or cardiac pacemakers, etc. In the following sections, non-military applications of nuclear energy will be introduced, mainly focusing on nuclear fission power generation and nuclear fusion power generation.

9.2 Nuclear Fission Power Generation

The core of nuclear fission power generation is the nuclear reactor, which is a device that can maintain and control the nuclear fission chain reaction, thus realizing the conversion of nuclear energy and heat energy. In 1942, the University of Chicago in the United States built the world's first self-sustaining chain reactor, opening up a new era of nuclear energy utilization.

9.2.1 Working Principle of Nuclear Power Plants

A nuclear power plant is a plant that uses the energy released by nuclear fission reaction to generate electricity. The basic principle is that the coolant flows through the surface of the nuclear fuel element, carries the heat generated by fission to the steam generator, and the heat carried will evaporate the water to generate steam, which drives the steam turbine generator unit to generate electricity.

9.2.2 Composition of Nuclear Reactor

The nuclear reactor consists of a core, cooling system, neutron moderator system, neutron reflector, control and protection system, shielding system, radiation monitoring system, etc.

Fuel in core: The fuel of the reactor is fissile or proliferative material. ^{235}U, which contains only 0.711% of natural uranium, is the only fissile material occurring on earth. In addition, ^{233}U and ^{239}Pu are two other types of fissile materials that are produced by reactors or accelerators. These fissile materials can be made into metals, alloys, oxides, carbides, and mixed fuels as fuel for reactors.

Fuel cladding: Since a large amount of fission product, especially fission gas, will be generated when the fissile material is irradiated in the reactor, in order to prevent the escape of fission products, it is necessary to put the nuclear fuel in a cladding. The materials of the cladding are mainly aluminum, zirconium alloy, and stainless steel.

Control rod and safety rod in control and protection system: In order to control the rate of the chain reaction at a predetermined level, it is necessary to use neutron-absorbing materials to make absorption rods, called control rods and safety rods. The control rod is used to compensate for fuel consumption and adjust the reaction rate, and the safety rod is used to quickly stop the chain reaction. The absorber materials are generally hafnium, boron, boron carbide, cadmium, silver indium cadmium, etc.

Cooling system: Since a large amount of heat is generated during nuclear fission, in order to maintain the safety of reactor operation, it is necessary to conduct the heat generated during nuclear fission reaction, thus the reactor must have a cooling system. Commonly used coolants include light water, heavy water, helium, and liquid metal sodium.

Neutron moderator System: Since slow neutrons are more likely to cause ^{235}U fission, and the neutrons generated by nuclear fission are fast neutrons, some reactors need to put materials that can slow down the neutron speed. This material is called a moderator. Commonly used moderators include water, heavy water, graphite, etc.

Neutron reflector: The reflector is set around the active zone, which can be heavy water, light water, beryllium, graphite, or other materials. It can reflect the neutrons escaping from the active zone and reduce neutron leakage.

Shielding system: The shielding system is installed around the reactor to attenuate neutron and γ-dose.

Radiation monitoring system: This system can monitor and detect radioactive leakage in nuclear reactors as soon as possible.

9.2.3 Structural Form and Classification of Nuclear Fission Reactor

According to the type of fuel, type of coolant, form of neutron energy distribution, special design requirements, and other factors, various types of reactors can be built. At present, there are thousands of large and small reactors in the world, and their classification is also diverse. Reactors are usually classified based on their energy spectrum, coolant type, and purpose of application.

According to the energy spectrum, there are thermal neutron reactors and fast neutron reactors that are caused by thermal neutrons and fast neutrons. According to coolant, there are light water reactors (further divided into pressurized water reactors and boiling water reactors), heavy water reactors, gas-cooled reactors, and sodium-cooled reactors. According to the purpose, there are research and experiment reactors (used to study neutron characteristics and use neutrons to carry out research in physics, biology, irradiation protection, and materials science), production reactors (mainly used to produce new fissile materials ^{233}U and ^{239}Pu), and power reactors (using the thermal energy generated by nuclear fission for the propulsion power of ships and nuclear power generation).

The following section will briefly introduce the types of reactors classified by purpose.

1. **Research and experiment reactor**

Research and experiment reactor refers to the reactor used for scientific experimental research. But it does not include reactors built for the research and development of specific reactor types, which are the research objects themselves, such as prototype reactors, zero-power reactors, various mode reactors, etc. This type of experimental reactor has a wide range of applications, including researching reactor physics, reactor engineering, biology, chemistry, physics, medicine, etc., and can be used to produce various radionuclides and train reactor engineering personnel. There are many types of research and experiment reactors, including pool reactors, tank reactors, heavy water reactors, homogeneous reactors, fast neutron reactors, etc.

Pool reactor: In this reactor, water not only acts as a moderator, reflector, and coolant but also plays a major shielding role. The reactor is named because the pool is often made in the shape of a swimming pool.

Tank reactor: Since higher working temperature and larger coolant flow can only be achieved in the pressurization system, the pressurization tank structure must be adopted.

Heavy water reactor (HWR): The small neutron absorption cross-section of heavy water allows the use of natural uranium as reactor fuel. This reactor is characterized by large critical mass and low neutron flux density. If the critical mass is to be reduced and a high neutron flux density is to be obtained, enriched uranium is used instead of natural uranium.

2. **Production reactor**

The production reactor is used for producing fissile materials or other materials, or for industrial-scale irradiation. Production reactors include plutonium-producing reactors, tritium-producing reactors, dual-use plutonium-tritium-producing reactors, isotope-producing reactors, and large-scale irradiation reactors. If not specifically specified, the production reactor is usually referred to as a plutonium-producing reactor. This reactor has a simple structure. The fuel elements in the production reactor are both fuel and raw materials for ^{239}Pu production. Neutrons come from ^{235}U in elements made of natural uranium. The neutron yield of ^{235}U fission is 2–3. In addition to the neutrons required to maintain the fission reaction, the remaining neutrons are absorbed by ^{238}U and can be converted into ^{239}Pu. On average, 0.8 plutonium atoms can be obtained for each ^{235}U atom "burned". In addition, the production reactor can also be used to produce tritium as thermonuclear fuel.

3. **Power reactor**

Power reactors can be divided into submarine power reactors and commercial power generation reactors. Nuclear submarines usually use pressurized water reactors as their power plants. The reactors used in commercial nuclear power plants mainly include pressurized water reactors, boiling water reactors, heavy water reactors, graphite gas-cooled reactors, and fast reactors.

Pressurized water reactor: It uses uranium dioxide with low abundance (about 3% for ^{235}U) as fuel and high-pressure water as moderator and coolant, which is the most mature reactor type in the world at present.

Boiling water reactors: It uses low abundance (about 3% for ^{235}U) of uranium dioxide as fuel and boiling water as moderator and coolant.

Heavy water reactor: It uses heavy water as a moderator and heavy water (or boiling light water) as a coolant and can use natural uranium as fuel. The heavy water reactor developed in Canada (the CANDU reactor) is in the leading position in the world, and it is the only reactor that has reached the commercial level at present.

Graphite gas-cooled reactor: It uses graphite as a moderator, carbon dioxide as a coolant, and natural uranium as the fuel. Its maximum operating temperature is 360 °C. This kind of reactor has accumulated rich operating experience and had operated for 650 reactor years by the early 1990s.

Fast neutron reactor: It uses plutonium or highly enriched uranium as fuel, and generally uses liquid alkali metals such as liquid metal sodium or gas as coolant, without moderators. According to different coolants, fast neutron reactors are divided into sodium-cooled fast reactors and gas-cooled fast reactors. The proliferation of ^{238}U, ^{232}Th, and other nuclear materials can be realized by using the fast reactor, and the utilization rate of natural uranium can be increased to 60–70%. This is an important way to expand nuclear fuel resources and is considered to be the second generation of reactor type after the thermal reactor. However, the nuclear reaction power density of fast reactors is higher than that of thermal reactors, requiring good thermal conductivity of the coolant and little moderating effect on neutrons. Liquid metal sodium has the advantages of a high boiling point (881 °C), high specific heat, and low neutron absorption, which is an ideal coolant for fast neutron reactors. But the chemical properties of metal sodium are extremely active, which is easy to react violently with oxygen in water and air metal sodium. Therefore, leakage must be strictly prevented in use, thus the technical difficulty of fast reactors has been increased. This is one of the reasons why the development of the fast reactor lags behind that of the thermal reactor for a long time. The nuclear reaction formulas of the ^{238}U proliferation process are as follows.

$$^{238}\mathrm{U} + \mathrm{n} \rightarrow {}^{239}\mathrm{U} + \gamma \tag{9.3}$$

$$^{239}_{92}\mathrm{U} \xrightarrow[23.45\ \mathrm{min}]{\beta^-} {}^{239}_{93}\mathrm{Np} \tag{9.4}$$

$$^{239}_{93}\mathrm{Np} \xrightarrow[2.3565\ \mathrm{min}]{\beta^-} {}^{239}_{94}\mathrm{Pu} \tag{9.5}$$

9.2.4 History and Current Situation of Nuclear Power Generation

The use of nuclear energy is one of the greatest scientific and technological achievements made by mankind in the twentieth century. At the end of the nineteenth century, the British physicist Thomson discovered the electron. In 1895, the German physicist Roentgen discovered X-ray. In 1896, the French physicist Becquerel discovered radioactivity. In 1898, Marie Curie discovered a new radioactive element polonium. In 1905, Einstein put forward the formula of mass and energy conversion in his famous theory of relativity: $E = mc^2$. This formula shows that a small amount of

mass loss can be converted into a very large amount of energy, revealing the physical law of the source of nuclear energy. The above findings have all laid an important theoretical foundation for the use of nuclear energy.

In 1938, German physical chemists Hahn and Strass discovered the fission phenomenon of ^{235}U: when the fission of uranium nuclear occurs, enormous energy will be released. This energy comes from the binding energy of the nucleons in the nucleus, which is exactly equal to the mass loss during nuclear fission. This discovery brought the use of nuclear energy from theory to reality, and mankind has since uncovered the secret of nuclear energy.

Like other most advanced technologies, the use of nuclear energy began with the manufacture of nuclear weapons. In 1942, Fermi, a famous American scientist, led dozens of scientists to build the world's first nuclear reactor at the University of Chicago in the United States, realizing the controllable nuclear fusion chain reaction for the first time. Based on the experimental results of the reactor, the United States built and put into operation the world's first nuclear weapon-grade plutonium reactor in 1945, marking the beginning of the era of nuclear energy.

The peaceful use of nuclear energy began in the early 1950s. In 1951, the United States used the residual heat of a plutonium-producing reactor to test power generation with a power of 200 kW. In 1954, the former Soviet Union built the world's first nuclear power plant with a power generation capacity of 5 MW. After that, the United Kingdom and France successively built a number of gas-cooled reactor nuclear power plants for both plutonium production and power generation. The United States then built the first pressurized water reactor nuclear power plant with 90 MW power by using its nuclear submarine technology. At that time, countries with nuclear power were racing to build nuclear power plants while seizing the arms race for nuclear weapons. In the mid-1970s, western countries entered the climax of building nuclear power plants. During this period, the growth rate of nuclear power plants was much higher than that of thermal power and hydropower.

Two major nuclear power plant accidents occurred in succession around the 1980s. One was the Three Mile Island nuclear power plant accident in the United States in 1979, and the other was the Chernobyl nuclear power plant accident in the former Soviet Union in 1986. These are the only two major accidents of commercial nuclear power plants during the cumulative operation of 12,000 reactor years in 32 countries. The main reason for the Chernobyl accident was that the reactor was not equipped with containment. In contrast, the Three Mile Island accident, in which a containment was installed, caused no radioactive damage to anyone. These two accidents brought a serious impact on the development of nuclear power in the world, especially the Chernobyl accident, which led to a sharp downward in the situation of global nuclear power development. This accident directly triggered the "anti-nuclear", "nuclear restriction" and even "nuclear abolition" movements in many countries, especially in Western Europe. In Belgium, Italy, Germany, the Netherlands, Sweden, Switzerland, and other countries, the development of nuclear power was been explicitly restricted by international and domestic political factors. In Canada, the Czech Republic, Finland, France, Hungary, Spain, the United Kingdom, the United States, and other countries, nuclear power was stabilized at a certain scale,

but the growth was slow. In the nearly 30 years after the Three Mile Island nuclear power plant accident, the United States did not even build a new nuclear power unit. Only in South Korea, Japan, India, and other countries, due to energy demand or resource constraint led by rapid economic growth, nuclear power was still actively developed. In addition, the final disposal of nuclear fuel and high-level radioactive waste was also an important reason for restricting the development of nuclear power at that time and even now. The development of nuclear power worldwide encountered a low point in the 1980s and 1990s.

At the end of the twentieth century, as the source of fossil fuel became increasingly tense, its supply and price fluctuated greatly under the impact of the international situation, and the pressure of environmental problems caused by greenhouse gases emission was increasing. In addition, the operating performance and technology of the world's nuclear power was been improved after the two major accidents, and many countries shifted their attention to the development of clean energy to nuclear energy. Three major events greatly promoted the recovery of global nuclear power. In the years from the end of the twentieth century to the beginning of the twenty-first century, the U.S. government launched the technology and policy research of the fourth generation of nuclear power (June 1999), Russian President Vladimir Putin issued an initiative to promote the development of world nuclear power at the World Millennium Summit (September 2000), and the United States formulated a new energy policy to revive the development of nuclear power (May 2001). From the formulation of policies, development strategies, and long-term planning to the practical actions taken, the development of nuclear power has been effectively promoted. After that, many countries began to build advanced nuclear power units on a large scale and continued to develop advanced nuclear power systems. The overall development route is: (a) extend the service life of existing nuclear power units, (b) construct the third generation nuclear power system, (c) develop the fourth generation nuclear power system, (d) develop nuclear energy to produce hydrogen.

According to the statistics published by the World Nuclear Association and the International Atomic Energy Agency, as of January 1st, 2020, a total of 442 nuclear power units in the world were operating in grid-connected power generation, distributed in 30 countries. The practice of many countries has proved that nuclear power is a safer, cleaner, and more economical industrial energy than thermal power, but the premise is to ensure the safety of nuclear power operations.

Table 9.1 shows the statistics of nuclear power installed capacity and power generation in the world by January 1st, 2020. It can be seen that the top ten countries in terms of the number of nuclear power units are the United States, France, China, Russia, Japan, South Korea, India, Canada, Ukraine, and the United Kingdom. The number of grid-connected nuclear power units in these ten countries accounts for 83.9% of the world's total, and their total installed capacity accounts for 85.7% of the world's total. In 2019, the global nuclear power supply accounted for 10–11% of the global power supply. Table 9.2 lists the top 10 nuclear power generation countries in 2019 and the proportion of nuclear power generation to the domestic power supply in that year. Among them, nuclear power generation in Japan before the Fukushima nuclear accident in 2011 accounted for about 30% of the domestic power supply,

Table 9.1 Statistics of operation and construction data of nuclear power units in the world by January 1, 2020

Country	Operating unit (grid-connected power generation)		Unit under construction (the first tank of concrete has been poured)	
	Number of units (set)	Total installed capacity (MWe)	Number of units (set)	Total installed capacity (MWe)
USA	96	97,896	4	5000
France	58	63,130	1	1750
China	51	49,407	13	13,695
Japan	33	31,679	2	2756
Russia	38	29,203	4	4903
South Korea	24	23,231	4	5600
India	22	6219	7	5400
Canada	19	13,553	0	0
Ukraine	15	13,107	0	0
UK	15	8883	1	1720
Sweden	7	7569	0	0
Spain	7	7121	0	0
Belgium	7	5943	0	0
Germany	6	8052	0	0
Czech	6	3932	0	0
Pakistan	5	1355	2	2322
Switzerland	4	2960	0	0
Finland	4	2764	1	1720
Hungary	4	1889	0	0
Slovakia	4	1816	2	942
Argentina	3	1702	1	27
Bulgaria	2	1926	0	0
Brazil	2	1896	1	1405
South Africa	2	1830	0	0
Mexico	2	1600	0	0
Romania	2	1310	0	0
Iran	1	915	1	1057
Slovenia	1	696	0	0
Netherlands	1	485	0	0
Armenia	1	376	0	0
The United Arab Emirates	0	0	4	5600
Bangladesh	0	0	2	2400
Belarus	0	0	2	2388

(continued)

Table 9.1 (continued)

Country	Operating unit (grid-connected power generation)		Unit under construction (the first tank of concrete has been poured)	
	Number of units (set)	Total installed capacity (MWe)	Number of units (set)	Total installed capacity (MWe)
Turkey	0	0	1	1200
Total	442	392,445	53	59,885

Note China's power generation includes the power generation of four operating units in Taiwan

Table 9.2 Generation capacity of the world's top 10 nuclear power generation countries in 2019 and the proportion of nuclear power generation in domestic power supply

Country	2019 generation (GW)	Share in domestic power supply (%)
U.S	98.2	≈ 20
France	63.1	≈ 70
China	51.2	≈ 5
Japan	32	7.5
Russia	28.5	19.7
South Korea	23.2	26
Canada	13.6	14.9
Ukraine	13.1	53.9
UK	8.9	15.6
Sweden	7.7	34

Note China's power generation includes the power generation of four operating units in Taiwan

which decreased to 0% from 2013 to 2015 after the accident, and gradually recovered to 7.5% in 2019. In addition, the nuclear power supply of Slovakia, Hungary, Belgium, Switzerland, Slovenia, the Czech Republic, and Finland in Europe accounts for more than 30% of the domestic power supply.

9.3 Research Progress of Fusion Power Generation and Thermal Fusion Reactor

Although nuclear fission power generation is a new source of energy to solve the current global energy crisis and has played an important role in the national economy and social life. However, due to the limited uranium resources on the earth and the insufficient development of the utilization technology of thorium resources, the currently proved uranium resources can only maintain the full power operation of the global power station for decades. In addition, the treatment and disposal of a large amount of high-level radioactive waste generated during the operation of nuclear

power plants have also been a problem that has plagued the world. Besides, the public has some concerns about the safety and reliability of nuclear fission reactors and has always maintained reservations about the current measures for the treatment of high-level radioactive waste. For the above reasons, the development of nuclear fission energy has been hindered to some extent. Compared with nuclear fission, nuclear fusion will hardly bring environmental problems such as radioactive pollution, and its raw material can be directly obtained from deuterium in seawater, which is almost inexhaustible. It is an ideal energy source. At present, mankind can realize uncontrollable nuclear fusion, such as the explosion of hydrogen bombs. However, to make effective use of the energy, the speed and scale of nuclear fusion must be reasonably controlled to achieve continuous and stable energy output. At present, the only simple and feasible method to control nuclear fusion is to use light atoms such as deuterium and tritium as fusion reaction materials and increase the kinetic energy of atomic nuclei through high temperature to overcome the Coulomb repulsion force between nuclei until the fusion of atomic nuclei, thus releasing energy. Once the nuclear fusion reactor is established, it is expected to permanently solve the energy demand of human society. At present, the research of nuclear fusion technology has become a hotspot in the world.

9.3.1 Advantages of Nuclear Fusion Energy

As another important form of nuclear energy, nuclear fusion has the following advantages:

(a) Nuclear fusion releases more energy than nuclear fission. For example, the fission reaction of ^{235}U turns one-thousandth of matter into energy, while the fusion reaction of deuterium turns nearly four thousandth of matter into energy. Thus, the energy released by unit mass deuterium fusion is about four times that released by unit mass ^{235}U fission. This is one of the outstanding advantages of fusion nuclear energy as a potential new energy.

(b) Nuclear fusion resources are sufficient. The seawater contains 2.34×10^{13} t of deuterium, and tritium can be produced by bombarding lithium nuclei with neutrons. The earth is also rich in lithium resources. Therefore, if controllable nuclear fusion using deuterium (or tritium) as raw material is realized, the problem of energy shortage in the world will be permanently solved.

(c) Nuclear fusion energy is a very safe energy source. Any operation accident in a nuclear fusion reactor can rapidly cool the plasma so that the nuclear fusion reaction can be extinguished in a very short time. At the same time, the energy stored in the plasma is very low, and the reactor accident caused by nuclear fission waste heat will not occur. Therefore, the safety of fusion reactors is very high theoretically.

(d) Nuclear fusion energy is fairly clean energy. Compared with fossil raw materials and nuclear fission, the final product of deuterium-deuterium (D-D) and

deuterium-tritium (D-T) fusion are only non-radioactive helium, nor do they produce long-lived radioactive waste, thus eliminating the problem of uranium and plutonium recovery and high-level radioactive waste treatment and disposal.

Therefore, in the long run, the development of nuclear fusion energy is crucial to solving the global energy shortage and protecting the global environment.

9.3.2 Basic Conditions for Realizing Nuclear Fusion

The process of nuclear fusion of light elements, such as D-D fusion or D-T fusion, is the combination reaction of positively charged atomic nuclei. Because the Coulomb repulsion between the nuclei is very strong, there must be enough kinetic energy to make the atomic nucleus overcome the coulomb repulsion and reach the range where the nuclear force can work ($< 10^{-15}$ m). Although the light nucleus can be accelerated to 0.05 meV by the accelerator and the deuterium target can be bombarded to trigger nuclear fusion, about one fusion occurs in one million accelerated deuterium nuclei, and the fusion energy obtained by fusion is far less than the electric energy consumed by the accelerator, which outweighs the loss. At present, the only feasible way to increase the kinetic energy of the atomic nucleus is to make the material participating in the fusion reaction reach a sufficiently high temperature, which is commonly known as the ignition temperature of nuclear fusion. For the D-D reaction, the ignition temperature is 5×10^8 K, and for the D-T reaction, the ignition temperature is 10^8 K. At such a high ignition temperature, any substance has dissociated into plasma.

To achieve a self-sustaining fusion reaction, it is not enough for the plasma to have a high enough temperature. It is also necessary that the energy generated by fusion can provide sufficient kinetic energy for secondary particles to maintain the fusion reaction, that is, the energy released by thermonuclear reaction should be at least equal to the energy used to heat the fuel (the ratio of the reaction released energy to the input energy $Q = 1$, called the gain and loss equivalence). To achieve $Q \geq 1$, in addition to high temperature, the following two conditions must be met: an appropriate plasma density and a sufficient time τ to maintain high temperature and density. The higher the density of the plasma, the greater the probability of a nuclear fusion reaction in a particle collision. The longer the high temperature and plasma are maintained, the more sufficient the fusion reaction will be.

In 1957, by calculating the energy balance of nuclear fusion plasma, Lawson put forward the condition to judge whether a fusion reaction can continue to occur at the ignition temperature, that is, Lawson's criterion, see formula 9.6.

$$n\tau \geq constant \tag{9.6}$$

where

n–plasma density (m^{-3});

τ–plasma maintenance time (s).

Lawson condition is a necessary condition for achieving self-sustaining nuclear fusion and obtaining energy gain.

Lawson criterion for the D-T and D-D reactions is as follows:

$$\text{D-T } reaction: \begin{cases} n\tau = 10^{20} m^{-3} \cdot s \\ T = 10^{8} K \end{cases} \text{D-D } reaction: \begin{cases} n\tau = 10^{22} \mathrm{m}^{-3} \cdot \mathrm{s} \\ T = 10^{9} \mathrm{K} \end{cases} \tag{9.7}$$

9.3.3 Plasma Confinement

It is clear from the above discussion that the key issue of achieving controllable nuclear fusion and obtaining energy gain is to generate a high-temperature and high-density plasma and maintain it for a certain time. Due to the extremely high ignition temperature of fusion (above 10^8 K), any substance has been melted down at this temperature, so it is impossible to find an actual solid container to hold such plasma. Thus, the restriction of the high-temperature plasma becomes the key to being solved in controlled thermonuclear reactions.

At present, there are many kinds of experimental devices to study controllable nuclear fusion, but according to the principle of realizing confinement, these devices can be divided into two types: magnetic confinement devices and inertial confinement devices. The former uses a magnetic field to confine the high-temperature plasma, while the latter uses an intense laser fuel reaction to heat the pellet. Only the principles of these two types of devices are briefly described here.

1. **Magnetic confinement device**

Magnetic confinement is the earliest restraint method of confinement proposed in controllable nuclear fusion research and is also the most promising way to achieve ignition conditions in the near future.

Since plasma is composed of charged particles, it will be subject to the force of the magnetic field when moving in the magnetic field. If the shape, intensity, and distribution of the magnetic field are reasonably designed, it is possible to keep charged particles moving in the specified region. In the early stage of fusion research, various types of magnetic confinement devices, such as fast pinch, magnetic mirror, and stellarator were proposed and studied. Until the 1970s, the relevant research was gradually concentrated on the Tokamak proposed by the former Soviet Union scientists, but the research on other types of magnetic restraint devices has not stopped.

Tokamak is two magnetic fields created in the annular vacuum reaction chamber. One is a very strong axial magnetic field along the annular axis generated by the energized coil outside the chamber, and the other one is a circular magnetic field generated by the strongly induced current (up to millions of amperes) excited by the pulse current of the transformer coil in the plasma. The circular magnetic field rotates

endlessly along the magnetic field line in the annulus. When the strongly induced current passes through the plasma, it can also play a heating role, which is conducive to realizing and maintaining nuclear fusion reactions.

Over the past 50 years, more than 100 Tokamaks have been built around the world, including many large ones, such as the large Tokamak Fusion Test Reactor (TFTR) built by the Princeton Plasma Physics Laboratory in December 1982, the Joint European Fusion Reactor (JER) in the UK, the T-15 of the former Soviet Union, the JT-60 in Japan, etc.

Since Tokamaks use pulsed current to heat plasma, and ohmic heating alone cannot reach the fusion temperature, it is necessary to develop high-power auxiliary heating and a non-inductive current drive. In addition, it is also necessary to prevent the plasma disruption caused by the instability of the magnetic fluid that restricts the plasma. For this reason, the shape and heating materials of Tokamaks have been improved. In the past two decades, a spherical ring device, also known as spherical Tokamak (ST), has developed rapidly. It is a Tokamak with a low annular diameter ratio (ratio of large radius to small radius of annular plasma). This device not only preserves the stability of plasma in traditional Tokamak devices but also greatly improves the very low confinement efficiency of Tokamak. Compared with the ordinary Tokamak, the magnetic lines of force and the particles moving along the magnetic lines of force stay more in the core of the magnetic field. Thus, a ST makes more effective use of magnetic energy and allows the plasma to reach a higher temperature and current density. At the same time, the confinement efficiency of the plasma is high, and plasma rupture is not easy to occur.

ST was promoted by Chinese American physicist YuanKai Peng in 1986. In the mid-1990s, with the formal support of the United States and Europe, mega-ampere ST devices were established and put into operation in Princeton and Kalam respectively. Since then, a large number of small and medium-sized ST devices have emerged, making ST the most challenging magnetic confinement approach for traditional Tokamaks. At present, the parameters that ST has reached are only second to those of the stellarator except for the traditional Tokamak.

However, the small central space of the ST device makes the central solenoid work under extremely high stress, thermal load, and neutron load, which puts forward higher requirements for the reliability of materials. At the same time, too small a central space reduces the efficiency of the central solenoid. Therefore, the center solenoid has become a major obstacle to the development of ST. The study of the plasma current of the centerless solenoid has become an important subject in the development of ST.

With the expansion of the Tokamak device and the lengthening of the pulse, the comprehensive use of superconducting magnets is an inevitable choice. The successful application of superconducting technology to the coil of Tokamak's strong magnetic field is a major breakthrough in the study of controllable thermonuclear fusion energy. The completion of the superconducting Tokamak has made the continuous and stable operation of the magnetic confinement configuration a reality. It is recognized as the most effective way to explore and solve the engineering and physical problems of future fusion reactors with superconducting cores. At present, only

Russia, Japan, France, and China have superconducting Tokamaks in the world. China's superconducting Tokamak HF-7 was built in 1994 under the joint efforts of China and Russia. The French superconducting Tokamak Tore–supra, which is 17.5 times larger than HT-7, is the world's first device to realize quasi-steady operation with high parameters. Under the condition that the discharge time is up to 120 s, the plasma temperature is 20 million degrees, the center density is 1.5×10^{19} per cubic meter, and the discharge time is hundreds of times the thermal energy constraint time.

2. **Inertial confinement device**

Inertial confinement fusion (ICF) is driven by an ultra-intense laser beam, relativistic electron beam, or ultra-intense heavy ion beam with high power and high energy density. The plasma formed by rapidly ablating the surface of the pellet is ejected outward to produce a super-strong recoil force (i.e., "rocket effect") towards the cohesive center, forming spherical implosion pressurization and centricity effect, so that the deuterium and tritium thermonuclear fuel in the spherical target can reach an extremely high temperature, extremely high pressure, and extremely high-density thermonuclear fusion ignition conditions, thus forming a self-sustaining thermonuclear fusion reaction and releasing a large amount of fusion energy. The above implosion and thermonuclear fusion process last for a very short time. Due to the inertial confinement of the target and thermonuclear fusion fuel, the thermonuclear fusion reaction process has been completed before the high temperature, high pressure, and high-density hot spots fly away.

Laser-driven inertial confinement fusion is a nuclear fusion scheme developed in the 1970s. It has developed rapidly in the past 50 years and has attracted much attention. Currently, the largest laser fusion device is the National Ignition Facility (NIF) located in the Lawrence Livermore National Laboratory in California, USA. The device, which was put into operation in 2009, is an ultraviolet laser system as large as a stadium (215 m in length and 120 m in width) and can provide 192 beams of laser, with a total energy of 1.8 MJ and a power of 500 TW. In addition to being used as a driving source for thermonuclear fusion, the device can also simulate extreme phenomena in the universe such as extremely high pressure, extremely high temperature, and ultra-strong magnetic field in neutron stars, planetary cores, and supernovae, enabling scientists to engage in astrophysics, extreme materials science, nuclear physics science, and other research in the laboratory.

9.3.4 History of Controllable Nuclear Fusion

Just after World War II, the United States and the former Soviet Union took the lead in the study of controllable thermonuclear fusion. After the 1960s, the United Kingdom, France, Germany, Japan, and China also successively participated in the research. In the early stage of controllable nuclear fusion research, the research mainly focused on the exploration of the plasma confinement pathway. It was not until the 1980s

that the research direction of inertial confinement mainly focused on laser fusion and magnetic confinement mainly focused on Tokamak gradually formed.

Since 1980, significant progress has been made in international research on magnetic confinement controllable nuclear fusion. A number of large and ultra-large Tokamak devices (TFTR of the United States, JET of the European Community, JT260U of Japan, T215 of the former Soviet Union, etc.) have been built and put into operation. By the mid-1990s, major research achievements had been made on the three Tokamak devices JET, JT-60, and TFTR: the output power of fusion has reached 16.1 MW, the plasma temperature has reached 4.4×10^9 °C, and the Q value has reached 1.25. These achievements show that the scientific feasibility of generating fusion energy on Tokamaks has been basically confirmed, and Tokamak is the most likely way to first realize the commercialization of fusion energy. The construction and experimentation of these large Tokamak devices have laid a solid scientific and technological foundation for the International Thermonuclear Experimental Reactor (ITER) project. The ITER program is another major international cooperation project after the International Space Station. The project plans to invest USD 5 billion to build a thermonuclear fusion reactor in France to verify the technical and engineering reality of the development of controllable nuclear fusion energy.

With the development of high-power laser technology and particle beam technology, inertial confinement fusion research has also made significant progress. In the 1990s, the United States began to build the world's largest and most complex laser optical system NIF. In this device, a beam of infrared laser is refracted and reflected by many surface lenses and concave mirrors to enhance its energy by 10,000 times, and then it is separated into 48 beams of laser and enhanced, further separated into 192 beams of laser and enhanced, and its total energy will increase to 3000 trillion times of the original energy. Each laser beam emits pulsed ultraviolet light that lasts about 3 billionths of a second and contains 1.8 million joules of energy. Its total energy will be more than 500 times the total energy generated by all power stations in the United States. When these pulses hit the target reaction chamber, they will produce X-rays. These X-rays will be concentrated on a plastic shell filled with heavy hydrogen fuel in the center of the reaction chamber. The X-ray will heat the fuel to 100 million degrees and produce 100 billion atmospheric pressure to make heavy hydrogen nucleate and fuse. The fusion reaction of the heavy hydrogen nucleus will release more than 15 times the input energy. The NIF project was originally planned to invest USD 2 billion to be completed around 2003. However, due to the complexity of the project, the actual investment has reached more than USD 3.5 billion, which has far exceeded the original budget. By 2021, 4 of the 192 laser beams have been working for 24 months and have emitted the strongest laser in the world. In December 2022, NIF crossed the fusion ignition threshold and achieved a historic net energy gain (energy gain of 1.5 times), confirming the scientific basis of inertial fusion energy. But NIF's laser can only be fired once every few hours. Therefore, a faster emission rate scheme (the Mercury laser device) has already been planned. It may not be as large as the NIF, but its goal is to emit 10 pulses of laser per second. Similar studies have been carried out in China and France.

9.3.5 Overview of the ITER Project

1. **Origin and development of the ITER project**

The ITER project was jointly proposed by Soviet leader Gorbachev and US President Reagan at the Geneva Summit in 1985. It has been highly concerned by governments since its introduction.

Initially, the project was only participated by the United States, Russia, Europe, and Japan, independent of the International Atomic Energy Agency (IAEA), with its headquarters in the United States, Japan, and Europe. At that time, the scientific theory and technical conditions were not mature enough, and the preliminary design scheme proposed by the four in 1996 was not reasonable. In 1998, due to the adjustment of domestic policies, the United States announced its withdrawal from the ITER project in the name of strengthening basic research. After the withdrawal of the United States, Europe, Japan, and Russia continued to cooperate. Based on the achievements of nuclear fusion research in the 1990s and the development of other high and new technologies, they greatly improved the design of the experimental reactor and completed the engineering design of the ITER device in 2001.

In 2002, Europe, Japan, and Russia started to negotiate an international agreement on the ITER project based on EDA, discussed the establishment of corresponding international organizations, and invited China and the United States to participate in the project. In January of the following year, China officially announced its participation in the consultation. At the end of the same month, President Bush announced that the United States would rejoin the ITER project. South Korea participated in the consultation in June 2003. After two years of negotiation, the six parties signed an agreement in June 2005 to build ITER in Cadarache, the French nuclear technology research center. In 2006, India joined the project. Finally, in November 2006, the governments of the seven members signed an international agreement on the construction of ITER. According to the latest development in the ITER project, the first plasma tests are expected to be conducted in late 2025 for the proof-of-concept of the reactor. The basic design parameters of ITER are shown in Table 9.3.

ITER plays a crucial role in fusion research. It can comprehensively demonstrate the engineering feasibility of the fusion reactor and carry out high-parameter plasma physics experiments with long pulse or steady state operation. Scientists are counting on this fusion reactor to make a qualitative leap in controllable fusion research and verify the technical and engineering reality of the development of controllable nuclear fusion energy.

2. **Scientific objectives of the ITER project**

(a) To obtain the combustion plasma with fusion power of 500,000 kW, Q (ratio of output power to input power) greater than 10, and a pulse time of 500 s by inductively driving the plasma current.

(b) To study the stable operation of the combustion plasma with fusion power greater than 350,000 kW, Q greater than 5, and a burn time duration of 3000 s by non-inductively driving the plasma current. If confinements permit, try

Table 9.3 Basic parameters of ITER

Subject	Design parameter
Total fusion power	500 MW (700 MW)
Q (fusion power/heating power)	> 10
14 meV neutron average wall load	0.57 MW/m^2 (0.8 MW/m^2)
Repeat fuel duration	> 500 s
Large radius of the plasma	6.2 m
Small radius of plasma	2.0 m
Small section elongation ratio	1.7
Central magnetic field intensity of plasma	5.3 T
Volume of plasma	837 m^3
Surface area of plasma	678 m^2
Total power of heating and driving current	73 MW

to explore the steady state of critical ignition or even ignition combustion plasmas with Q greater than 30.

(c) To verify the engineering feasibility of controlled thermonuclear fusion energy and accumulate information on how to design and build fusion reactors in the future.

3. **Future development of fusion energy in the ITER project**

If the operation and experiment of ITER are successful, fusion energy demonstration power plants with the capacity of generating nearly one million kilowatts will be built in 2030 (cooperative or individually arranged), and a fusion energy commercial power station will be built in 2050. According to this assumption, by the end of this century, thermonuclear fusion energy may account for 10–20% of the total energy, and thermonuclear fusion energy will play an important role in this century.

9.4 Other Forms of Nuclear Energy Utilization

In addition to the nuclear fission energy and nuclear fusion energy described in the previous two sections, nuclear energy also has other extensive applications, such as direct heating by nuclear energy. Other forms of nuclear energy, such as nuclide decay energy, can be used to make space reactors or miniature isotope batteries. The radiation emitted by the decay of nuclides is also widely used in nuclear agriculture, radiation breeding, nuclear medicine treatment, medical equipment sterilization, etc. This section mainly introduces some other important applications of nuclear energy, such as space nuclear energy, radionuclide batteries, heating (nuclear hydrogen production, seawater desalination, direct heating, etc.).

9.4.1 Space Nuclear Energy

With the increasing exploitation, development, and utilization of space, space energy with appropriate power, lightweight, long service life, low cost, and safety and reliability is needed to ensure the power supply and propulsion of space activities. Space nuclear energy has incomparable advantages over ordinary energy (chemical energy, solar energy, etc.) in terms of power range, service life, independence, anti-interference, etc. It can be used as both a short-time high-power explosive power supply (space nuclear propulsion) and a low-power long-term power supply (space nuclear power supply), which can meet the energy requirements of almost all space activities.

The main forms of nuclear energy in space are nuclear fission energy and nuclide decay energy. Space nuclear energy systems include radionuclide power systems, space nuclear reactor power systems, nuclear thermal propulsion systems, nuclear propulsion systems, dual-mode (power/propulsion) space nuclear power systems, etc.

The nuclear thermal propulsion system directly heats the propellant to a high temperature by the fission energy of the reactor, then ejects the working agent of high temperature and high pressure from the nozzle at a high speed, thus generating a huge propulsion, which can be used as the propulsion power of the space vehicle. A nuclear propulsion system was used in the Cassini space exploration spacecraft launched by NASA in 1997.

Other types of system convert nuclide decay energy or reactor fission energy into electrical energy through various mechanisms to provide power for spacecraft or heat the fuel of the spacecraft to generate propulsion. Over the past 40 years, a total of 38 nuclear power supplies have been installed on 22 US spacecraft, of which 37 use radionuclide batteries and only one uses nuclear reactor power.

Currently, most of the nuclear batteries used in space use β-decay energy of the radionuclide ^{238}Pu to convert thermal energy directly into electrical energy through the temperature effect. The power of the nuclear battery is generally from tens of watts to two or three hundred watts, and its service life is from several years to ten years.

Radioisotope batteries can provide power support for earth satellites (navigation and communication), lunar landings, and space planet exploration, and have successfully completed many tasks. When Apollo landed on the moon, astronauts left nuclear batteries on the surface of the moon to provide power for the Apollo lunar science experiment module, so that the experiment module can send back valuable scientific data to the earth for a long time. The unmanned spacecraft Pioneer and Voyager also used such nuclear batteries to fly over Jupiter and Saturn and head for the farther solar system. Nuclear reactors, powered by space reactors use ^{235}U with a concentration of more than 90% as nuclear fuel, including thermal reactors and fast reactors. Its electric power is large, ranging from thousands of watts to tens of kilowatts, and its service life can reach 3–5 years. The former Soviet Union mainly chose space reactor power supply because it can meet the requirements of military space missions for

high-power nuclear power supply. The former Soviet Union launched many military satellites into space, including 35 nuclear reactor power supplies and a small number of radioisotope batteries to provide power for the Cosmos series of military reconnaissance satellites. In addition, the reactor power supply can further meet the requirements of future space flight for larger scale, higher power, and longer-life space missions.

9.4.2 Radionuclide Decay Energy Power Generation—Radioisotope Battery

The decay energy of radionuclides is another important type of nuclear energy in addition to fission energy and fusion energy. Through certain energy conversion methods, radionuclides can be used to produce special power radioisotope batteries. Because the amount and speed of energy released during the decay of radionuclides are not affected by the temperature, pressure, electromagnetic field, and light waves in the external environment, as well as the characteristics of high energy density (see Table 9.4) and long life of the radionuclides used (e.g. 12.3 a for ^{3}H, 18.1 a for ^{244}Cm, 87.7 a for ^{238}Pu, 100 a for ^{63}Ni), isotope battery has the advantages of long service life, no maintenance, compact structure, high specific capacity, strong resistance to external environmental interference, safety, and reliability. It can be used as the power of spacecraft, deep-sea sonar, polar wasteland investigation, unmanned weather stations, and other extreme situations, as well as cardiac pacemakers and micro machinery.

1. **History of radioisotope battery**

Radioisotope battery was first proposed by British physicist Henry Mosley in 1913. The battery he designed was a spherical capacitor whose energy conversion mechanism is a direct charging mechanism. Due to the very small current (10^{-11} A) and extremely high voltage (150 kV), the battery was of little practical use at that time. Over the next 30 years, the radioisotope battery no longer attracted widespread attention. By the 1950s, the field of arms competition between the United States and the Soviet Union began to expand from the mainland to the sea and space. In these special environments, stable and reliable power supply with high power density, no maintenance, and replacement for long-term operation is required. At that time, the

Table 9.4 Comparison of electric energy provided by different batteries per unit weight

Battery type	Electric energy provided ($mW{\cdot}h{\cdot}mg^{-1}$)
Chemical battery (lithium-ion)	0.3
Fuel cell (methanol, conversion efficiency 50%)	3
^{210}Po isotope battery (conversion efficiency 5%)	3000
^{3}H isotope battery (conversion efficiency 5%)	500

existing solar cells, chemical cells, and fuel cells could no longer meet the actual needs, and the research and development of radioisotope batteries entered a rapid development period.

The first radioisotope battery developed and successfully applied is the radioisotope thermoelectric generator (RTG). It uses the principle of thermoelectric power generation to convert the decay heat of ^{238}Pu and other nuclides into electrical energy. This type of battery has been used for the power supply of space detectors such as Apollo-12, Apollo-14, and Apollo-15 lunar experiment station, and Pioneer-10 and Pioneer-11 Jupiter detectors developed by the United States. In addition, due to the advantages of being noiseless, vibration-free, and concealment, the RTG was officially listed as military equipment by the United States in the late 1980s.

After that, the research on the energy conversion mechanism of multi-isotope batteries was been carried out in succession. Among them, some radioisotope batteries with energy conversion mechanisms, such as those with thermionic emission mechanisms, have been successfully used in space detectors.

The initial research and development of radioisotope batteries were to meet the energy demand of space exploration. After the 1950s, semiconductor components began to develop towards miniaturization, which promoted the development of microelectronic processing technology, especially at the beginning of the twenty-first century, the research and development of microelectromechanical systems (MEMS) became very rapid. However, due to the lack of a long-term stable power supply, the application of MEMS was greatly limited. The radiation generated by isotopes and semiconductor materials can be used to make miniature batteries, which can solve the problem of MEMS power supply. In addition to the common characteristics of conventional radioisotope batteries, miniature radioisotope batteries also have the following characteristics: power in the range of nanowatts to microwatts, current in the range of nano-amperes to microamperes, the voltage in the range of a few volts to a few volts, can be integrated with micro-nano electronic devices and micro-nano electromechanical systems, and the size matches the size of micro-nano electronic devices and micro-nano electromechanical systems. Because of these characteristics, miniature radioisotope batteries have very important potential applications in embedded sensors, distributed systems, wireless communications, aerospace, ocean exploration, and other occasions where battery charging and fuel replacement cannot be achieved. The research and development of this kind of battery have been a hot spot in the field of international radioisotope battery R&D since the 1980s and have been paid attention to by more and more countries and scientific research institutions.

2. **Energy conversion mechanism of radioisotope battery**

The performance of the radioisotope battery is greatly influenced by the energy conversion mechanism and the structure of the energy conversion unit, etc. In order to improve the energy conversion efficiency, prolong the service life, increase the applicability of energetic particles of various types and energy ranges, and reduce the preparation cost, scientists have been committed to the research of radioisotope batteries for various conversion mechanisms and energy conversion units.

Up to now, there are more than 10 kinds of decay energy-electric energy conversion mechanisms of radioisotope batteries. According to the different ways of using decay energy, the conversion mechanism of radioisotope batteries can be divided into two categories. One is the conversion of heat released by the decay energy of radioisotopes into electric energy, that is, the thermoelectric conversion mechanism, in which the radioisotope thermoelectric generator (RTG) is representative of this kind of isotope battery. The other category is to convert the radioactive particles of radioisotopes directly or indirectly into electric energy, of which the radiation volt effect battery is representative of this type of radioisotope battery.

The classification of the main energy conversion mechanism of the isotope battery is shown in Fig. 9.1. For thermoelectric conversion mechanisms, there are static conversion mode and dynamic conversion mode. The static conversion mode includes thermoelectric conversion mechanism (the corresponding power generation device is RTG), thermionic emission mechanism, alkali-metal thermal-to-electric conversion (AMTEC) mechanism, and thermophotovoltaic effect, etc. The principle of RTG is similar to the thermoelectric conversion in the semiconductor thermocouple, with a conversion efficiency of about 5%. With the emergence of new high-efficiency thermoelectric materials, the conversion efficiency can be increased to 10% or even higher. The thermionic emission mechanism is to emit thermions through the thermoelectric electrode and realize thermoelectric conversion in the atmosphere filled with cesium and other metal vapors. The conversion efficiency is generally 8%, up to 18%. AMTEC is a thermoelectric energy direct conversion device using beta alumina solid electrolyte as an ion-selective permeation membrane and alkali metal as the working medium. At present, only the sodium medium AMTEC with low efficiency has been successfully manufactured. If potassium can be used as the medium, the

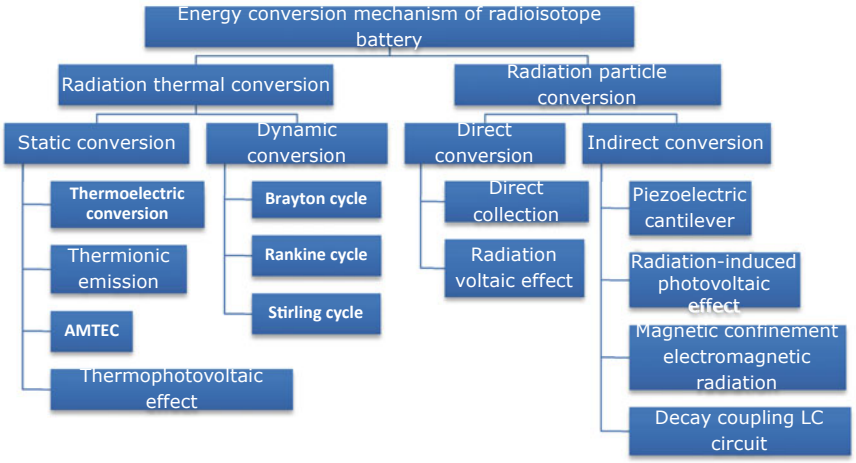


Fig. 9.1 Main conversion mechanism of radioisotope batteries

theoretical conversion efficiency can reach 30%. The thermophotovoltaic effect is an indirect conversion method that uses the heat released by radioactive isotope decay energy to generate light and then uses the photovoltaic effect to generate current. Its theoretical conversion efficiency is about 20–30%. The dynamic conversion methods mainly include the Brayton cycle, the Rankine cycle, and the Stirling cycle. These three cycles convert heat energy into mechanical energy and then convert mechanical energy into electric energy. In the Brayton cycle, the heat-carrying material used is inert gas (such as neon or argon). The inert gas drives the turbine after heating and then drives the generator to generate electricity to realize thermoelectric conversion. The heat-carrying material of the Rankine cycle is generally liquid metal (such as mercury or alkali metal) or organic material. After heating, the liquid material is converted into steam, which drives the turbine to drive the generator. The Stirling cycle is characterized by the use of reciprocating reversible engines instead of turbines. The theoretical energy-conversion efficiency of dynamic conversion (up to 40%) is higher than that of static conversion. However, there are still three bottlenecks in the engineering application. Firstly, high efficiency requires a high hot end temperature and low waste heat discharge temperature, while low waste heat discharge temperature leads to an increase in radiation heat dissipation area. Secondly, it is difficult to lubricate high-speed running parts. Thirdly, the impact of the inertia vector generated by high-speed rotation on the stability of the system (such as spacecraft). So far, the publicly reported applications in the aerospace field are all based on the static conversion method of isotope batteries.

The conversion mechanism of using radioisotope ray particles mainly includes direct conversion (including direct collection and radiation voltaic effect) and indirect conversion (including piezoelectric cantilever, radiation-induced photovoltaic effect, magnetic confinement electromagnetic radiation, and decay coupling LC circuit). The direct collection mechanism is that the collecting electrode directly collects the charge of charged particles released by the decay of radioactive isotopes to generate electric energy. The mechanism of the radiation voltaic effect is to use the built-in electric field of semiconductor devices to separate the semiconductor materials and generate electron–hole pairs under the action of high-energy particles emitted by radioisotopes, thus generating current. The mechanism of the piezoelectric cantilever is to collect and accumulate charged particles released by radioisotopes using the microcantilever, and periodically contact and discharge the radioactive source under the action of static electricity. This process is accompanied by the periodic deformation of the micro-cantilever, which is converted into current output through the piezoelectric material closely attached to it. The mechanism of the radiation-induced photovoltaic effect is to use particles released by radioisotopes to excite fluorescent substances to emit fluorescence and then generate current under the photovoltaic effect. The collection mechanism of electromagnetic radiation of particles under magnetic confinement is to use magnetic fields to constrain β-particles radiated by radioisotopes to emit energy in the form of electromagnetic waves in the cyclotron motion and use metal to collect electromagnetic waves and convert them into current output. The decay coupling LC circuit power generation mechanism does not directly use the decay energy of radioisotopes to supply energy but couples its decay energy

into the stored LC oscillation circuit, compensates the attenuation of oscillation by the inherent impedance of the oscillation circuit, maintains and amplifies the LC oscillation, and supplies power to the external circuit through the alternating current transformer.

At present, the nuclear decay energy generation mechanism that has been applied in practice mainly includes the thermal radioisotope thermal electric generator. In contrast, the mechanism of radiation voltaic effect is not widely used but has great development potential.

3. **Miniature radioisotope battery**

Micro-Electro-Mechanical System (MEMS) technology is considered one of the most important scientific and technological achievements at the beginning of the twenty-first century. It covers a wide range of applications such as medicine, biotechnology, aerospace, consumer electronics, communications, measurement, computer technology, security technology, automation devices, and environmental protection. Current commercial products produced by MEMS technology include pressure gauges, accelerometers, biochemical sensors, inkjet printer nozzles, and many disposable medical supplies. At present, the main obstacle restricting the application and promotion of MEMS is the lack of a miniature power supply that can match with this micro device and supply power stably for a long time. Therefore, solving the power supply problem of MEMS is one of the important topics to promote the development and application of MEMS technology.

The isotope battery that converts the decay energy of radionuclides into electric energy is one of the effective ways to solve this problem. When radionuclides decay, charged particles are released. Directly capturing these charged particles or through the PN junction of semiconductor materials can generate current and voltage to supply power for the miniature electromechanical system. Among various types of radioisotope batteries, the radiation voltaic isotope battery might be one of the best solutions. The research of radiation voltaic batteries began in the 1950s, but due to the lagging development of isotope preparation, semiconductor manufacturing, and other related technologies, there has been no breakthrough in this field for a long time. Since the late 1990s, driven by the demand for airborne power supply of micro systems such as MEMS, and with the development of isotope and semiconductor technology, the research of radiation voltaic batteries has received renewed attention. From then on, a large number of studies have focused on the improvement of semiconductor energy exchange unit devices such as the attempt of new structures, new materials, and new types of semiconductor devices, in order to increase the effective loading capacity and utilization rate of low-energy isotopes and enhance the ability of energy exchange unit to resist the radiation damage of high-energy isotopes, so as to improve the overall performance of radiation voltaic batteries.

The types of radiation voltaic battery energy exchange unit devices that have been studied so far are listed in Fig. 9.2. Compared with PN junction devices, non-PN junction devices have a wider range of material choices. Although the energy conversion efficiency of these devices as the energy conversion unit of radiation voltaic battery is not ideal, it can be expected that through continuous optimization of materials and

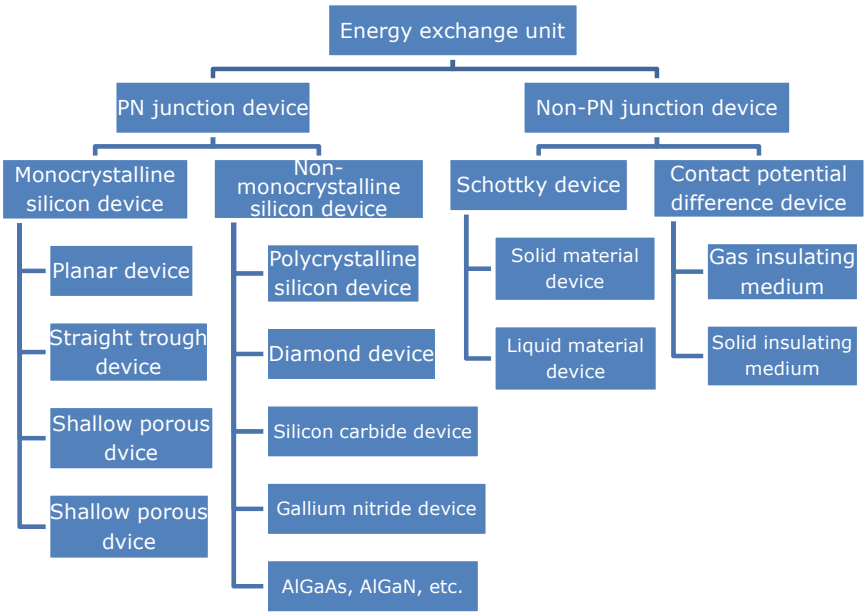


Fig. 9.2 Energy exchange unit of radiation voltaic isotope battery

structures, the device property will have great room for improvement. The development of Schottky devices made of liquid semiconductor materials deserves attention. It not only greatly improves the utilization rate of radioactive isotope particle radiation but also does not cause lattice damage of device material irradiated by radiation, which avoids the problem of degradation of device performance under long-term irradiation due to this reason. The development of such new materials and devices plays an important role in promoting the development and application of radiation voltaic batteries.

Radioisotopes are critical to the performance of radiation voltaic batteries. The final service life of a radiation voltaic battery depends on the half-life of the radioisotope applied. The property and density of the radioisotope rays determine the input power, thus directly affecting the output power of the battery. The interaction between the ray and the material of the energy exchange unit produces the electron–hole pair, and at the same time, it also produces other radiation damage effects. This will cause the deterioration of the output current or voltage of the battery during the long-term energy supply process, that is, the actual attenuation amplitude of the current or voltage exceeds the attenuation caused by the spontaneous decay of the isotope.

Generally speaking, the selection principles of driving radioisotopes used in radiation voltaic batteries are as follows: (a) High power density; (b) Long half-life; (c) Low toxicity, with an appropriate chemical form that is difficult to be absorbed by organisms and accumulated in the human body; (d) High purity, less harmful impurities, no emission of neutrons and high-energy γ-rays; (e) Good chemical stability.

It uses radioisotopes with certain chemical forms, which are resistant to oxidation, corrosion, deliquescence, volatilization, and other materials in the battery. Even in the case of packaging failure, it will not cause serious chemical pollution; (f) Low cost and easy to obtain.

The emission of low-energy pure β-radioisotopes is not easy to cause radiation damage to the device, and there is no need to add a shielding layer. As a driving source of radiation voltaic battery, it has more advantages than α and γ nuclides. However, its low energy density makes the output power of the corresponding radiation voltaic battery smaller. If a semiconductor material with strong radiation resistance is used as the energy conversion unit, the high-energy β-isotope or even an α-isotope can be selected as the driving source.

The combination of miniature isotope batteries and MEMS can be applied in many research fields. The miniature pressure sensor powered by the long-life miniature isotope battery can detect the pressure change of one-thousandth of a pascal, and is used for the pressure monitoring of a low-pressure environment (such as a vacuum chamber). The miniature pressure (stress) sensor can be permanently placed in the wall of the building, the cavity wall of the aircraft, and the outer wall of the ship to provide information about the structural change of the wall and cavity under various conditions (such as before and after the earthquake, the action of huge waves, etc.), and provide timely and reliable data for safety evaluation and accident prevention. The application of MEMS in the field of aerospace will lead to the transformation of aerospace systems, and the composition of microsatellites with a weight of less than 0.1 kg and a size reduced to the minimum. With a medium carrier rocket, hundreds of microsatellites can be launched into low earth orbit, forming a constellation layout covering the whole world.

9.4.3 Radioluminescence

Radioluminescence uses the energy of radionuclides to generate light energy, which is also known as permanent self-luminescence. It uses the radiation emitted by radioisotopes to emit visible light and obtain light energy by exciting some materials (fluorescent, phosphorescent materials, etc.). Therefore, radioluminescence consists of two important parts: radionuclides that provide rays (energy sources) and luminescent substrates that are excited to generate light energy. Early radionuclides used in radioluminescence are α-nuclides. But due to protection and toxicity considerations, β-sources are currently used as the majority of self-luminescent materials. Radioluminescence has been used in engineering technology to produce luminescent radioactive coatings since its discovery in 1906, commonly known as permanent luminescent materials. As a self-luminescent microlight source, it has a wide range of applications, such as low-intensity lighting, luminous signals, display devices, and luminous markers, due to its characteristics of no external excitation, simplicity and reliability, and long-lasting stability. It can be used on the instrument panel of aircraft, submarines, tanks, and other instruments, and can also be painted on the

sight of guns and guns. Meanwhile, it can work normally in a harsh environment and can be used for lighting and safety signs in underground mines and tunnels, as well as in aerospace equipment.

Tritium luminescent material is a kind of radionuclide luminescent material with mature technology and wide application. It is a self-luminescent material composed of a tritium carrier and fluorescent agent. Tritium luminescent material is the preferred light source for small-field illumination under dark conditions. The research and development of tritium luminescent materials in the United States, France, Russia, Canada, Switzerland, and other countries started early, and the quality of related products is good. At present, they have been widely used for traffic signs, building escape signs, watch pointers, fishing lights, and other lighting purposes.

9.4.4 Nuclear Heating

In the world's energy structure, the heat source used for low temperatures (such as heating) accounts for about half of the total heat consumption. This part of the heat is mostly obtained by direct coal combustion, causing serious pollution to the environment.

In 1964, the former Soviet Union put forward the technical scheme of nuclear heating. Both nuclear raw material production reactor and research reactor will generate a lot of heat while completing the main production and research tasks, and the heat must be dissipated by the heat dissipation system. If the heat dissipation system and the heating system are combined, the production and living places can be heated by nuclear energy in cold winter. Later, nuclear thermal power plants, low-temperature nuclear heating reactors, and floating nuclear thermal power plants with heat supply as the main or important function were successively developed.

Among them, the low-temperature nuclear heating reactor can operate at low temperatures and pressures with a simple structure, low cost, and high safety. Floating nuclear thermal power plants mainly supply electricity and heat to isolated islands. Nuclear heating can greatly reduce the emission of smoke and dust by replacing a large amount of coal heating.

Nuclear heating has received extensive attention internationally because it is economical, safe, and clean. Northern Europe, Germany, France, Switzerland, Canada, China, and other countries have also conducted research and development on nuclear heating reactors.

9.4.5 Hydrogen Production by Nuclear Energy

Hydrogen is an energy carrier with a high calorific value, no pollution, and no greenhouse gas generation. Thus, hydrogen energy is considered an ideal secondary energy

in the twenty-first century. In addition to being directly used as fuel to generate thermal energy, hydrogen can also be used for fuel cells and metal hydrogen.

The commonly used methods for hydrogen production methods include steam methane reforming (SMR), water electrolysis, biomass conversion, partial oxidation of petroleum, pyrolysis or gasification of coal or biomass, etc. The two dominant methods in industry are SMR and water electrolysis.

The use of fossil fuels such as methane to produce hydrogen will cause environmental pollution and the greenhouse effect, while the electricity consumption of hydrogen production by water electrolysis is large. Therefore, in order to realize the non-pollution and zero emission of hydrogen energy production and utilization, sustainable, clean, and low-cost primary energy must be found. As nuclear energy just meets the above requirements, it is likely to become the primary energy for hydrogen production in the future.

Nuclear hydrogen production technology mainly includes electrolytic hydrogen production and thermochemical hydrogen production. Producing hydrogen by electrolysis of water from nuclear power is a method of hydrogen production, which has been applied in practice. But this method has high energy consumption (4–6 kW h/m^3) and low efficiency (the total efficiency of hydrogen production is about 30%). In contrast, using the high temperature generated by the nuclear fission process in the reactor directly for thermochemical hydrogen production has a higher total hydrogen production efficiency (> 50%), thus this technology has been widely studied.

The principle of thermochemical hydrogen production is based on the thermochemical cycle, which makes water undergo catalytic thermal decomposition at 800–1000°C to produce hydrogen and oxygen. One of the keys to this method is to use the low-cost high-temperature heat source generated by nuclear fission in the reactor as the heat source for hydrogen production in the thermochemical cycle. After the 1970s, the United States, Japan, and the European Union invested billions of dollars to develop more than 100 thermochemical cycle processes, among which the iodine sulfur (IS) cycle first developed by GA (in the US) and the UT-3 cycle proposed by the University of Tokyo (in Japan) are considered as the best processes. In 2004, the IS cycle built a bench unit with a hydrogen production capacity of 50 NL L^{-1}.

As thermochemical hydrogen production has the advantages of high efficiency and no greenhouse gas emissions, with the continuous deepening of research, it will be an ideal large-scale hydrogen production method after solving the problems of equipment corrosion under high temperatures.

9.4.6 Desalination of Seawater by Nuclear Energy

Many countries in the world are short of fresh water. Some of them have excessively used groundwater for many years, causing an increasing scarcity of underground freshwater resources. Therefore, the development of desalination of seawater has become an urgent need to obtain fresh water and improve the structure of water resources.

The main methods of seawater desalination are distillation and membrane separation, of which distillation is the main method of seawater desalination industrial device. However, the distillation of seawater itself consumes a lot of energy, thus how to improve the efficiency ratio is the key to promoting the large-scale development of distillation desalination of seawater. Nuclear energy used for seawater desalination mainly uses the thermal energy of the reactor, which is similar to the idea of nuclear heating. Combine the nuclear power plant or low-temperature nuclear reactor with the desalination plant, use the residual heat of the nuclear power plant to heat the desalination distillation unit, or directly use the low-temperature nuclear reactor to provide steam for the distillation unit. The advantages of low-temperature nuclear reactors are described in the nuclear heating section.

9.4.7 Other Applications of Nuclear Energy

In addition to the above-mentioned applications of nuclear energy, there are other applications such as digging canals, building caverns, and bombing asteroids that may hit the earth. The wide application of nuclear energy plays an important role in solving the problems of sustainable development of human society, such as the environment and resources on which human beings rely for survival, and protecting the earth from the impact of cosmic asteroids.

9.5 Sustainable Development of Nuclear Energy

The extensive use of nuclear energy has greatly promoted the rapid development of the world economy and the improvement of human living standards. In particular, the development of nuclear fusion power plants will permanently solve the energy problems that have plagued the development of human society. Before the development and application of nuclear fusion energy, it is necessary to vigorously develop nuclear fission energy to alleviate the situation of current and long-term global energy supply tension. Although compared with fossil fuels, nuclear fission power generation has the advantages of low cost and relatively clean, it also brings many problems that are difficult to solve, such as the problem of the treatment and disposal of spent fuel, the contradiction between the lack of uranium resources and the vigorous development of nuclear power. In order to achieve sustainable development of nuclear fission energy, two main problems must be solved.

9.5.1 Challenges for Nuclear Energy Development

As mentioned before, the treatment and disposal of a large number of high-level radioactive wastes and the lack of uranium resources are two major worldwide problems restricting nuclear fission power generation.

1. **Treatment and disposal of large amounts of radioactive waste**

After the worldwide recovery of nuclear power, many countries have made great efforts to develop nuclear power. The operation of a large number of nuclear power plants generated huge amounts of radioactive waste. How to deal with and dispose of these radioactive wastes has become a difficult problem for the development of nuclear power in the world.

By 2015, the nuclear waste discharged from the world's existing nuclear reactors reached about 2.5×10^5 t (metal weight), of which 2.9×10^3 t was transuranic elements, 1.15×10^4 t was fission products, and 2.356×10^5 t was uranium. These nuclear wastes contain a large amount of U, Pu, minor actinides (MA), and fission products (FP), among which actinides (e.g., Pu, Np, Am, and Cm) and long-lived fission products (LLFP) constitute the main long-term radioactive hazards to the Earth's biological and human environment. However, the global industrial reprocessing capacity of spent fuel was 3.9×10^3 t per year, accounting for only 1/3 of the annual output. Its treatment was only for the recovery of uranium and the extraction of military plutonium, while other actinides and long-lived fission elements remain in radioactive waste. As a reliable deep geological disposal repository has not been built around the world, most of the spent fuel is still temporarily stored in temporary storage.

The large amount of radioactive waste generated by nuclear power is bound to bring great psychological pressure on the public. The shadow left by the Chernobyl nuclear power plant accident in the former Soviet Union, the Three Mile Island accident in the United States, and the Fukushima nuclear accident in Japan have raised concerns about the safety and reliability of the treatment and disposal of high-level radioactive waste. If this problem cannot be properly solved, the sustainable development of nuclear energy will be restricted.

For this reason, in recent decades, countries around the world have invested a lot of human, material, and financial resources to carry out research on the safe disposal of high-level radioactive waste. Since 2000, Russia, the United States, and IAEA have launched various initiatives related to nuclear fuel disposal. At the IAEA plenary meeting in 2003, Director-General ElBaradei proposed the Multilateral Nuclear Approvals (MNA), which is a multinational cooperation approach for the nuclear fuel cycle (including uranium enrichment, reprocessing, and spent fuel disposal). In 2005, Russia put forward the so-called "Putin Initiative" or the Global Nuclear Power Infrastructure (GNPI) initiative. In 2006, the US Department of Energy released the Global Nuclear Power Partnership (GNPP) initiative. These initiatives aim to solve the problems of nuclear waste treatment and disposal that currently impeding the

world's nuclear power development through cooperation among all countries in the world on the premise of preventing nuclear proliferation.

2. **Current world nuclear power scale and uranium storage**

By January 1st, 2020, the total installed capacity of nuclear power worldwide is 392 GWe (442 grid-connected generator units), with an annual uranium demand of 6.8×10^4–7.2×10^4 tU. It is predicted that the total installed capacity of nuclear power in the world will be 449–533 GWe by 2025. If only counted by pressurized water reactor (PWR), the annual uranium demand will be 8.2×10^4–1.0×10^5 tU. Based on the 60-year life cycle, the total uranium demand is 4.9×10^6–6.0×10^6 tU.

In 2004, the world's proven uranium reserves with a recovery cost of no more than \$80/kgU were 3.804×10^6 tU, those with a recovery cost of no more than \$130/kgU amounted to 4.743×10^6 tU, and the resources to be identified did not exceed 1.3×10^7 tU. In other words, according to the current consumption capacity, the proven uranium reserves in the world can only maintain the normal operation of all nuclear power units for up to 60 years. Even if the resources to be identified are included, it can only maintain the normal operation of all nuclear power units in the world for about 200 years. Until fusion power is successfully developed, the shortage of uranium resources will inevitably affect the subsequent development of fission nuclear power.

To solve the above problems, the following measures need to be taken:

(a) Increase investment to further explore the storage capacity of uranium ore.
(b) Develop advanced nuclear energy systems to make full use of uranium and thorium resources and reduce the generation of high-level radioactive waste.
(c) Strengthen the development and utilization of other renewable energies, such as fusion energy and solar energy.

9.5.2 Current Spent Fuel Disposal Method

At present, there are two ways to deal with spent fuel, namely, "one-time pass" and "post-treatment".

1. **One-time pass**

The "one-time pass" approach means that the spent fuel elements are cooled for a long period and packaged and then sent as waste to the permanent storage built in the deep stratum for final disposal. This type of nuclear waste final disposal method is relatively simple and potentially less expensive, with a low risk of nuclear proliferation. But large amounts of nuclear resources (uranium and plutonium) are buried underground, so the utilization rate of natural uranium will be very low. At the same time, because spent fuel contains all radionuclides, some of which are radioactive, calorific, toxic, and have a long half-life, thus they need to be isolated from the human living environment for a long time and reliably. However, it will take

more than 100,000 years for these nuclides to decay below the radioactive level of natural uranium ore in the process of deep geological disposal. Due to the complexity of the geological environment in the deep geological layer, the reliability of various packaging materials, and other factors, this disposal method poses a great long-term threat to environmental safety, and the public recognition of this method is low.

The "one-time pass" method uses the geological disposal of high-level radioactive waste, which is an extremely complex system engineering. It involves many disciplines such as engineering, geology, hydrogeology, chemistry, and environmental safety, and is a comprehensive research project integrating basic, application, engineering, and other disciplines.

It has been more than 70 years since American scientists put forward the idea of "geological disposal" of high-level radioactive waste in 1950. Geological disposal has gone from the original concept assumption, basic research, and underground experimental research to the stage of pre-selection of the disposal site, and a few countries such as Finland, the United States, and China have determined the site. In the past 20 years, important progresses have been made in the research of geological disposal of high-level radioactive waste. However, up to now, no geological repository for high-level radioactive waste has been built in the world, and the global high-level radioactive waste is still stored in a temporary repository.

2. **Reprocessing**

Compared with the "one-time pass" method, the "reprocessing" technology has proved its safety and effectiveness on an industrial scale. It has been successfully operated in several countries since the 1970s, and its technology is still improving.

At present, the post-treatment of spent fuel mainly adopts the Purex process. Through this process, U and Pu in spent fuel can be extracted for recycling to make full use of uranium resources. Long-life fission products and minor actinides enter the highly radioactive waste liquid. Through cement solidification and other technologies, high radioactive waste is made into stable solidified blocks such as silicate glass and sent to permanent storage in a deep geological layer for disposal.

Although current reprocessing methods can realize the recycling of U and Pu, the long-life fission products and secondary actinides are still left in the high-level radioactive waste liquid, which still requires 106 years of isolation from the geological circle in deep geological disposal to reach the environmental radioactivity level. That's to say, the current post-treatment method has not yet solved the environmental problems caused by high-level radioactive waste.

9.5.3 Establish an Advanced Nuclear Fuel Cycle System to Ensure the Sustainable Development of Nuclear Energy

The radioactive risk of deep geological treatment mainly comes from the minor actinides (MA) and long-lived fission products (LLFP) in high-level radioactive waste. If these MA and LLFP are separated from high-level radioactive waste, the remaining radioactive waste will be made into glass-solidified waste and stored for 1000 years, and its radioactive toxicity will be reduced to the level of natural uranium ore. If the separated MA and LLFP are transformed into short-lived or stable nuclides through transmutation, the possible radioactive hazard of nuclear energy production to the environment can be reduced to a very low level. At the same time, the energy released during MA transmutation can also be utilized, thus further improving the utilization rate of uranium resources. Hence an advanced concept of the fuel cycle system has been formed.

The "advanced fuel cycle" system refers to the combination of a thermal reactor fuel cycle with a fast neutron reactor or accelerator-driven system (ADS) to realize the transmutation of MA and LLFP while realizing the closed cycle of U and Pu.

Compared with the existing fuel cycle system, the fuel cycle process in the advanced system will be further simplified, and the Purex process can be adopted on the premise of meeting the requirements of the fast reactor fuel cycle. Under a low FP decontamination factor, U and Pu are separated from spent fuel simultaneously to make mixed oxide fuel for the fast reactor, and then ^{238}U is multiplied into fissionable ^{239}Pu by the fast reactor, which leads to higher uranium utilization rate, better nuclear power economy (investment cost reduced by 1/2–1/3), and stronger nuclear proliferation ability (low FP decontamination). At the same time, the combustion or transmutation of MA and LLFP generated during the fuel cycle in the fast reactor or ADS can reduce its long-term radioactive hazards and ensure environmental safety. Therefore, the advanced fuel cycle system also has the characteristics of small nuclear waste generation. The establishment of an advanced fuel cycle system is a necessary condition for the sustainable development of nuclear energy.

It is important to note that although the "advanced fuel cycle" system has greatly eliminated the radioactive hazards of long-lived nuclides, it will inevitably produce strong radioactive waste that needs geological treatment eventually.

From the above discussion, it is clear that the advanced fuel cycle system is based on advanced spent fuel reprocessing technology and an advanced nuclear reactor or accelerator drive system. Among them, separation is the key to the advanced fuel cycle system.

1. **Development of advanced reprocessing technology**

The most important trend of future fuel cycle development is to realize the transformation to the complete recycling of actinides (Pu, U, MA), namely the so-called advanced fuel cycle. The implementation of an advanced fuel cycle will not only improve the utilization rate of uranium resources but also help to solve the problem

of safe disposal of high-level radioactive waste, which is most concern by the public. In the implementation of the advanced fuel cycle, the separation and transmutation of MA have shortened the isolation time between nuclear waste and the biosphere to 1000–1500 years. At the same time, in addition to the complete recycling of actinides, other toxic and long-lived nuclides such as ^{90}Sr, ^{137}Cs and ^{99}Tc in spent fuel should also be separated to control or reuse.

Developing the advanced reprocessing technology and establishing the advanced nuclear fuel cycle system that includes the treatment of high-level radioactive waste liquid and the transmutation of long-lived nuclides have become the focus of global research. Advanced reprocessing technology, including spent fuel reprocessing technology that can adapt to high burnup and short cooling periods, advanced water separation technology for separating minor actinides, and advanced dry technology for reprocessing spent fuel from the fast reactor, is also one of the main research contents of advanced fuel cycle technology in the future. Among them, the good separation between trivalent actinides and lanthanides is a problem that must be solved in the "separation transmutation" nuclear fuel cycle.

Since the current spent fuel reprocessing is mainly established for the recovery of U and Pu, it does not involve the separation of MA and LLFP. Therefore, it cannot meet the requirements of the advanced fuel cycle system, so it is necessary to carry out research on advanced reprocessing technologies.

(1) Improvement of aqueous reprocessing

At present, there are two technical schemes for advanced reprocessing, namely, the total separation scheme and the "reprocessing-partitioning" scheme. The total separation scheme refers to a new separation process for separating U, Pu, MA, LLFP, and other nuclides from spent fuel. But the implementation of this plan is difficult. The "reprocessing-partitioning" scheme is to separate trivalent MA from high-level radioactive waste and realize the separation of lanthanides and actinides on the basis of improving the Purex process (such as increasing the separation of Np, Tc, etc.).

(a) Study on the improvement of aqueous reprocessing

At present, the international improvement of the conventional Purex process is mainly to strengthen the separation of Np and Tc based on the separation of U and Pu and improve and strengthen the control of ^{14}C and ^{129}I gas emissions. For example, the PARC process developed by JAER in Japan, the method of extracting Np from the Purex process with salt-free reagent developed by JNC in Japan, and the "one cycle" Purex process jointly developed by BNFL in the UK and the Russian Radium Research Institute.

The above various improvement schemes based on the conventional Purex process have the advantage that they can be realized only by slightly adjusting the process of the mature Purex process. Near the existing commercial reprocessing plant, the construction of a plant to separate MA from HLLW can realize the complete separation of nuclides. Therefore, the scheme is relatively mature in technology, easy to

implement, and low in investment cost. At present, most countries are carrying out research along this line.

(b) Separation of MA from high-level waste

After extraction of U and Pu, the highly radioactive waste liquid contains trivalent MA (mainly Am and Cm) with high radiotoxicity. The separation is complicated and involves the separation of actinides and lanthanides. Because the content of lanthanide in HLLW is one order of magnitude higher than actinide, and the chemical behavior of trivalent actinides and lanthanides is very similar, the separation of the two is extremely difficult.

Since the 1970s, more than 20 processes for separating MA from HLLW have been developed in various countries, but there are only four representative processes: the TRUEX process proposed by the United States, the TRPO-Cyanex 301 process proposed by China, the DIDPA-TALSPEAK process by Japan, and the DIAMEX-SESAME process proposed by France.

Among the four processes mentioned above, the DIAMEX process and the TRUEX process are internationally recognized as the better ones. The German Institute of Transuranium Elements has carried out several thermal experiments of typical separation processes with real feed liquid. The results show that bisamide is the best extractant for the co-extraction of MA and lanthanides from the highly radioactive waste liquid of the Purex process. It not only does not need seasoning but also can be completely burned as it only contains C, H, O, and N. which can be completely incinerated because they contain only C, H, O, and N. For the separation between An (III) and Ln (III), bis(triazinopyridine) (BTP) is the best extractant. Its separation coefficient is high, and it does not need to adjust the acid of the feed liquid. Under the condition of continuous countercurrent extraction, the content of lanthanide in Am/cm products can be lower than 1%.

In short, the separation of MA from HLLW is still in the laboratory research stage in various countries, and the An/Ln separation is in the exploratory research stage. It will take more than 10 years to realize the industrial application. In terms of An/Ln separation, it is necessary to continue to find efficient separation methods and minimize the generation of secondary waste (it is required to use salt-free reagents as much as possible).

(2) Dry reprocessing

The further deepening of fuel burnup of power reactor and the requirement to shorten the cooling time of spent fuel due to the economic considerations of the nuclear fuel cycle will lead to the radiation enhancement of the spent fuel to be treated, which makes the aqueous reprocessing with organic solvent as extractant difficult to be competent. Dry reprocessing has become a very active research field. Currently, the countries that are actively developing dry reprocessing include the United States, Russia, Japan, France, India, and South Korea.

In dry reprocessing, the oxide fuel is first chlorinated into chloride molten salt, and then electrochemically treated at high temperature to selectively separate the target

nuclide. Compared with aqueous reprocessing, dry reprocessing has the following advantages: (a) The inorganic salt medium used has good resistance to high temperature and irradiation; (b) Simple process flow, compact equipment structure, and good economy; (c) The reagent is recycled and the amount of waste is small; and (d) Pu and MA are recycled together to prevent nuclear proliferation.

However, the technical difficulties of dry reprocessing are great: (a) The strong irradiation of components requires that the whole process must be remotely operated; (b) The atmosphere needs to be strictly controlled to prevent hydrolysis and precipitation reaction; (c) Structural materials must have good high-temperature resistance and corrosion resistance.

At present, most countries are still in the stage of laboratory research in dry reprocessing. Only the United States has completed the simulation experiment of the laboratory scale (50 g heavy metal) and engineering scale (10 kg heavy metal) and is preparing the thermal experiment of the pilot scale (about 100 kg heavy metal).

2. **Develop fast reactor technology to realize ^{238}U and ^{232}Th fast reactor proliferation**

If the uranium and plutonium extracted from the spent fuel produced by the thermal reactor nuclear power plant are returned to the thermal reactor for recycling, the utilization rate of uranium resources can only be increased by 2–3 times. Due to the limited ^{235}U resources on the earth, the development scale and operation time of thermal reactor power stations mainly burning ^{235}U is also limited. Because ^{238}U in spent fuel and natural uranium ore accounts for the majority, only after many cycles in a fast neutron reactor (fast reactor) and burning most ^{238}U can the utilization rate of uranium resources be increased by several times (see Table 9.5), and the volume and toxicity of nuclear waste be reduced by more than 10 times. This means that using fast reactor technology and its corresponding advanced nuclear fuel closed cycle can enable the known conventional uranium resources on the earth to be utilized for thousands of years. For this reason, the technical development roadmap of the international "fourth generation" nuclear power system led by the United States lists the fast reactor and its fuel cycle as the main direction of nuclear energy development, and sets the sustainable goal of nuclear energy development: (a) waste minimization and safe management of waste; (b) maximize the use of resources. Russian President Putin also proposed the development of the fast reactor nuclear power system at the Millennium Summit, which shows that the sustainable development of nuclear fission energy places high hopes on the fast reactor and its closed fuel cycle.

Table 9.5 Uranium utilization rate under different reactor types and fuel cycle modes

Reactor type	Processing method	Uranium utilization rate (%)
Pressurized water reactor	"One-time pass"	0.45
Pressurized water reactor	Reprocessing; U, Pu cycle	1
Pressurized water reactor, fast reactor	Reprocessing; U, Pu recycle in the fast reactor	60–70

In addition, the earth is rich in thorium data. Its geological reserves are four times that of uranium resources. The energy it can provide is about equal to the total reserves of uranium, coal, and oil. ^{232}Th is not a fissile material, but it can proliferate into fissionable ^{233}U under the action of fast neutrons. ^{233}U has superior nuclear properties than ^{235}U and ^{239}Pu in a wider neutron spectrum range, and its thermal neutron parasitic capture is less than ^{235}U and ^{239}Pu. The amount of actinide waste, especially transuranium elements, is small, and the Th-U cycle can achieve a high conversion ratio (close to 1) in the thermal reactor. At the same time, the 232U and its daughter nuclides generated after the ^{232}Th (n, 2n) reaction emit strong γ-rays (e.g., the γ-ray energy of ^{208}Tl is 2.6 meV), which makes the thorium cycle inherently strong in nuclear non-proliferation.

For the above reasons, the research on the Th-U cycle by using the fast reactor-thermal reactor technology will help to alleviate the shortage of nuclear power resources in the long term.

3. **Transmutation of long-lived fission products and actinides**

Transmutation refers to the transformation of long-lived nuclides into short-lived or stable nuclides through the absorption of neutrons, fission, or spallation of heavy atoms and other nuclear reactions. Transmutation facilities that can provide neutron sources include thermal neutron reactors, fast neutron reactors, and accelerator drive systems (ADS).

In the partition-transmutation (P-T) process, the concept of long-lived high radioactive waste was put forward in the 1960s. In the 1970s, scientists from the United States, Britain, and other countries carried out extensive exploratory research on P-T. However, due to the limitations of various technical levels at that time, P-T research had been considerably controversial. Some countries have even obtained negative results on the use of P-T technology in nuclear waste treatment, thus P-T research has once turned into a low tide. With the development of reactor technology, accelerator technology, post-processing, and separation technology, as well as the complexity and uncertainty of long-term risk exposed in deep formation disposal research, especially in the late 1980s and early 1990s, France and Japan put forward the SPIN (Separation-integration) calculation and OMEGA (Options making extra Gains of action and fusion products generated in nuclear fuel reprocessing) plans respectively, the research on P-T has been paid attention again in the world and has made great progress. Transmutation disposal of nuclear waste through fast reactors, fusion-fission hybrid reactors, and spallation neutron source subcritical reactors has been carried out successively.

Whether the P-T of high-level radioactive waste can achieve the goal of eliminating long-term risks depends on the cleanliness of the separation of long-life highly radioactive waste. No matter how efficient and thorough the transmutation is, the final residual toxicity depends on the loss rate of separation. If the loss rate is 1%, the final residual toxicity will not be less than 1%. The worse the transmutation efficiency, the more cycles, and the higher the residual toxicity. The transmutation of MA and LLFP in which reactor type is used affects the composition of advanced nuclear power systems and the final amount of radioactive waste. The neutron sources currently used

for transmutation research include thermal neutron reactors, fast neutron reactors, and accelerator drive systems (ADS). France, Japan, Russia, and the United States are the main countries that have systematically studied evolution.

(1) Transmutation of long-lived fission product

Long-life fission products in spent fuel mainly include ^{99}Tc, ^{129}I, ^{89}Sr, ^{135}Cs, ^{137}Cs, ^{93}Zr, ^{151}Sm, and other nuclides. Among these nuclides, ^{151}Sm is a strong neutron absorber in the thermal neutron spectrum, which is easy to burn in the reactor. ^{107}Pa, ^{135}Cs, ^{137}Cs, and ^{93}Zr can be diluted and discharged due to low radioactivity. ^{90}Sr and ^{137}Cs have the highest radioactivity and the strongest toxicity and are not easy to transmute because of their small thermal neutron capture cross-section (only when the neutron fluence rate is 10^6 cm^{-1} s^{-1}–107 cm^{-1} s^{-1} can it transmute). However, because their half-life is relatively short (about 30a), they can be placed for a long time until it decays into stable ^{90}Zr and ^{137}Ba. ^{99}Tc and ^{129}I have long life, high toxicity, and are easy to migrate and penetrate the biosphere, which must undergo transmutation treatment. Because these two nuclides have large thermal neutron capture cross-sections, they can effectively transmute in the epithermal neutron spectrum, and their annual transmutation rates can reach 5% and 10% respectively.

(2) Transmutation of actinide nuclides

Actinide nuclides can be transmuted by (n, γ), (n, 2n), and (n, 3n) reactions. Its products are still actinide nuclides, which can be transmuted into fission products only through the fission reaction.

Only a few actinides in spent fuel are fissile nuclides, such as ^{239}Pu and ^{241}Pu, which have large fission cross-sections in the thermal neutron spectrum, while the fission cross-sections of other nuclides are far less than the neutron capture cross-sections. Therefore, the transmutation in the thermal reactor is dominated by thermal neutron capture. The actinide waste produced during transmutation is often more than that through fission transmutation, and the high toxicity of some new MA such as ^{244}Cm makes the multi-stage cycle almost impossible to operate. Only when the thermal neutrons in the thermal reactor are abundant can the fission be conducted after multiple neutron capture. Therefore, actinide nuclides cannot be transmuted effectively in thermal reactors.

For actinide elements, only by using fast neutron irradiation and increasing the fission fraction can an efficient transmutation be achieved. For example, after one cycle, the transmutation rate of Np is 40–50%. The result is that the long-term radioactive hazard of ^{237}Np is reduced, but ^{238}Pu with high toxicity is produced. After one cycle, the transmutation rate of Am is 73%, producing mixed nuclides with ^{238}Pu and ^{240}Pu as the main toxicants with medium and long life. While the fast neutron reactor using Pu as fuel transmutes MA, part of Pu will produce new MA through neutron capture. Therefore, in the fast reactor, there is a balance of MA growth and decline for a long time.

When transmuting MA in the fast reactor, the reactor safety is reduced due to the improvement of core reactivity, thus the amount of MA added in the fast reactor

cannot exceed 21.5% of the total fuel. For the transmutation of MA in ADS, the subcritical device driven by the accelerator ensures good safety. As mentioned before, in the process of fast reactor transmutation, the generation of new MA will lead to a long-term balance of the growth and decline of An, while in the process of ADS transmutation of MA, due to the high fission share, almost no new and heavier MA will be produced. Studies have shown that the transmutation capacity of ADS is one order of magnitude higher than that of fast reactors. Although ADS has high transmutation capability, there are still many problems with its safe and long-term stable operation. The road to the practical application of this technology is still long, and its development costs a lot.

It must be pointed out that neither fast reactors nor ADS can eliminate MA and LLFP but can only reduce them. Therefore, geological disposal is still inevitable, but the amount of high-level radioactive waste to be disposed of can be greatly reduced. In order to minimize waste and maximize resource utilization, the advanced nuclear fuel cycle system must have advanced reprocessing technology (separation of U, Pu, MA, and LLFP) and advanced nuclear reactor technology (fast reactor or accelerator-driven nuclear power system, used for the proliferation of ^{238}U and ^{232}Th, and the transmutation of MA and LLFP). Only by establishing an advanced nuclear fuel cycle system can the sustainable development of nuclear energy be realized.

9.5.4 Solutions to Uranium Resource Shortage

Faced with the shortage of uranium raw materials on land, scientists have turned their attention to the ocean. The vast ocean contains about 4.5 billion tons of natural uranium, which can be used by 1000 million kilowatt nuclear power units for 100,000 years. Therefore, scientists have proposed the strategy of extracting uranium from seawater. The difficulty of extracting uranium from seawater first lies in the extremely low concentration of uranium in seawater (about 3.3 mg/m^3), followed by the interference of a large number of K^+, Na^+, Ca^{2+}, Mg^{2+}, and other ions in seawater. Among the various technical methods proposed, such as adsorption, extraction, ion exchange, precipitation, biological conversion, and electrochemical extraction, adsorption is the most promising. The key to the adsorption method is the design and preparation of adsorption materials with high selectivity, high adsorption capacity, easy elution, good recycling performance, and resistance to marine biological pollution. Some examples include polypropylene fiber materials containing the amidoxime group developed in Japan, hollow gear-shaped polyethylene fiber with a high specific surface area containing the amidoxime group developed in the United States, and polypropylene fiber materials containing amidoxime group and polyhexamethylguanidine hydrochloride developed in China. Currently, the extraction

of uranium from seawater has not yet entered industrial production. Once a breakthrough is achieved, it will solve the source problem for the long-term use of fission energy.

Exercise

1. Briefly describe the working principle of nuclear power plants.
2. Briefly describe the types and principles of nuclear fusion confinement.
3. Why is nuclear fusion an inexhaustible source of clean energy?
4. Try to discuss how to realize the sustainable development of nuclear energy.
5. It is known that the mass loss when protons and neutrons combine to form deuteron is 0.0040×10^{-27} kg, how much energy is released during this process? Knowing that $c = 2.9979 \times 10^8$ m/s, 1 eV $= 1.6022 \times 10^{-19}$ J.
6. After capturing a neutron, the static lithium nucleus ${}^{5}_{3}\mathrm{Li}$ generates a deuterium nucleus and an α-particle and releases 4.8 meV of energy. (1) Write the equation of nuclear reaction; (2) calculate the mass loss during the reaction.

Bibliography

Ao, J. X., Xu, X., Li, Y. N., Wu, G. Z., Li, Q. A., & Ma, H. J. (2019). Haishui Tiyou Yanjiu Jinzhan [Research progress in uranium extraction from seawater]. *Fushe Yanjiu Yu Fushe Gongyi Xuebao., 37*(02), 3–28.

Dai, D., & Wu, H. S. (2020). Quanqiu Hedian Zhuangji Rongliang 2019nian Xiaofu Jiangdi [The installation capacity of global nuclear power decreased slightly in 2019]. *Guowai Hexinwen, 1*, 23–25.

El-Genk, M. S. (2008). Space nuclear reactor power system concepts with static and dynamic energy conversion. *Energy Conversion and Management, 49*(3), 402–411. https://doi.org/10.1016/j.enconman.2007.10.014

Feng, B. (2016). ICF Jiguang Qudongqi Shuba Ouhe Miaozhun Dingwei Yanjiu [Research on laser alignment and target positioning of ICF laver driver]. Haerbin Gongye Daxue.

Hao, Q. (2013). Hefeiliao Chuli Fangfa ji Guanli Celve Yanjiu [Research on nuclear waste treatment and management strategies]. Huabei Dianli Daxue.

He, K. H., Luo, D. L., Wang, Harty, R. B., Otting, W. D., & Kudija, C. T. (1994). Applications of brayton cycle technology to space power. *IEEE Aerospace and Electronic Systems Magazine, 9*(1), 28–32. https://doi.org/10.1109/62.257140

Liu, C. A., & Shi, X. M. (2013). Meiguo Jiguang Guangxing Yueshu Jubian Nengyuan Yanjiu Zongshu [A review of laser inertial confinement fusion energy research in the United States]. *Yuanzi Hewuli Pinglun, 30*(1), 89–93.

Luo, S. Z., Wang, G. Q., & Zhang, H. M. (2011). Fushe Fute Xiaoying Tongweisu Dianchi Yanjiu Jinzhan [Advance in radiation—voltaic isotope battery]. *Tongweisu, 24*(1), 1–11.

Li, H. M., Wen, J., & Wang, X. L. (2020). Jugua Xiushi Kangjunxing Haishui Tiyou Cailiao [Polyguanidine Modified antibacterial adsorbent for uraniumextraction from seawater]. *Sichuan Daxue Xuebao(Ziran Kexueban), 57*(03), 569–576.

Moses, E. I., Campbell, J. H., Stolz, C. J., & Wuest, C. R. (2003). The National Ignition facility: the world's largest optics and laser system. SPIE LASE.

Nishitani, T., Garin, P., Sugimoto, M., Nakajima, N., Heidinger, R., Kimura, H., & Baluc, N. (2012). Progress of fusion nuclear technologies in the broader approach framework. *Fusion Engineering and Design, 87*, 535–542. https://doi.org/10.1016/j.fusengdes.2012.01.018

Nuclear Power in a Clean Energy System. (2019). Vancouver: IEA Publications.

Prelas, M. A., Weaver, C. L., Watermann, M. L., Lukosi, E. D., Schott, R. J., & Wisniewski, D. A. (2014). A review of nuclear batteries. *Progress in Nuclear Energy, 75*, 117–148. https://doi.org/10.1016/j.pnucene.2014.04.007

Solomykov, A., & Zhao, J. L. (2019). Eluosi Heneng Gongre Jishu Fazhan Yu Xianzhuang Fenxi [Development and present status analysis of Russian nuclear energy heating technology]. *Quyu Gongre, 5*, 126–132. https://doi.org/10.16641/j.cnki.cn11-3241/tk.2019.05.020

Su, G. H., Zhang, J., & Wang, C. L. (2020). Heneng Zai Weilai Zairen Hangtian Zhongde Yingyong [Application of nuclear energy in future manned space flight. Manned spaceflight]. *26*(01), 1–13. https://doi.org/10.16329/j.cnki.zrht.2020.01.001

Tao, Q., Yu, F., & Pang, B. (2020). ITER Jihua Guoji Dakexue Gongcheng Gongzuo Jinzhan [Progress in the international huge science and engineer project of ITER]. *Zhongguo Hedian, 13*(06), 736–740.

Wang, Z., Wu, H. S., Guo, X. Y., & Dan, L. (2021). Quanqiu Hedian Zhuangji Rongliang 2020nian Baochi Wending [The installation capacity of global nuclear power remained stable in 2020] *Guowai Hexinwen,1*, 27–28.

Wu, H. S., & Zhao, H. (2017). IAEA Yuji Hedian Zhuangji Rongliang Dao 2050nian Jiang Fanfan [IAEA estimates a one-fold increase in installation capacity of global nuclear power plants by 2050]. *Guowai Hexinwen, 9*, 12–13.

Ye, H. L. (2020). Hejubian Nengyuan De Kaifa Yu Liyong [Development and utilization of nuclear fusion energy]. *Zhongguo Gaoxin Keji., 83*(23), 41–42.

Zelenina, E. V., Sychov, M. M., Kostylev, A. I., & Ogurtsov, K. A. (2019). Prospects for the development of tritium-based solid-state radio luminescent light sources. *Radiochemistry, 61*(1), 55–60. https://doi.org/10.1134/S1066362219010089

Zheng, W. Q., Li, Q. J., & Wang, H. C. (2016). Heneng Zai Haishui Danhua Zhongde Yingyong Tanjiu [Application exploration of desalination of seawater by nuclear energy]. *Chanye yu Keji Luntan, 15*(05), 78–79. https://doi.org/10.3969/j.issn.1673-5641.2016

Appendix A
International System of Units (SI)

1. SI base unit

Basic units and corresponding symbols

Base quantity	Base unit	
Mass	Kilogram	kg
Length	Meter	m
Time	Second	s
Current	Ampere	A
Thermodynamic temperature	Mole	mol
Amount of substance	Kelvin	K
Luminous intensity	Candela	cd

2. SI derived unit

SI (including SI supplementary unit) derived unit

Quantity	SI derived unit		
	Name	Symbol	Relationship with SI base unit
Frequency	Hertz	Hz	$1\ \mathrm{Hz} = 1\ \mathrm{s}^{-1}$
Force	Newton	N	$1\ \mathrm{N} = 1\ \mathrm{kg} \cdot \mathrm{m} \cdot \mathrm{s}^{-1}$
Pressure	Pascal	Pa	$1\ \mathrm{Pa} = 1\ \mathrm{N} \cdot \mathrm{m}^{-2}$
Energy	Joule	J	$1\ \mathrm{J} = 1\ \mathrm{N} \cdot \mathrm{m}$
Power	Watt	W	$1\ \mathrm{W} = 1\ \mathrm{J} \cdot \mathrm{s}^{-1}$
Electric charge	Coulomb	C	$1\ \mathrm{C} = 1\ \mathrm{A} \cdot \mathrm{s}$
Resistance	Ohm	Ω	$1\ \Omega = 1\ \mathrm{V} \cdot \mathrm{A}^{-1}$
Conductance	Siemens	S	$1\ \mathrm{S} = 1\ \Omega^{-1}$
Capacitance	Farad	F	$1\ \mathrm{F} = 1\ \mathrm{C} \cdot \mathrm{V}^{-1}$

(continued)

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6

(continued)

Quantity	SI derived unit		
	Name	Symbol	Relationship with SI base unit
Celsius temperature	Degree Celsius	°C	x°C = $(x + 273.15)$ K
Magnetic flux	Weber	Wb	1 Wb = 1 V · s
Magnetic flux density	Tesla	T	1 T = 1 Wb · m^{-2}
Radioactivity	Becquerel	Bq	1 Bq = 1 s^{-1}
Absorbed dose	Gray	Gy	1 Gy = 1 J · kg^{-1}
Dose equivalent	Sievert	Sv	1 Sv = 1 J · kg^{-1}

3. Multiples and fractions of SI unit

Common SI prefixes that form units of decimal numbers and Fractions

Factor	Name	Symbol
10^{24}	Yotta	Y
10^{21}	Zetta	Z
10^{18}	Exa	E
10^{15}	Peta	P
10^{12}	Tera	T
10^{9}	Giga	G
10^{6}	Mega	M
10^{3}	Kilo	k
10^{2}	Hecto	h
10^{1}	Deca	da
10^{-1}	Deci	d
10^{-2}	Centi	c
10^{-3}	Milli	M
10^{-6}	Micro	μ
10^{-9}	Nano	n
10^{-12}	Pico	p
10^{-15}	Femto	f
10^{-18}	Atto	a
10^{-21}	Zepto	z
10^{-24}	Yocto	y

Appendix B
Legal Unit of Measurement

Main legal unit of measurement that can be used together with SI

Quantity	Name	Symbol	Relationship with SI unit
Time	Annum	a	1 a = 365 d = 3.153600×10^7 s
	Day	d	1 d = 24 h = 8.64×10^4 s
	Hour	h	1 h = 60 min = 3.6×10^3 s
	Minute	min	1 min = 60 s
Length	Kilometer	km	1 km = 10^3 m
	Decimeter	dm	1 dm = 10^{-1} m
	Centimeter	cm	1 cm = 10^{-2} m
Angle	Degree	°	1° = (π/180) rad
	Minute	′	1′ = (1/60) °
	Second	″	1″ = (1/60) ′
Mass	Ton	t	1 t = 10^3 kg
	Gram	g	1 g = 10^{-3} kg
	Atomic mass unit	u	1 u ≈ 1.660540×10^{-27} kg
Volume	Liter	L	1 L = 1 dm^3 = 10^{-3} m^3
Rotational speed	Revolution per minute	$r \cdot min^{-1}$	$r \cdot min^{-1}$ = (1/60) s^{-1}
Energy	Electron volt	eV	1 eV ≈ 1.602177×10^{-19} J
Magnetic flux density	Gauss	G	1 G = 10^{-4} T
Magnetic flux	Maxwell	Mx	1 Mx = 10^{-8} Wb
Radioactivity	Curie	Ci	1 Ci = 3.7×10^{10} Bq

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6

Appendix C
Fundamental Physical Constant

Physical quantity	Symbol	Quantity value
Speed of light in vacuum	c	$2.997924 \times 10^{8}\ \mathrm{m \cdot s^{-1}}$
Planck constant	h	$6.626076 \times 10^{-34}\ \mathrm{J \cdot s}$
Elementary charge	e	$1.602177 \times 10^{-19}\ \mathrm{C}$
Electron mass	m_e	$9.109390 \times 10^{-31}\ \mathrm{kg}$
Proton mass	m_p	$1.660540 \times 10^{-27}\ \mathrm{kg}$
Neutron mass	m_n	$1.674929 \times 10^{-27}\ \mathrm{kg}$
Atomic mass unit	u	$1.602177 \times 10^{-27}\ \mathrm{kg}$
Standard atmospheric pressure	atm	101,325 Pa
Avogadro's number	N_A	$6.022137 \times 10^{23}\ \mathrm{mol^{-1}}$
Molar gas constant	R	$8.314511\ \mathrm{J \cdot kg^{-1} \cdot mol^{-1}}$
Classical electron radius	r_e	$2.817941 \times 10^{-15}\ \mathrm{m}$

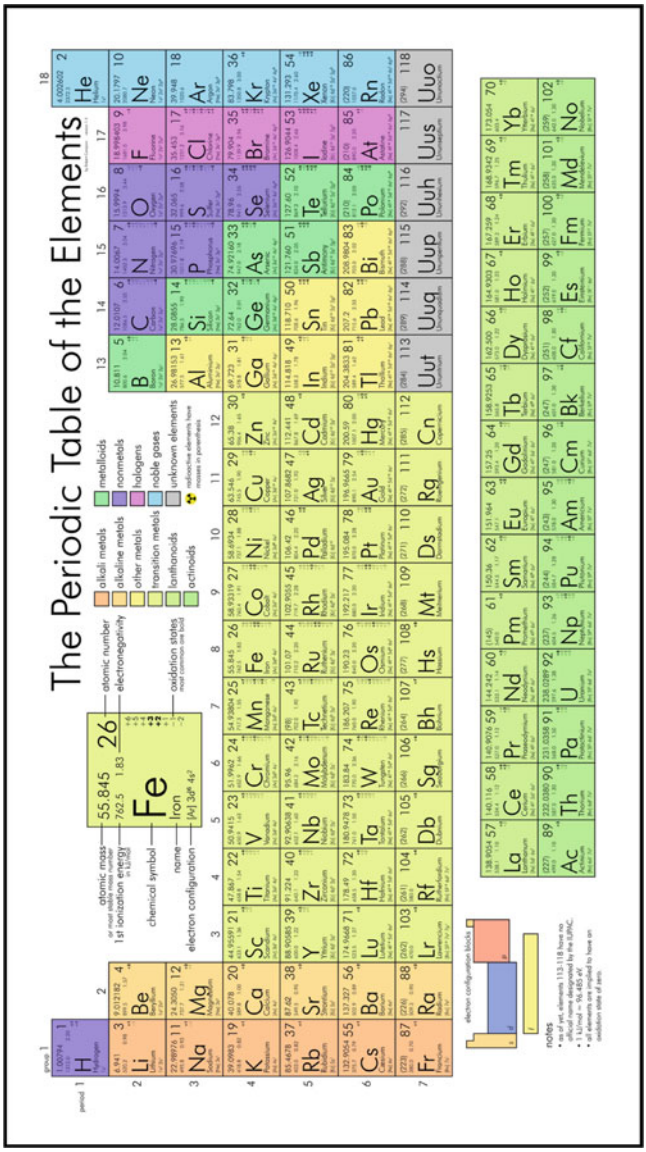
© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6

Appendix D
Periodic Table of the Elements

© Harbin Engineering University Press 2023

S. Luo, *Nuclear Science and Technology*, Nuclear Science and Technology,
https://doi.org/10.1007/978-981-99-3087-6


The Periodic Table of the Elements
group 1
period 1
2
3
4
5
6
7
18
13
14
15
16
17
atomic mass
or most stable isotope
1st ionization energy
in kJ/mol
chemical symbol
name
electron configuration
atomic number
electronegativity
oxidation states
most common are bold
alkali metals
alkaline metals
other metals
transition metals
lanthanoids
actinoids
metalloids
nonmetals
halogens
noble gases
unknown elements
radioactive elements, have masses in parentheses
electron configuration blocks
notes
• atomic weights in parentheses are those of the most stable or most common isotope
• elements 113-118 have not yet been officially named by the IUPAC
• 1 kJ/mol = 9.65 eV
• all elements are a solid at room temperature unless otherwise noted