Cementitious Materials for

Nuclear Waste Immobilization

Rehab O. Abdel Rahman • Ravil Z. Rakhimov
Nailia R. Rakhimova • Michael I. Ojovan

WILEY

Cementitious Materials for Nuclear Waste Immobilization

PROFESSOR REHAB O. ABDEL RAHMAN

Hot Laboratory and Waste Management Centre,
Atomic Energy Authority of Egypt, Egypt

PROFESSOR RAVIL Z. RAKHIMOV

Kazan State University of Architecture and Engineering,

PROFES[illegible]HIMOVA

Kazan State University of Architecture and Engineering,
Russian Federation

PROFESSOR MICHAEL I. OJOVAN

Imperial College London, UK

WILEY

This edition first published 2015

Registered Office
John Wiley & Sons, Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at www.wiley.com.

Library of Congress Cataloging-in-Publication Data

Rahman, Rehab O. Abdel.
Cementitious materials for nuclear waste immobilization / professor Rehab O. Abdel Rahman, professor Ravil Z. Rakhimov, professor Nailia R. Rakhimova, professor Michael I. Ojovan.
pages cm
Includes bibliographical references and index.
ISBN 978-1-118-51200-5 (cloth)
1. Radioactive waste repositories–Materials. 2. Cement composites. 3. Hazardous wastes–Solidification. I. Rakhimov, Ravil Z. II. Rakhimova, Nailia R. III. Ojovan, Michael I. IV. Title.
TD898.17.R35 2014
621.48′38–dc23

2014024526

A catalogue record for this book is available from the British Library.

ISBN: 9781118512005

Set in 10/12pt Times by SPi Publisher Services, Pondicherry, India
Printed and bound in Malaysia by Vivar Printing Sdn Bhd

1 2015

Cementitious Materials for Nuclear Waste Immobilization

"To emeritus mathematician Vladimir Rolinskyi".

About the Authors

Rehab O. Abdel Rahman is Associate Professor of Chemical Nuclear Engineering in the Radioactive Waste Management Department, Hot Laboratory and Waste Management Centre, Atomic Energy Authority of Egypt.

She received her PhD degree in Radioactive Waste Management from the Nuclear Engineering Department, Faculty of Engineering, Alexandria University, Egypt. Her research interests include different aspects of radioactive waste management, including radioactive waste treatment, conditioning and disposal. She has authored more than 25 peer-reviewed scientific papers and book chapters on radioactive waste management. She serves as a reviewer for some international journals, as Managing Editor for the *International Journal of Environment and Waste Management* and the *International Journal of Environmental Engineering* and was Editor of the book *Radioactive Waste* (InTech, 2012). She was awarded the State Incentive Award in Engineering Sciences, 2011 and selected as one of the 'Top 100 Engineers 2011' by the International Biographical Centre.

Ravil Z. Rakhimov is a Professor and Head of Department in the Department of Building Materials of the Kazan State University of Architecture and Engineering, Russian Federation.

He has been awarded DSc and PhD degrees in polymer research. He is a Fellow of the Russian Academies of Architecture and Building Sciences, Informatisation, and of Quality Problems, an Honoured Scientist of the Russian Federation, an Honorary Builder of the Russian Federation, and Laureate of the State Prize of the Government of the Russian Federation. He has authored over 600 scientific papers, has 32 patents, and published 39 monographs and textbooks on development and investigation of different mineral binders and building materials.

Nailia R. Rakhimova is a Professor in the Department of Building Materials of the Kazan State University of Architecture and Engineering, Russian Federation.

She has been awarded a DSc degree in alkali-activated slag-blended cements research and a PhD degree in polymer coatings research. She has authored over 100 scientific papers (in Russian) and 15 peer-reviewed scientific papers, has 6 patents, and published 1 monograph on alkali-activated slag cements and concretes.

Michael I. Ojovan has been Visiting Professor in the Department of Materials of Imperial College London and Associate Professor in the Department of Engineering Materials of the University of Sheffield. He is currently a Nuclear Engineer at the International Atomic Energy Agency Headquarters in Vienna, Austria.

He has been awarded a DSc degree in Physical Chemistry and a PhD degree in Solid State Physics. He is a Fellow of the Russian Academy of Natural Sciences and a Member of the Materials Research Society and International Commission on Glass. He has authored over 300 peer-reviewed scientific papers, has 42 patents, and published 11 monographs on nuclear materials including the second edition of *An Introduction to Nuclear Waste Immobilisation* (Elsevier, 2005, 2014). He is known for the two-exponential universal viscosity equation and the connectivity–percolation theory of glass–liquid transition.

Preface

Approaches and current practices of use of cementitious materials for nuclear waste immobilization are summarized in this book, with a focus on the most important aspects of cements as nuclear wasteforms. The topics covered include an introductory background on nuclear waste management, description of Portland cements and cements with mineral and chemical admixtures, alternative cementitious binders, radioactive waste cementation and equipment used, wasteform durability requirements and testing, and performance assessment.

Hydration of Portland cement as well as interaction of Portland cements with water and soil are described in detail. Also covered are mineral and chemical admixtures, chemical admixtures to control the structure and properties of Portland cements such as accelerators and retarders, plasticizers, and super-plasticizers, air-entraining agents, water-retaining agents and water permeability reducing admixtures, biocidal admixtures, mineral admixtures in the control of the composition, structure and properties of cements and mineral admixtures from natural rocks and minerals. Alternative binders are considered including calcium aluminate cements, calcium sulphoaluminate cements, phosphate cements such as magnesium and calcium phosphate cements, as well as alkali-activated cements. Cement properties relevant to waste immobilization are analysed including characterization and testing.

Radioactive waste streams suitable for cementation are described including both aqueous and organic waste, bulk and fragmented (dispersed) solid wastes as well as the description of cement-based wasteform optimization. Waste cementation technology and equipment are considered including methods of liquid and dispersed solid waste cementation and methods for cementation of bulk solid waste. Quality control of technological processes and materials obtained is discussed.

Cementitious wasteform durability requirements are examined along with the role of material performance and expected performance of cements. Wasteform leaching parameters and testing protocols such as IAEA/ISO 6961-82, ASTM C1220-98 (MCC-1), ANS-2009 (ANS/ANSI 16.1) and ASTM C1662-10 are given. Long-term field tests of cementitious materials are described as well as the effects of radiation, biological activities and role of filling materials. Performance assessment gives a brief overview of historical disposal practice, disposal facility design, modelling approaches, and safety case developed for disposal facilities.

Overall the book provides the reader with both a scientific and technological basis of using cementitious materials for immobilization of nuclear waste.

Contents

About the Authors **xi**
Preface **xiii**

1 Introduction **1**

1.1 Background of Nuclear Waste Problem 1
1.2 Nuclear Industry Facilities 2
1.2.1 NFC Facilities 2
1.2.2 Radioisotope Production and Application 8
1.3 Nuclear Waste Sources and Classification 10
1.4 Nuclear Waste Management 13
1.4.1 Development of Policy Principles, Strategy and Legal Framework 14
1.4.2 Technical Options for a Waste Management System 16
1.4.3 Technical Factors that Affect Technology Selection 22
1.5 Wasteform Materials 23
References 25

2 Cements: Portland Cement **27**

2.1 Cements 27
2.2 Portland Cement: Manufacture, Mineral Composition, Properties 28
2.3 Phase and Mineral Composition of Ordinary Portland Cement 30
2.4 Properties of Portland Cement 31
2.5 Hydration of Portland Cement 32
2.5.1 Hydration and Hydraulic Activity of Clinker Phases and Portland Cement 32
2.5.2 Process Chemistry, Products and Hydration Stages 35
2.5.3 Microstructure, Phases and Properties of Fresh and Hardened Cement Paste 40
2.6 Interaction of Portland Cements with Water and Soil 44
2.6.1 Ground Waters and Their Interaction with Cement Hydration Products 44
2.6.2 Soil and Its Interaction with Cement Hydration Products 48
References 51

3 Portland Cements with Mineral and Chemical Admixtures 53

3.1 Chemical Admixtures to Control the Structure and Properties of Portland Cements 53
3.1.1 Accelerators 55
3.1.2 Retarders 56
3.1.3 Plasticizers, Super-Plasticizers and Hyperplasticizers 57
3.2 Mineral Admixtures in the Control of the Composition, Structure and Properties of Cements 61
3.2.1 Classification of Mineral Admixtures for Cements 62
3.2.2 Portland Cements with Mineral Admixtures from Natural Rocks and Minerals 66
3.2.3 Portland Cements with Mineral Admixtures from Wastes of Various Industries 67
3.2.4 Portland Cements with Synthetic Mineral Admixtures 69
3.2.5 Portland Cements with Hybrid Mineral and Organic-Mineral Admixtures 70
References 74

4 Alternative Binders 79

4.1 Calcium Aluminate Cements 80
4.1.1 Chemical and Mineralogical Composition of CACs 80
4.1.2 Hardening of CACs 81
4.1.3 Properties of CACs 82
4.2 Calcium Sulphoaluminate Cements 83
4.2.1 Chemical and Mineralogical Composition of CSACs 84
4.2.2 Hardening of CSACs 84
4.2.3 Properties of CSACs 86
4.3 Phosphate Cements 87
4.3.1 Properties of Phosphate Cements 89
4.3.2 Magnesium Phosphate Cements 90
4.3.3 Calcium Phosphate Cements 90
4.4 Alkali-Activated Cements 92
References 99

5 Cement Properties, Characterization and Testing 105

5.1 Water/Cement Ratio, Water Requirement, Workability and Water Retention 105
5.2 Setting Time 109
5.3 Specific Surface Area and Particle Size Distribution 111
5.4 Heat Evolution 113
5.5 Strength 114
5.6 Freeze–Thaw Resistance 119
5.7 Microstructure and Analysis 121
References 124

6 Radioactive Waste Cementation **127**

6.1 Radioactive Waste Streams for Cementation 127
6.2 Liquid Waste 130
6.2.1 Organic Liquid Waste for Cementation 130
6.2.2 Aqueous Waste for Cementation 132
6.3 Bulk Solid Radioactive Wastes 138
6.3.1 Bulk Metallic Wastes 138
6.3.2 Bulk Concrete Wastes 140
6.3.3 Bulk Graphite 142
6.3.4 Bulk Hazardous Wastes 143
6.4 Fragmented (Dispersed) Solid Wastes 143
6.4.1 Compactable, Combustible Wastes 144
6.4.2 Non-compactable, Non-combustible Wastes 145
6.5 Additives for Radioactive Waste Cementation 147
6.5.1 Lime 148
6.5.2 Blast Furnace Slag 149
6.5.3 Clay Minerals 149
6.6 Cement-Based Composite Materials 152
6.7 Cement-Based Wasteform Optimization 153
References 154

7 Waste Cementation Technology **159**

7.1 Methods of Liquid Waste Cementation 159
7.1.1 Regular Mixer Technology 161
7.1.2 Disposable Stirrer Technology 163
7.1.3 Slant Mixer Technology 167
7.1.4 High Energy and High Shear Mixer Technology 168
7.1.5 In-line Mixing Technology 168
7.2 Methods for Cementation of Fragmented (Dispersed) Solid Waste 168
7.3 Methods for Cementation of Bulk Solid Waste 173
7.4 Quality Control of Technological Processes and Materials Obtained 174
References 175

8 Cementitious Wasteform Durability **177**

8.1 Wasteform Durability Requirements 177
8.2 Role of Material Performance 181
8.3 Expected Performance of Cements 182
8.4 Wasteform Leaching Parameters 185
8.5 Laboratory Tests 186
8.6 Long-Term Field Tests 188
8.6.1 Mound Type Repository Field Tests 189
8.6.2 Vault Repository Field Tests 194

8.7 Effect of Radiation 195
8.8 Biological Effects 196
8.9 Role of Filling Materials 197
References 198

9 Performance Assessment **201**

9.1 Historical Disposal Practice 202
9.2 Disposal Facility Design 204
9.2.1 Shallow Land Disposal Options 206
9.2.2 Underground Disposal Option 208
9.3 Modelling Approaches 210
9.4 Performance Assessment 212
9.5 Safety Case 216
References 217

10 Future Trends and Concluding Remarks **221**

10.1 Role of Cementitious Materials 221
10.2 Novel Cementitious Materials 222
10.3 Concluding Remarks 224
References 225

Index **227**

1
Introduction

1.1 Background of Nuclear Waste Problem

By definitions a waste is a material for which no further use is foreseen. For legal and regulatory purposes a radioactive (nuclear) waste is that waste which contains or is contaminated with radionuclides at concentrations or activities greater than clearance levels as established by the regulatory body. It is always recognized that this definition is purely for regulatory purposes, and that material with activity concentrations equal to or less than clearance levels is still radioactive from a physical viewpoint, although the associated radiological hazards are considered negligible [International Atomic Energy Agency (IAEA), 2003a]. Over recent years large amounts of radioactive waste have been generated during the production and application of radioactive materials both for peaceful and military purposes. The knowledge of the hazard associated with exposure to these wastes led to the adaptation of waste management strategies that relies on the concepts of containment and confinement. In radioactive waste repository, confinement may be provided by the wasteform and its container, whereas containment may be provided by the surrounding host rock (IAEA, 2013). The selection of the wasteform type and disposal option is determined based on the hazard imposed by the wastes. Although containment and confinement concepts have proven efficiency in isolating nuclear waste, there were some cases dating back to the early 1950s where radioactive wastes were disposed of unsolidified in unlined trenches. These practices led to radioactivity leaks in many sites, such as in Hanford, Washington, USA. The evaluation of the remediation costs and the hazard imposed from these practices on human health and the environment resulted in recognition of the need to have more rigorous confinement and containment strategies. This led to the development of new waste management systems which utilize volume reduction techniques and solidification/stabilization technologies to produce stable wasteforms and implement the multi-barrier disposal concept to ensure safe disposal of these wastes.

Cementitious Materials for Nuclear Waste Immobilization, First Edition. Rehab O. Abdel Rahman, Ravil Z. Rakhimov, Nailia R. Rakhimova and Michael I. Ojovan.

Currently safe management of nuclear wastes is a subject that is receiving considerable attention from public and different governmental, regional and international bodies. This recognition has not only stemmed from the huge volume of the cumulative wastes and the diversity of their chemical, biological and radiological hazards but also because the public relates their acceptance for new nuclear power programmes to their confidence in the waste management practice (Abdel Rahman, 2012). In the following sections, the facilities that generate nuclear wastes will be briefly introduced, different waste classification schemes and waste management activities will be presented and matrix material for nuclear waste immobilization will be highlighted.

1.2 Nuclear Industry Facilities

The nuclear fuel cycle (NFC) and radioisotope production and application facilities are considered the main generators for nuclear wastes. The NFC includes all operations associated with the production of nuclear energy, namely mining and milling, processing and enrichment of uranium or thorium; manufacture of nuclear fuel; operation of nuclear reactors (including research reactors); reprocessing of nuclear fuel; any related research and development activities and all related waste management activities (including decommissioning). During the lifecycle activities of these facilities, different amounts of wastes with varying characteristics are produced. Within the operational and decommissioning phases only nuclear wastes are generated whereas other phases produce non-nuclear wastes, for example soils from excavation, building materials and so on. Nuclear wastes produced within the operational phase are usually characterized by their limited amounts; on the other hand, a much larger volume of waste is generated during the decommissioning phase (IAEA, 2007). This section will introduce operational processes that take place in different nuclear facilities and lead to generation of radioactive wastes, whereas the wastes generated during the decommissioning phase of these facilities will be discussed in Chapter 6.

1.2.1 NFC Facilities

The NFC refers to activities associated with the production of electricity using nuclear reactors (IAEA, 2003a). They are classified based on the existence of recycling option into two categories, namely open and closed NFCs, as illustrated in Figure 1.1 (Ojovan and Lee, 2005). Facilities that operate from nuclear ore extraction to fuel loading into a nuclear reactor are known as front-end NFC facilities; these include mines, mills, fuel enrichment and fuel fabrication facilities. After using the fuel in the reactor, the facilities that deal with used (spent) fuel and radioactive waste are referred to as back-end NFC facilities; they include fuel storage and/or fuel reprocessing plants. The operation of each facility is associated with the generation of different types of nuclear wastes. It is worth mentioning that nuclear materials generally can pose chemical, radiological and flammability hazards. Accordingly, there is a need to specify these hazards and implement certain safety measures to counter these hazards. Table 1.1 lists the safety aspects associated with the hazard of nuclear wastes at NFC facilities (IAEA, 2005a).

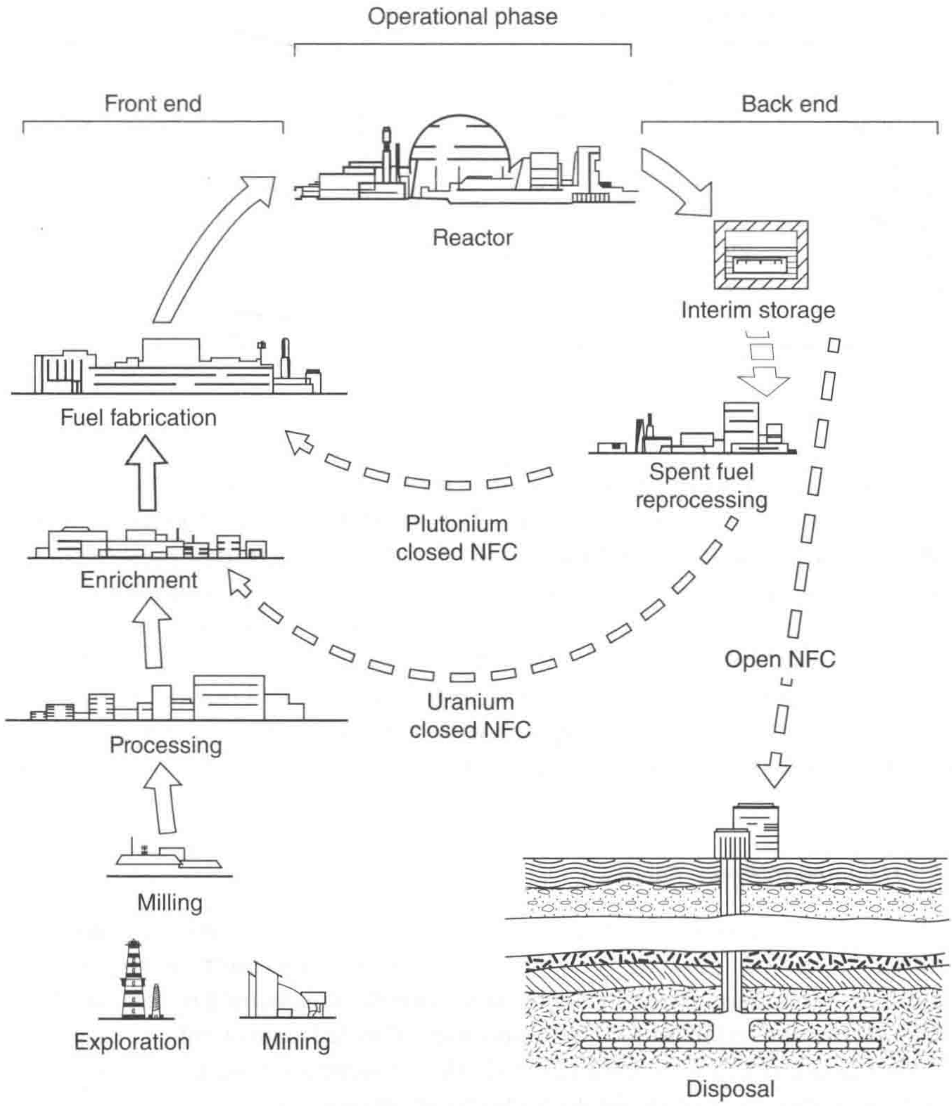

Figure 1.1 *Open and closed NFCs. Reproduced with permission from Ojovan and Lee, 2005. © 2005, Elsevier*

1.2.1.1 Mining and Milling Facilities

Mining uranium ore is the first step in any NFC, where uranium is extracted from a mine and then concentrated in a mill. The uranium mill is usually located near the mine to reduce shipping charges. The concentration processes involved include crushing, grinding, leaching, precipitation, solvent extraction and ion exchange (Benedict *et al.*, 1981). The concentrate is composed of uranyl nitrate solution, $[UO_2(NO_3)_2]$, and solid ammonium diuranate, $[(NH_4)_2U_2O_7]$, which is known as yellow cake. The operation of these facilities generates large amounts of solid wastes in the form of natural materials, that is displaced soil, and radioactive contaminated tailings. The radioactivity content in tailings is above the background level; usually they are returned to the pit from where the uranium ore was

Table 1.1 *Hazard identification at different NFC facilities*

Facility	Criticality	Radiation	Chemical toxicity	Flammability
Mining/milling	—	XX	XX	X
Conversion	X	XX	XX	XX
Enrichment	X	XX	XX	XX
Fuel fabrication	XX	XX	XX	XX
Reprocessing	XX	XX	XX	XX
Storage	XX	XX	—	—
Transportation	X	XX	X	XX

X, hazard may be of concern; XX, hazard of concern.
Reproduced with permission from IAEA, 2005a. © 2005, IAEA.

originally extracted and the site rehabilitated for further use (see Section 6.4). In some cases this operation is not economically feasible, so the tailings are stored then transported to a long-term stable structure and the site is rehabilitated for further use (Alexander and McKinley, 2007). Also, large volumes of effluent are generated during the operation of mines and mills; historically these effluents were held in storage ponds and eventually evaporated to solids (Benedict *et al.*, 1981). Currently the treatment of these effluents and their control is becoming a concern because of the strengthened regulatory requirements. The main problems that arise when dealing with these effluents are due to their large volumes and the nature of contaminants where both radioactive and non-radioactive toxicants exist (IAEA, 2004).

1.2.1.2 Uranium Refining Facilities

Refining uranium concentrate is performed by purifying the concentrate, where chemical impurities are removed, followed by conversion of purified concentrate into a suitable chemical form. The purification is conducted by dissolving the concentrate in nitric acid and then applying solvent extraction to remove impurities. Purified concentrate is then converted to uranium trioxide (UO_3) or uranium dioxide (UO_2), depending on the type of reactor. To produce UO_3, either thermal denitration (TDN) or ammonium diuranate (ADU) could be used, where ammonium uranyl carbonate (AUC) is used to obtain UO_2. TDN is a one-step process from which fine UO_3 powder is produced. With ADU and AUC, the purified uranium is subjected to precipitation, filtration and calcinations/calcinations with hydrogen; Figure 1.2 illustrates these processes. The wastes arising from refining processes are mainly generated during the purification step. They include liquid effluent sludge, insoluble and filter aid, and drums (IAEA, 1999a).

If enrichment is required, UO_3 will be transformed to uranium hexafluoride (UF_6) according to the following reaction:

$$UO_3 \xrightarrow{H_2} UO_2 \xrightarrow{HF} UF_4 \xrightarrow{F_2} UF_6 \qquad (1.1)$$

Figure 1.3 illustrates the sequence of the chemical process to produce UF_6; these chemical processes generate wastes in the form of solid calcium fluoride, calcium hydroxide, water

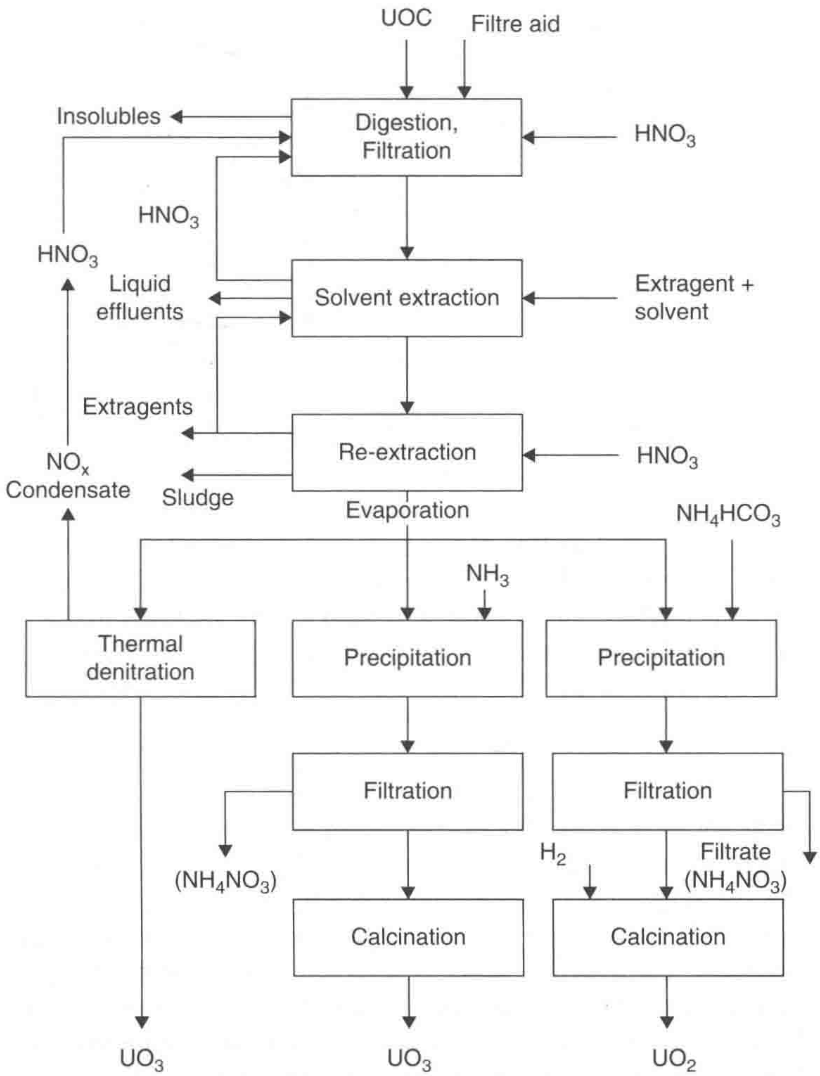

Figure 1.2 *Flowchart for the production of uranium trioxide and uranium dioxide. Reproduced with permission from IAEA, 1999a. © 1999, IAEA*

contaminated by uranium and gaseous wastes that contain UF_6, F_2 and HF (IAEA, 1999a, 2008). UF_6 is then directed to the enrichment plant to increase the percentage of uranium fissionable isotope (^{235}U) to the required ratio depending on the reactor type. There are several technologies available for enriching uranium; these include electromagnetic isotope separation, thermal diffusion, aerodynamic uranium enrichment process, chemical exchange isotope separation, ion exchange process, the plasma separation process, gaseous diffusion process, gas centrifuge process and laser isotope separation. Gas diffusion and gas centrifuge are considered the most widely used commercial methods (IAEA, 2005a). The enrichment process generate wastes in the form of depleted UF_6, which can be converted to stable, insoluble and non-corrosive U_3O_8 that can be safely stored pending reuse (IAEA, 2009a).