

AN INTRODUCTION TO NUCLEAR WASTE IMMOBILISATION

M I OJOVAN & W E LEE



AN INTRODUCTION
TO NUCLEAR WASTE
IMMOBILISATION

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AN INTRODUCTION TO NUCLEAR WASTE IMMOBILISATION

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(1956–2004)

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Foreword

We now realise it is time to do something about radioactive waste. Many countries with large volumes of nuclear waste from civil power and military programmes have started cleaning up contaminated sites and advance design and construction of repositories. The USA has the Waste Isolation Pilot Plant (WIPP) in Carlsbad and is in the process of developing the Yucca Mountain storage facility. French legislation decrees that options for taking care of its radioactive waste are presented, assessed and progressed in 2006. The UK has set up the Nuclear Decommissioning Authority (NDA) to manage the clean up and the Committee on Radioactive Waste Management (CoRWM) to advise government on suitable options by Summer 2006. The UK budget for the clean up is currently £50 billion.

The World's energy supply must come from a balanced portfolio of sources including renewables such as wind, solar and hydro. A great benefit of energy produced from nuclear fission in common with renewables is that it does not generate CO₂. If we are to protect the planet from destruction wrought by CO₂-induced global warming, nuclear power has to contribute a significant part of our energy production. The two arguments most commonly used against nuclear power are that it is uneconomical and we have not taken care of the waste problem. Rising oil and gas prices are taking care of the former and this book illustrates how we are taking care of the latter. This legacy from the past, which has to be dealt with in any event, should not preclude future generations from the considerable benefits and opportunities of modern nuclear energy systems.

Sue E. Ion
President
British Nuclear Energy Society

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Preface

This book, drawing on the authors' experience in the processing and disposal of wastes, examines the gamut of nuclear waste issues from the natural level of radionuclides in the environment to geological disposal of waste-forms and their long-term behaviour. It is intended for readers with technical background who wish to know more about this regrettably modern but nonetheless important topic. It focuses on the fundamental principles that underpin the processing and design of waste-forms as well as repositories in which it planned to locate them forever. The book explains the hazards associated with both toxic and nuclear waste and methods for their recycling or safe disposal. It describes sources of nuclear waste, the main types and their characteristic properties. It summarises current methods of nuclear waste management and established immobilisation technologies such as vitrification and cementation. The potential for more advanced immobilisation methods and concepts for difficult wastes using novel glasses, cements, ceramics and composite materials are also discussed. Some of the geological disposal and storage options available are also considered; a key topic in which we should all take an interest as some of these wastes will be radioactive for many thousands of years.

The book consists of 20 chapters. These are organised to follow the lifetime of any nuclear waste from its formation and alteration through various processing and separation methods to its eventual burial including analysis of the environmental impact of any planned repository. Chapters 1–6 introduce basic concepts such as radiation dose highlighting that excessive levels of any substance (not only radioactive materials) present a threat to the environment as well as describing how to quantitatively assess the hazard. The focus is on the most hazardous heavy metals and radionuclides, most of which are man-made. This common approach emphasises the evolution of the potential hazard with time and reveals the most problematic long-lived radionuclides. Chapters 7–12 describe the regulatory basis of nuclear waste issues leading to basic schemes of waste management. While many nuclear wastes may become non-radioactive within reasonable time and so be released from regulatory control, this is not the case for long-lived and highly radioactive wastes. Chapters 13–18 describe

state-of-the-art techniques in nuclear waste processing and immobilisation. The focus here is on basic immobilisation methods: cementation, bituminisation and vitrification, giving also a brief introduction to some of the emerging challenges and potential solutions. Finally, Chapters 19 and 20 are dedicated to nuclear waste disposal and quantitative assessment of its safety.

The book is intended as an introductory overview for postgraduate students and researchers in this field but will also be useful for undergraduates studying physics, chemistry, geography, geology and environmental or other engineering disciplines with an interest in the welfare of the planet.

Michael I. Ojovan
William E. Lee

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Chapter 1

Introduction to Immobilisation

1.1. Introduction

We are living in a naturally radioactive world. Our universe developed 1.5×10^{10} years ago from a high energy density singularity, the so-called “Big Bang”. It then expanded and was cooled by this expansion, the current 3-K background radiation being remnant radiation from the first seconds after the Big Bang (Fig. 1.1).

Everything we see around us is the substance from a supernova star which exploded 4.6×10^9 years ago. At that moment all possible isotopes of all elements entered the composition of the supernova. The shortest-lived radionuclides decayed quickly, still in the plasma and gaseous phase as revealed by the presence of these radionuclides in the radiation spectrum of newer supernovae. Cooled gas condensed and formed solid dust particles that agglomerated to form the first universal bodies, which collided with each other to form the first protoplanets. Long-lived radionuclides such as ^{99}Tc , ^{239}Pu and ^{242}Pu , which became part of the composition of the protoplanets, gradually decayed although longer lived radionuclides such as ^{235}U , ^{238}U and ^{232}Th did not decay completely. These are left as a reminder of the natural radioactivity evolution over the 4.6 billion year lifetime of the Earth.

Until the invention of the X-ray tube by Roentgen in 1885 natural radiation was the only ionising radiation in existence. In 1896 natural radioactivity was discovered by Becquerel and since then it has been used for medical and research purposes. Since the first artificial radioactive materials were produced by the Curies in the 1930s they have been utilised for society’s benefit in science, medicine, industry and agriculture. However, using natural and artificial radioactivity leads to waste products, many of which contain significant levels of radionuclides.

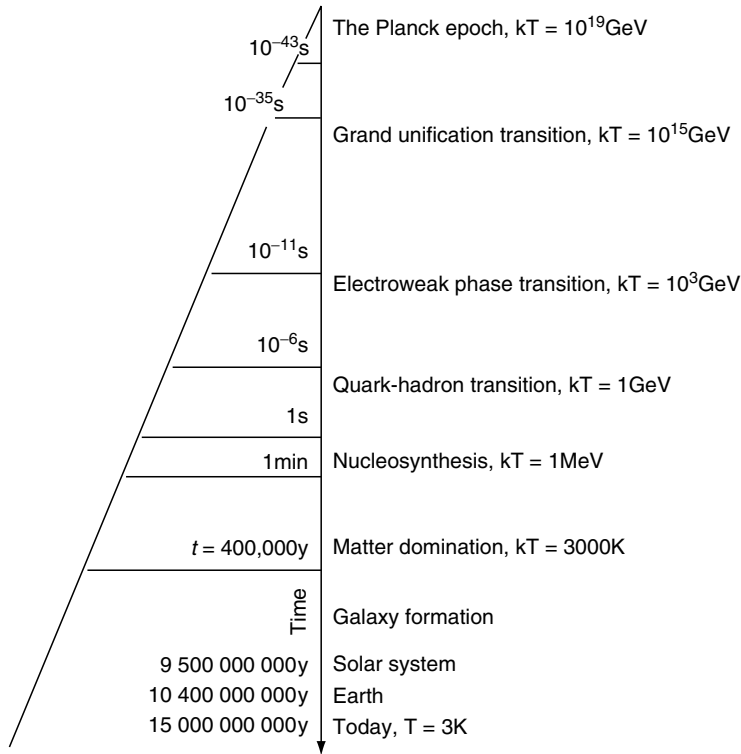


Figure 1.1: Schematic of universe expansion, t = time, T = temperature and k = Boltzmanns constant

1.2. Importance of Waste

Waste has accompanied human society from prehistory to today and no doubt will accompany our future. Historically, we have been careless about managing the waste we produce. Disposal of waste into the surrounding habitat has been the usual practice with little concern for the environment. However, we now realise that waste has to be managed properly to preserve the planet for generations to come. To quote the American Indian saying “We do not inherit the Earth from our ancestors but we borrow it from our children”. This realisation has been slow to come about and not even the so-called developed countries have in place functioning, comprehensive policies for waste management.

Waste from use of radioactivity is, in many but not all cases, radioactive. Society has approached the management of radioactive waste differently from the management of other waste types. Rather than diluting and dispersing it

into the environment, we have decided to contain and confine it. This is the first time in the history of human civilisation that such a decision has been taken consciously, as a matter of ethical principle; encouragingly, this prudent approach is now being extended to other wastes.

1.3. Radioactive Waste

Radioactive waste is defined as material that contains, or is contaminated with, radionuclides at concentrations or activities greater than clearance levels as established by individual countries' regulatory authorities, and for which no use is foreseen. The higher the concentration of radionuclides above established levels the greater the hazard the waste possesses. The hazard of radioactive waste also depends on the nature of the radionuclides and, at the same concentration, different radionuclides have different levels of hazard. This definition of radioactive waste is purely for regulatory purposes. A waste with activity concentrations equal to, or less than, clearance levels is considered nonradioactive. From a physical viewpoint, however, it is radioactive – although the associated radiological hazards are negligible. Radioactive waste is in part waste like any other which is nonradioactive. However, radioactive waste may be accompanied by significant levels of radiation hence it requires not only immobilisation to prevent radionuclides spreading around the biosphere, but also shielding and, in some cases, remote handling.

While most of the nuclear wastes from military and civil uses of radioactivity have been stored safely, in some cases, such as at Hanford in the USA, ill-defined highly active sludges were stored in massive but leaky steel drums (Fig. 1.2a) and it is only now that the site is being cleaned up. At Hanford all the liquid contained in the drums has been removed and construction of massive facilities for waste immobilisation is underway. The financial cost of cleaning up such sites and others where accidental releases of radioactivity have occurred such as in Chernobyl, Ukraine (Fig. 1.2b) is enormous.

In the UK the development and operation of the nuclear industry has left a legacy of waste that will cost >£50 billion to clean up. Worldwide, public perception of, and hence acceptance for, any future developments of new generating capacity involving nuclear power plants will rely upon safe and efficient waste management. It is vital to demonstrate that these current waste problems can be resolved efficiently and safely and that new technology solutions can be applied directly to future wastes that may arise from new nuclear build.

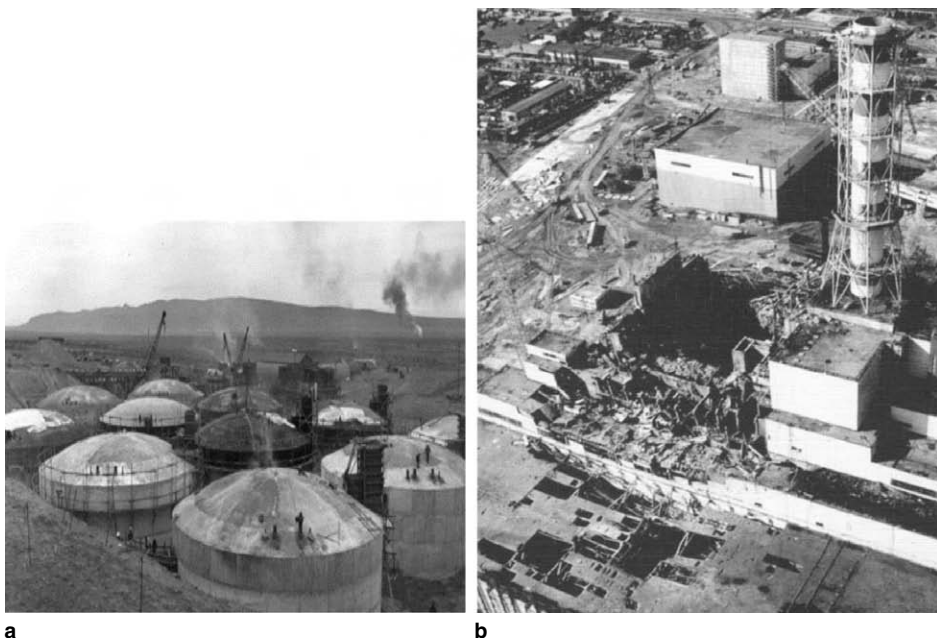


Figure 1.2: (a) Early picture of waste containers at Hanford. (b) The crater from the accident at Chernobyl, 1986. Courtesy B.E. Burakov, Radium Institute, Russia.

1.4. Recycling

Recycling means recovery and reprocessing of waste materials for use in new products. Recycled waste can be substituted for raw materials reducing the quantities of wastes for disposal as well as potential pollution of air, water and land resulting from mineral extraction and waste disposal. However, recycling has certain limitations when applied to radioactive materials. Due to their inherent radiation radionuclides are much more difficult to recover from contaminated materials. Recovery usually presumes concentration of species into a smaller volume even though this may result in more dangerous materials. Waste radionuclides recovered from contaminated materials are difficult to recycle in new devices or compounds. Hence even materials which contain large amounts of radioactive constituents (e.g. sealed radioactive sources as used in industry, medicine and research) are often immobilised (conditioned) and safely stored and disposed of rather than recycled.

One example of recycling in the nuclear industry is of spent nuclear fuel. A typical nuclear power plant (NPP) generating 1 GW(e) produces annually

approximately 30 t of spent nuclear fuel. The 433 or so NPP currently operating worldwide produce about 10 000 t of spent fuel a year. During use only about 5% of the U and Pu in the fuel is burnt generating electricity but also forming transmutation products that may poison the fuel. After use, the fuel elements may be placed in storage facilities with a view to permanent disposal or be reprocessed to recycle their reusable U or/and Pu. Most of the radionuclides generated by the production of nuclear power remain confined within the sealed fuel elements. Currently, most spent fuel is treated as waste and only a small fraction of it is reprocessed in countries such as France and the UK. Recycling of fissile elements (U, Pu) from spent nuclear fuel, despite the complexity of such a process, results in a significant reduction of toxicity of the radioactive wastes.

Another potential example of recycling in the nuclear industry is of military grade Pu much of which is stockpiled in the USA, Russia and the UK; a legacy of the cold war. It is technically possible to convert this material into a mixed U/Pu oxide (MOX) reactor fuel so that it can be used to generate energy in a suitable nuclear reactor. A potential new development is “inert matrix” fuel (IMF) which contains no U and in which Pu is the only fissionable component. This type of fuel would be optimised for burning of Pu leaving a less dangerous spent fuel waste product.

1.5. Waste Minimisation

Waste minimisation is a process of reducing the amount and activity of waste materials to a level as low as reasonably achievable. Waste minimisation is now applied at all stages of nuclear processing from power plant design through operation to decommissioning. It consists of reducing waste generation as well as recycling, reuse and treatment, with due consideration for both primary wastes from the original nuclear cycle and secondary wastes generated by reprocessing and clean up operations.

Waste minimisation programmes were largely deployed in the 1970s and 1980s. The largest volume of radioactive waste from nuclear power production is low-level waste (LLW). Waste minimisation programmes have achieved a remarkable 10-fold decrease of LLW generation over the past 20 years, reducing LLW volumes to $\sim 100 \text{ m}^3$ annually per 1 GW(e). As a result of these waste minimisation programmes the volume of waste from nuclear power generation is incomparably smaller than that of fossil fuel generating the same amount of electricity. If all spent fuel was reprocessed, the high level radioactive waste (HLW) from one year of global production of nuclear electricity could be accommodated by vitrification within the volume of a 10 m^3 .

1.6. Immobilisation

Immobilisation reduces the potential for migration or dispersion of contaminants including radionuclides. The IAEA defines immobilisation as the conversion of a waste into a waste form by solidification, embedding or encapsulation. It facilitates handling, transportation, storage and disposal of radioactive wastes. As we shall see in later sections these terms can be further defined. Immobilisation of waste is achieved by its chemical incorporation into the structure of a suitable matrix (typically glass or ceramic) so it is captured and unable to escape. Encapsulation of waste is achieved by physically surrounding it in materials (typically bitumen or cement) so it is isolated and radionuclides are retained. Another term closely linked with immobilisation is conditioning. Conditioning means those operations that produce a waste package suitable for handling, transportation, storage and disposal. Conditioning may include, e.g. the conversion of waste to a solid waste form and enclosure of waste in containers. Conditioning thus is similar to immobilisation with the difference being in the scale; conditioning is the engineering process dealing with large entities – packages.

1.7. Time Frames

Immobilisation is not a term used solely for radioactive waste. Many substances need a level of immobilisation or packaging during and after use. Immobilisation or packaging protects the substances contained and prevents access of the environment to them or their escape into the environment. However, in many applications immobilisation is for relatively short time periods: from hours in medicine; days and months for food; months, years, to several tens of years for industrial chemicals. In the case of radioactive waste the immobilisation time is extended to hundreds of years in the case of short-lived radionuclides, and thousands and hundreds of thousands of years for long-lived radionuclides. In addition radioactive materials are continuously irradiating the immobilising medium, sometimes at significant levels of radiation. In the case of a reasonably short time these changes can be understood and correspondingly taken into account. “Wait and see” is not an option for time frames lasting hundreds of years. These two features – extended times and irradiation – make immobilisation of radioactive wastes an issue which has no simple solutions.

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Chapter 2

Nuclear Decay

2.1. Nuclear Decay

Nuclides (X) are the nuclei of atoms of a specific isotope. They are characterised by the number of positively charged protons (Z), neutrons (N) and the energy state of the nucleus. In terms of mass (A) and atomic number (Z) a nuclide is

$${}^A_Z\text{X}_N \quad (2.1)$$

where $A = Z + N$. To be regarded as distinct a nuclide must contain enough energy to have a measurable lifetime, usually more than 10^{-10} s. An isotope refers to a type of atom whereas a nuclide refers to its nucleus. Isotopes have the same atomic number Z as the nuclide, but different numbers of neutrons and hence atomic mass A :

$${}^A_Z\text{X}_N, {}^{A+1}_Z\text{X}_{N+1} \quad (2.2)$$

Nuclides may be stable or unstable. Radionuclides are nuclides that possess properties of spontaneous disintegration. About 1700 nuclides are known, of which about 300 are stable and the rest radioactive.

The spontaneous decay of unstable nuclides with the emission of particles or photons is a statistical process termed radioactive decay. The decay modes are alpha, beta, gamma, electron capture, proton emission, neutron emission, cluster radioactivity and spontaneous fission.

$${}^A_Z\text{X}_N \rightarrow {}^{A+\Delta A}_{Z+\Delta Z}\text{Y}_{N+\Delta N} + \text{particles, photons} \quad (2.3)$$

Depending on the mode of decay radionuclides change their parameters as shown in Table 2.1.

Table 2.1: Modes of radioactivity

Decay mode	Change		
	ΔZ	ΔN	ΔA
α -Decay	-2	-2	-4
β -Decay (e^+ or e^-)	± 1	∓ 1	0
γ -Decay (photon)	0	0	0
Electron capture	-1	+1	0
Proton emission	-1	0	-1
Neutron emission	0	-1	-1
Cluster radioactivity	$-Z_{\text{cluster}}$	$-N_{\text{cluster}}$	$-(Z_{\text{cluster}} + N_{\text{cluster}})$
Spontaneous fission	$\sim 0.5Z$	$\sim 0.5N$	$\sim 0.5A$

Every radionuclide has a unique decay constant $\lambda(\text{s}^{-1})$ independent of space and time, which specifies the probability of a certain radioactive decay mode. For radioactive isotopes that may decay via several modes (k):

$$\lambda = \sum_k \lambda_k \quad (2.4)$$

2.2. Decay Law

The number of nuclei dN decaying per time interval dt is given by the decay law:

$$dN = -\lambda N dt \quad (2.5)$$

where N is the number of radionuclides. Radioactive decay follows the exponential decay law:

$$N(t) = N_0 e^{-\lambda t} \quad (2.6)$$

where N_0 is the number of radionuclides at time $t = 0$.

The mean lifetime of a radionuclide τ (s) is the reciprocal value of the decay constant:

$$\tau = \frac{1}{\lambda} \quad (2.7)$$

The time interval $T_{1/2}$ (s) after which the number of radioactive nuclei drops to half of the initial number is called the half-life:

$$T_{1/2} = \frac{\ln 2}{\lambda} \quad (2.8)$$

Figure 2.1 illustrates the decay of ^{60}Co and ^{134}Cs radionuclides. At $t = T_{1/2}$ a half of the initial number of nuclides have decayed. At time $t = \tau$ the number of remaining radionuclides is $N(\tau) = N(0)/e$, where $e = 2.718$ is the natural logarithm basis number.

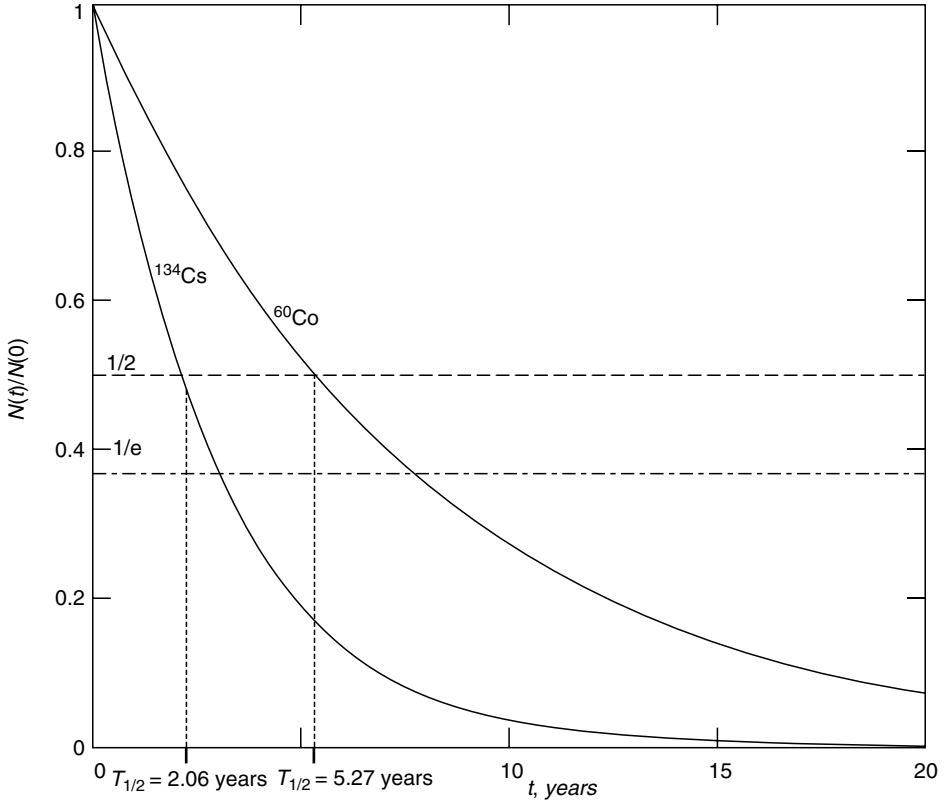


Figure 2.1: Radioactive decay of ^{60}Co and ^{134}Cs .

2.3. Radioactive Equilibrium

Decay chains arise when a nuclide produced in a radioactive decay is also radioactive (Fig. 2.2).

For the number of parent (N_p) and daughter (N_d) nuclides present at time t the following decay law holds:

$$\frac{dN_d}{dt} = \lambda_p N_p - \lambda_d N_d \quad (2.9)$$

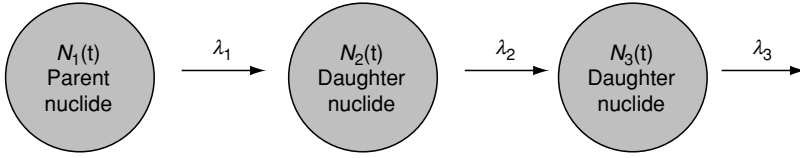


Figure 2.2: Schematic of a decay chain.

Radioactive equilibrium is the stationary state of a daughter isotope with an equal number of production and decay reactions in a certain time interval. At equilibrium:

$$\frac{N_d}{N_p} = \frac{\lambda_p}{\lambda_d} = \frac{T_{1/2,d}}{T_{1/2,p}} \quad (2.10)$$

For example, radium is a daughter element in the uranium decay series and at equilibrium:

$$\frac{N_{\text{Ra}}}{N_{\text{U}}} = 0.36 \times 10^{-6} \quad (2.11)$$

Hence 1 t of natural uranium contains only 0.36 g of ^{226}Ra .

2.4. Activity

Activity is defined as the number of decays per unit time:

$$A = -\frac{dN}{dt} \quad (2.12)$$

It can be expressed in terms of the mass of the radioactive substance m (kg):

$$A = \lambda N_A \frac{m}{M} \quad (2.13)$$

where N_A is Avogadro's number and M is the molar mass of the substance (kg/mol). The SI unit of activity is Becquerel (Bq) which is one disintegration per second:

$$1 \text{ Bq} = 1 \text{ decay/s} \quad (2.14)$$

The non-SI unit of activity is the Curie (Ci) where $1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$, which is the activity of 1 g of ^{226}Ra .

The specific activity of a substance is defined either per unit of mass or per unit of volume:

$$a(\text{Bq/kg}) = \frac{A(\text{Bq})}{m(\text{kg})} \quad (2.15)$$

$$a(\text{Bq/m}^3) = \frac{A(\text{Bq})}{V(\text{m}^3)} \quad (2.16)$$

For example, the specific activity of pure ^{60}Co is $4.85 \times 10^{16} \text{ Bq/kg}$ ($1.31 \times 10^3 \text{ Ci/g}$), whereas the specific activity of pure ^{134}Cs is $4.77 \times 10^{16} \text{ Bq/kg}$ ($1.29 \times 10^3 \text{ Ci/g}$).

2.5. Alpha Decay

Alpha decay of a nucleus can occur despite the presence of the potential repulsion barrier. This penetration of the potential barrier is often called tunnelling. The maximum potential energy of the barrier can be calculated as 30 MeV but alpha particles with energy of 4.18 MeV are emitted from ^{238}U by tunnelling as illustrated in Fig. 2.3. This cannot be explained by classical physics. Using quantum mechanics it can be shown that the α particle has a finite probability of penetrating the barrier leading to alpha particle emission.

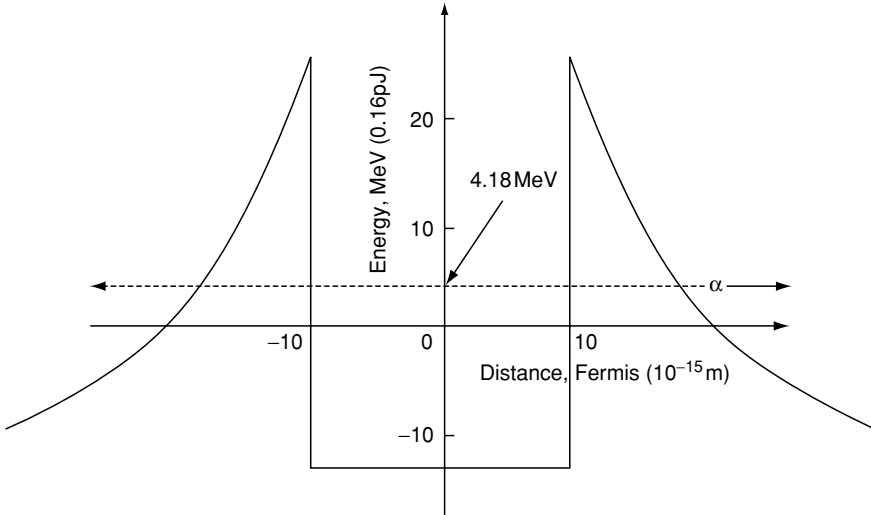


Figure 2.3: Schematic of an alpha decay.

When this probability is quite low the half-life of α emitters will be relatively long.

The equation of alpha decay is

$${}^A_Z\text{X}_N \rightarrow {}^{A-4}_{Z-2}\text{Y}_{N-2} + {}^4_2\alpha_2 \quad (2.17)$$

Figure 2.4 shows alpha decay of uranium, which has six groups of alpha particles in its decay spectrum. These correspond to different energy levels of the alpha particles in the U-nucleus (see Fig. 2.4).

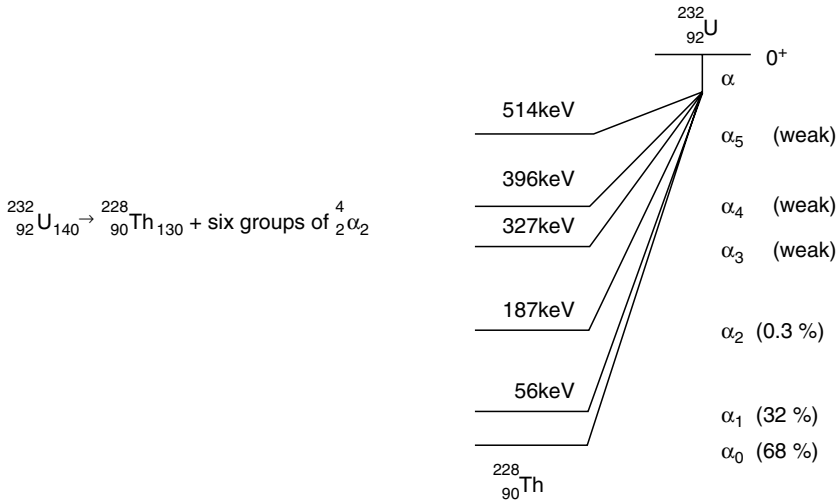


Figure 2.4: Alpha decay of uranium into thorium: left – equation, right – spectrum of decay comprising intensity in brackets and kinetic energies in keV of α particles.

2.6. Beta Decay

Beta decay of radionuclides is caused by weak interactions. The equation of beta decay is

$${}^A_Z\text{X}_N \rightarrow {}^{A}_{Z\pm 1}\text{Y}_{N\mp 1} + e^\mp + \begin{pmatrix} \bar{\nu}_e \\ \nu_e \end{pmatrix} \quad (2.18)$$

where e^\mp is either an electron or positron, ν_e and $\bar{\nu}_e$ are a neutrino and an antineutrino, respectively. Electrons, positrons and neutrinos do not exist in the nucleus as constituents. They are generated just at the moment of decay

by the weak interaction between the nucleons. The energy spectrum of electrons and positrons emitted in beta decay is continuous up to a maximum energy (Fig. 2.5).

2.7. Gamma Decay

Gamma decay of radionuclides occurs through emission of a photon by an excited nucleus. As a rule the excitation is preceded by an α - or β -decay, by a nuclear reaction, or an inelastic collision with another nucleus. Atomic nuclei have discrete energy levels and will therefore emit electromagnetic radiation with characteristic line spectra. The equation of gamma decay is



Figure 2.6 shows gamma decay of an excited radionuclide of nickel-60 preceded by the beta decay of cobalt-60.

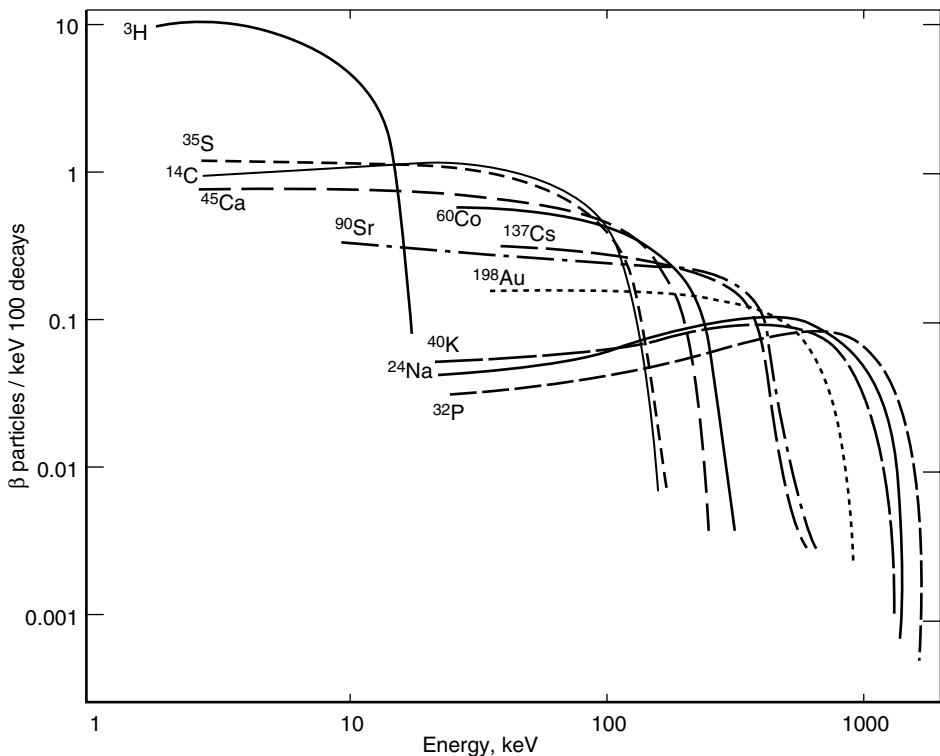


Figure 2.5: Beta decay spectra of common radionuclides.

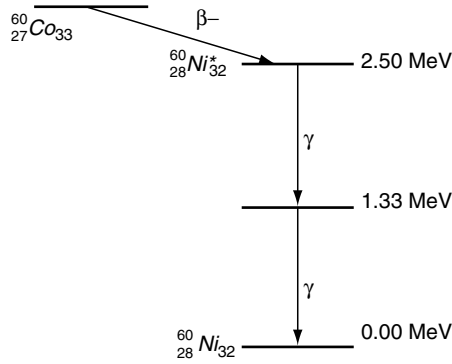


Figure 2.6: Gamma decay of nickel with preceding formation of an excited state of nickel from cobalt

2.8. Spontaneous Fission

Nuclear fission is the process whereby a heavy nucleus decomposes into two fractions termed fission products and several neutrons. Nuclear fission can be induced by capture of neutrons or photons by the nucleus. Fission of a nucleus described in the droplet model is caused by vibrations, which can break the nucleus into smaller nuclei. At low excitation energy, the nucleus undergoes small amplitude surface vibrations about the equilibrium shape in the ground state. However, its surface tension creates a potential barrier against deformation. If the excitation energy increases, this barrier may be overcome: the nuclear deformation increases until the nucleus forms a neck and finally breaks into two parts, which separate under the influence of the repulsive Coulomb potential. Spontaneous fission is characteristic of radionuclides with $Z^2/A > 17$ and occurs by tunnelling through the fission barrier. The spontaneous fission reaction is:

$${}^A_Z\text{X}_N \rightarrow {}^{A_1/2}_{Z_1/2}\text{Y}_{N_1/2} + {}^{A_2/2}_{Z_2/2}\text{W}_{N_2/2} + \text{light nuclei, particles, photons} \quad (2.20)$$

where approximately $A_1 \sim A/2$, $A_2 \sim A/2$, $N_1 \sim N/2$, $N_2 \sim N/2$, $Z_1 \sim Z/2$, $Z_2 \sim Z/2$. Usually, the mass distribution of fission products is asymmetric with mass ratio $A_1/A_2 \sim 3/2$. The kinetic energy of the fission products nearly equals the total energy released in fission. Many fission products are radioactive and decay preferentially by neutron emission, γ - and β -decay. The probability of spontaneous fission is smaller than that of alpha decay, correspondingly the half-life for spontaneous fission is larger than that of α -decay. The half-life for

^{235}U alpha decay is $T_{1/2} = 7.1 \times 10^8$ years but for spontaneous fission it is $T_{1/2} = 1.8 \times 10^{17}$ years.

Nuclear fission can be induced by capture of neutrons or photons. Slow neutrons efficiently induce fission of ^{235}U resulting in an energy release of ~ 200 MeV per disintegration ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$). Controlled self-sustaining fission is utilised in nuclear reactors to produce energy. The induced fission reaction of ^{235}U proceeds via:



where X and Y are fission products and $k = 2.43 \pm 0.07$ is the number of fission neutrons. Figure 2.7 shows the mass distribution for the fission products of ^{235}U .

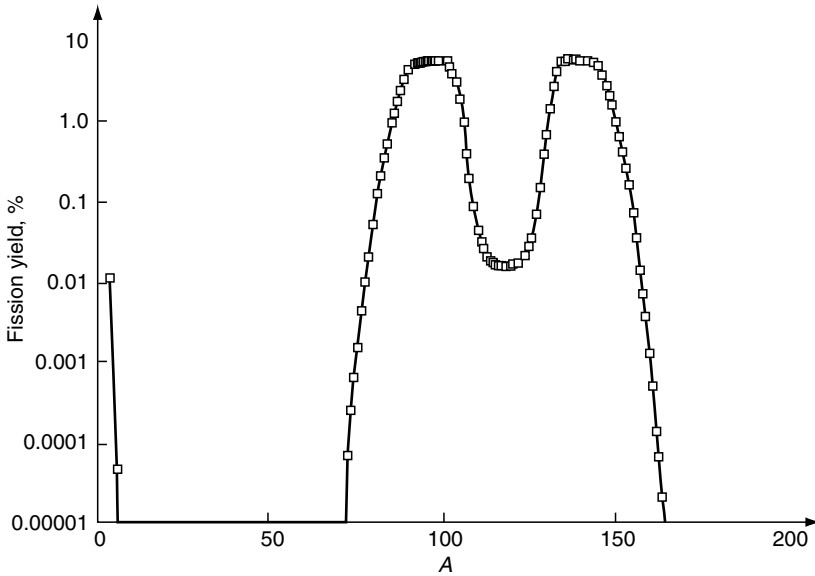


Figure 2.7: Mass distribution of fission products from ^{235}U .

2.9. Radionuclide Characteristics

Important characteristics of radionuclides, which are often present in radioactive wastes, are given in Table 2.2. Indicated in the table are the decay modes, which include α and β emission, electron capture (EC), isomeric transition to a lower energy (IT) and spontaneous fission (SPF). Table 2.2 also gives the major radiation energies in MeV/disintegration for the total electron (ϵ), gamma and X-ray photon (γ) emissions and the sum of the average energies (termed

Table 2.2: Characteristics of radionuclides

Nuclide	Atomic number	Half-life	Principal mode(s) of decay	Major radiation energies (MeV/dis)			Q-value		Specific activity (Ci/g)	Daughter(s)
				α	ϵ	γ	MeV/dis	W/Ci		
³ H	1	12.33 years	β		0.00568		5.68×10^{-3}	3.37×10^{-5}	9650	³ He
¹⁴ C	6	5730 years	β		0.0495		4.95×10^{-2}	2.93×10^{-4}	4.457	¹⁴ N
⁶⁰ Co	27	5.271 years	β		0.0958	2.5058	2.6016	1.541×10^{-2}	1131	⁶⁰ Ni
⁵⁹ Ni	28	7.5×10^4 years	EC		0.0043	0.0024	6.72×10^{-3}	3.98×10^{-5}	8.079×10^{-2}	⁵⁹ Co
⁶³ Ni	28	100.1 years	β		0.0171		1.71×10^{-2}	1.01×10^{-4}	61.68	⁶³ Cu
⁷⁹ Se	34	$<6.5 \times 10^4$ years			0.0529		5.29×10^{-2}	3.13×10^{-4}	6.966×10^{-2}	⁷⁹ Br
⁸⁵ Kr	36	10.72 years	β		0.2505	0.0022	2.53×10^{-1}	1.50×10^{-3}	392.3	⁸⁵ Rb
⁹⁰ Sr	38	28.5 years	β		0.1958		1.96×10^{-1}	1.16×10^{-3}	136.4	⁹⁰ Y
^{93m} Nb	41	13.6 years	IT		0.0281	0.0018	2.99×10^{-2}	1.77×10^{-4}	282.6	⁹³ Nb
⁹⁴ Nb	41	2.03×10^4 years	β		0.1454	1.5715	1.7169	1.018×10^{-2}	1.873×10^{-1}	⁹⁴ Mo
⁹³ Mo	42	3500 years	EC		0.0051	0.0107	1.58×10^{-2}	9.37×10^{-5}	1.10	⁹³ Nb
⁹⁹ Tc	43	2.13×10^5 years	β		0.0846		8.46×10^{-2}	5.01×10^{-4}	1.695×10^{-2}	⁹⁹ Ru
¹⁰⁶ Ru	44	1.020 years	β		0.1004		1.004×10^{-1}	5.951×10^{-4}	3346	¹⁰⁶ Rh
¹⁰⁷ Pd	46	6.5×10^6 years	β			0.0093	9.3×10^{-3}	5.5×10^{-5}	5.143×10^{-4}	¹⁰⁷ Ag
¹¹³ Cd	48	9.3×10^{15} years	β		0.0933		9.13×10^{-2}	5.412×10^{-4}	3.402×10^{-13}	¹¹³ In
^{113m} Cd	48	13.7 years	β (99.9%) IT (0.1%)			0.1834	1.83×10^{-1}	1.08×10^{-3}	216.8	¹¹³ In ¹¹³ Cd
¹²⁶ Sn	50	$\sim 1 \times 10^5$ years	β		0.1249	0.0573	1.82×10^{-1}	1.08×10^{-3}	2.837×10^{-2}	¹²⁶ Sb
¹²⁵ I	53	60.14 days	EC		0.0179	0.0423	6.02×10^{-2}	3.57×10^{-4}	17370	¹²⁵ Te
¹²⁹ I	53	1.57×10^7 years	β		0.0556	0.0248	8.04×10^{-2}	4.77×10^{-4}	1.765×10^{-4}	¹²⁹ Xe
¹³⁴ Cs	55	2.062 years	β		0.1639	1.5555	1.719	1.019×10^{-2}	1294	¹³⁴ Ba
¹³⁵ Cs	55	3.0×10^6 years	–		0.0563		5.63×10^{-2}	3.32×10^{-4}	1.151×10^{-3}	¹³⁵ Ba
¹³⁷ Cs	55	30.17 years	β (94.6%) β (5.4%)			0.1708	1.71×10^{-1}	1.01×10^{-3}	86.98	^{137m} Ba ¹³⁷ Ba
¹³³ Ba	56	10.54 years	EC		0.0547	0.4045	4.592×10^{-1}	2.722×10^{-3}	250.0	¹³³ Cs

¹⁴⁶ Pm	61	5.53 years	EC (66.1%) β (33.9%)		0.0928	0.7542	8.47×10^{-1}	5.02×10^{-3}	442.8	¹⁴⁶ Nd
¹⁴⁷ Pm	61	2.6234 years	β		0.6196		6.20×10^{-2}	3.67×10^{-4}	927.0	¹⁴⁶ Sm
¹⁵¹ Sm	62	90 years	β		0.1251		1.25×10^{-1}	7.41×10^{-4}	26.31	¹⁴⁷ Sm
¹⁵² Eu	63	13.33 years	EC (72.08%) β (27.92%)		0.1275	1.1628	1.290	7.646×10^{-3}	172.9	¹⁵¹ Eu
¹⁵⁴ Eu	63	8.8 years	β		0.2794	1.2531	1.532	9.081×10^{-3}	269.9	¹⁵² Sm
¹⁵⁵ Eu	63	4.96 years	β		0.0650	0.0633	1.28×10^{-1}	7.59×10^{-4}	465.1	¹⁵² Gd
¹⁵³ Gd	64	241.6 days	EC		0.0399	0.1015	1.414×10^{-1}	8.381×10^{-4}	3526	¹⁵⁴ Gd
¹⁵⁷ Tb	65	150 years	EC		0.0031	0.0050	8.10×10^{-3}	4.802×10^{-5}	15.19	¹⁵⁵ Gd
¹⁵⁸ Tb	65	150 years	EC (82%) β (18%)				9.02×10^{-1}	5.347×10^{-3}	15.08	¹⁵³ Eu
¹⁸⁷ Re	75	4.6×10^{10} years	β		0.0007		2.59	1.535×10^{-2}	3.823×10^{-8}	¹⁵⁷ Gd
²¹⁰ Pb	82	22.32 years	β		0.0343		3.43×10^{-2}	2.029×10^{-4}	76.30	¹⁵⁸ Gd
²⁰⁹ Po	84	102 years	α (99.74%) EC (0.26%)				4.9645	2.943×10^{-1}	16.8	¹⁵⁸ Dy
²²⁶ Ra	88	1600 years	α	4.7741	0.0035	0.0067	4.784	2.836×10^{-2}	9.887×10^{-1}	¹⁸⁷ Os
²²⁷ Ac	89	21.77 years	β (98.62%); α (1.38%)	0.0673	0.0125	0.0002	8.00×10^{-2}	4.74×10^{-4}	72.33	²¹⁰ Bi
²²⁹ Th	90	7340 years	α	4.8620		0.0343	4.896	2.902×10^{-2}	2.127×10^{-1}	²⁰⁵ Pb
²³⁰ Th	90	7.54×10^4 years	α	4.6651		0.0004	4.665	2.765×10^{-2}	2.109×10^{-2}	²⁰⁹ Bi
²³² Th	90	1.405×10^{10} years	α	4.0056		0.0002	4.006	2.375×10^{-2}	1.097×10^{-7}	²²² Rn
²³¹ Pa	91	3.276×10^4 years	α	4.9230	0.0483	0.0399	5.011	2.970×10^{-2}	4.723×10^{-2}	²²⁷ Th
²³² U	92	68.9 years	α	5.3065		0.0002	5.307	3.146×10^{-2}	21.40	²²³ Fr
²³³ U	92	1.592×10^5 years	α	4.8141	0.0055	0.0013	4.821	2.857×10^{-2}	9.680×10^{-3}	²²⁵ Ra
²³⁴ U	92	2.454×10^5 years	α	4.7732		0.0001	4.773	2.829×10^{-2}	6.248×10^{-3}	²²⁶ Ra
²³⁵ U	92	7.037×10^8 years	α	4.3785	0.0426	0.1561	4.577	2.713×10^{-2}	2.161×10^{-6}	²²⁸ Ra
²³⁶ U	92	2.342×10^7 years	α	4.4793	0.0108	0.0015	4.492	2.662×10^{-2}	6.469×10^{-5}	²²⁷ Ac
²³⁸ U	92	4.468×10^9 years	α	4.1945	0.0095	0.0013	4.205	2.492×10^{-2}	3.362×10^{-7}	²²⁸ Th
²³⁶ Np	93	1.550×10^5 years	EC (91%) β (8.9%) α (0.20%)		0.1967	0.1411	3.38×10^{-1}	2.00×10^{-3}	1.317×10^{-2}	²²⁹ Th
										²³⁰ Th
										²³¹ Th
										²³² Th
										²³⁴ Th
										²³⁶ U
										²³⁶ Pu
										²³² Pa

(continued)

Table 2.2: Continued

Nuclide	Atomic number	Half-life	Principal mode(s) of decay	Major radiation energies (MeV/dis)			Q-value		Specific activity (Ci/g)	Daughter(s)
				α	ϵ	γ	MeV/dis	W/Ci		
²³⁷ Np	93	2.140 × 10 ⁶ years	α	4.7604	0.0640	0.0327	4.857	2.879 × 10 ⁻²	7.049 × 10 ⁻⁴	²³³ Pa
²³⁶ Pu	94	2.851 years	α	5.7521	0.0126	0.0020	5.767	3.418 × 10 ⁻²	531.3	²³² U
²³⁸ Pu	94	87.74 years	α	5.4871	0.0099	0.0018	5.499	3.2593 × 10 ⁻²	17.12	²³⁴ U
²³⁹ Pu	94	2.411 × 10 ⁴ years	α	5.1011		0.0001	5.101	3.024 × 10 ⁻²	6.216 × 10 ⁻²	²³⁵ U
²⁴⁰ Pu	94	6563 years	α	5.1549			5.155	3.056 × 10 ⁻²	2.279 × 10 ⁻¹	²³⁶ U
²⁴¹ Pu	94	14.4 years	β	0.0001		0.0052	5.3 × 10 ⁻³	3.2 × 10 ⁻⁵	103.0	²⁴¹ Am
²⁴² Pu	94	3.763 × 10 ⁵ years	α	4.8901	0.0081	0.0014	4.900	2.904 × 10 ⁻²	3.818 × 10 ⁻³	²³⁸ U
²⁴⁴ Pu	94	8.26 × 10 ⁷ years	α (99.875%) SPF (0.125%)	4.5751	0.0007	0.0001	4.576	2.712 × 10 ⁻²	1.774 × 10 ⁻⁵	²⁴⁰ U (fission products)
²⁴¹ Am	95	432.7 years	α	5.4801	0.0304	0.0287	5.539	3.283 × 10 ⁻²	3.432	²³⁷ Np
^{242m} Am	95	141 years	IT (99.55%) α (0.45%)	0.0232	0.0403	0.0049	6.84 × 10 ⁻²	4.05 × 10 ⁻⁴	9.718	²⁴² Am ²³⁸ Np
²⁴³ Am	95	7380 years	α	5.2656		0.0481	5.3137	3.1496 × 10 ⁻²	1.993 × 10 ⁻¹	²³⁹ Np
²⁴³ Cm	96	28.5 years	α (99.76%) EC (0.24%)	5.8380	0.1129	0.1316	6.083	3.605 × 10 ⁻²	51.62	²³⁹ Pu ²⁴³ Am
²⁴⁴ Cm	96	18.1 years	α	5.7965		0.0016	5.798	3.437 × 10 ⁻²	80.90	²⁴⁰ Pu
²⁴⁵ Cm	96	8500 years	α	5.3631	0.1342	0.1178	5.615	3.329 × 10 ⁻²	1.717 × 10 ⁻¹	²⁴¹ Pu
²⁴⁶ Cm	96	4730 years	α	5.3764	0.0072	0.0014	5.385	3.192 × 10 ⁻²	3.072 × 10 ⁻¹	²⁴² Pu
²⁴⁷ Cm	96	1.56 × 10 ⁷ years	α	4.9475		0.3152	5.263	3.119 × 10 ⁻²	9.278 × 10 ⁻⁵	²⁴³ Pu
²⁴⁸ Cm	96	3.40 × 10 ⁵ years	α (91.74%) SPF (8.26%)	4.6524			4.6524	2.7577 × 10 ⁻²	4.251 × 10 ⁻³	²⁴⁴ Pu (fission products)
²⁵² Cf	98	2.645 years	α (96.908%) SPF (3.092%)	5.9308	0.0051	0.0011	5.9370	3.5191 × 10 ⁻²	537.8	²⁴⁸ Cm (fission products)

^m a metastable radionuclide

Q -values) for different radiation types in MeV/disintegration or W/Ci, which includes alpha and beta particles, discrete electrons and photons. The Q -value indicates the amount of energy that could be deposited in the form of heat in a radioactive material from each decay event if none of the radiation escapes from the material (neutrinos are not included). Problems with particular radio-nuclides present in waste arise from their ability to deliver high doses associated with long radioactive half-lives, high radiotoxicity (e.g. from α particle or high energy β emission), high mobility (Section 3.2), ease of assimilation and long biological half-lives (Table 4.1).

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 Nuclear physics: <http://www.rarf.riken.go.jp/rarf/np/nplab.html>
 Waste link: www.radwaste.org
 WWW table of radioactive isotopes: <http://ie.lbl.gov/toi/perchart.html>
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Chapter 3

Contaminants and Hazards

3.1. Elemental Abundance

Ten elements O, Na, Mg, Al, Si, P, K, Ca, Ti and Fe constitute 99% of the Earth's crust although it is the minor and trace elements which are often key for living organisms. Figure 3.1 shows the relative abundance of the chemical elements.

Geochemical processes have concentrated some minor elements in specific deposits, so they are readily accessible by mining. On the other hand other elements that are relatively abundant may be widely dispersed in small amounts and they seldom or never occur in concentrated large deposits. A typical example is titanium, which is present in practically all igneous rocks in amounts ranging up to several per cent, but which, in spite of its useful properties as a metal has only recently become widely used. This is partly because of its dispersed nature and partly because of the technical difficulties in extracting the element from the minerals in which it occurs.

The distribution of minor and trace elements in igneous rocks is largely controlled by their ionic radii or size. Minor and trace elements with radii similar to those of major elements can substitute for these elements in the common minerals of the igneous rocks. The crystal structures of these minerals act as tiny filters, accepting those atoms of appropriate size and rejecting others. Thus, rubidium with a radius of 1.47 Å is incorporated in potassium feldspar, KAlSi_3O_8 , because its radius is close to that of potassium (1.33 Å). Similarly, gallium and germanium occur in aluminium-containing and silicate minerals, respectively. Caesium, with a considerably larger radius (1.67 Å), is not accepted into the feldspar structure; it remains in the igneous liquid during the crystallisation of the major minerals until its concentration increases to such an extent that it can form the independent mineral pollucite ($\text{CsAlSi}_2\text{O}_6$).

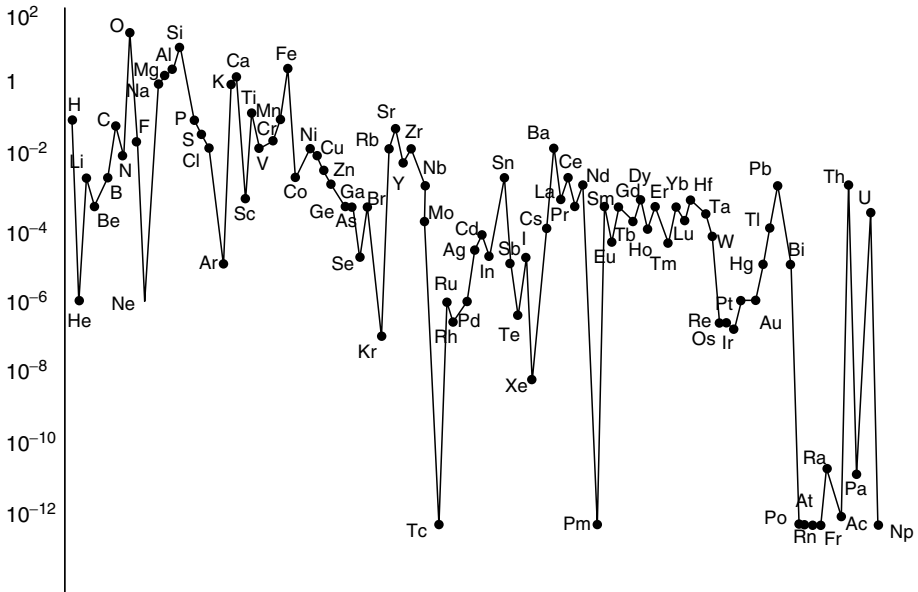


Figure 3.1: Average content of elements in the Earth's crust (in wt.%).

Thus elements that are similar in size and geochemical affinity to major elements are dispersed in small amounts in common minerals while those that do not readily enter the common minerals of igneous rocks remain in the residual melt as crystallisation proceeds. Fractional crystallisation of magmas (igneous melts) normally results in a residual liquid of granitic composition. Under suitable conditions this residual liquid solidifies as a coarse-grained rock known as a pegmatite. Pegmatites are well known for containing rare and unusual minerals, which incorporate many of the minor and trace elements, and are the commercial sources of lithium, beryllium, scandium, yttrium, the rare earths, caesium, niobium and tantalum, all elements that concentrate in the residual liquid because of their specific geochemical properties. Table 3.1 gives elemental distributions in soil, crust, deposits and igneous rocks.

3.2. Migration and Redistribution

Three basic processes lead to migration and redistribution of elements in the Earth's environment: primary due to volcanic activity, secondary due to atmospheric factors; and anthropogenic due to the action of living species. Migration and redistribution of elements by atmospheric factors induces rock failure and extraction of elements into water sources. It is important to point out

Table 3.1: Average natural occurrence of elements in ppm.

Element	Soil	Crust	Deposits	Igneous rock
Mn	850	975	760	1000
Ba	500	450	690	640
Zr	300	190	200	170
Sr	300	385	450	350
Cr	200	150	130	117
V	100	145	130	90
Zn	50	125	80	80
Ce	50	46	50	40
Ni	40	95	95	100
Li	30	45	60	50
Ga	20	15	30	20
Cu	20	75	57	70
Nb	15	20	20	20
Pb	10	15	20	16
Sn	10	40	16	32
B	10	10	56	13
Co	10	35	22	18
Be	6	4.5	5	4.2
Ge	5	4	4.5	2
As	5	3.4	6.6	2
Cs	5	1	10	10
Mo	2.5	2.3	2	1.7
Ag	1	0.06	0.5	0.2
Cd	0.5	0.2	0.5	0.13
Se	0.5	0.07	0.6	0.01
W	–	1.2	2	2
Sb	–	0.6	1.25	0.3
Hg	0.01	0.07	0.04	0.06
Bi	–	0.34	0.01	0.1
Au	–	0.001	–	0.001

that in nature equilibrium is practically never established between water solutions and solid minerals.

An element's mobility depends on the environmental (predominantly reducing/oxidising [redox]) conditions. Table 3.2 gives data on relative mobility of elements depending on the redox state of the environment. Table 3.2 indicates that many elements have lower mobility in a reducing rather than oxidising wet environment. This is why the majority of radwaste repository designs (where

Table 3.2: Relative mobility of elements in the environment.

Relative mobility	Environment			
	Oxidising	Acidic	Neutral to basic	Reducing
Very high	Cl, I, Br, S, B	Cl, I, Br, S, B	Cl, I, Br, S, B, Mo, V, U, Se, Re	Cl, I, Br
High	Mo, V, U, Se, Re, Ca, Na, Mg, F, Sr, Ra, Zn	Mo, V, U, Se, Re, Ca, Na, Mg, F, Sr, Ra, Zn, Cu, Co, Ni, Hg, Ag, Au	Ca, Na, Mg, F, Sr, Ra	Ca, Na, Mg, F, Sr, Ra
Medium	Cu, Co, Ni, Hg, Ag, Au, As, Cd	As, Cd	As, Cd	
Low	Si, P, K, Pb, Rb, Ba, Be, Bi, Sb, Ge, Cs, Tl, Li	Si, P, K, Pb, Li, Rb, Ba, Be, Bi, Sb, Ge, Cs, Tl, Fe, Mn	Si, P, K, Pb, Li, Rb, Ba, Be, Bi, Sb, Ge, Cs, Tl, Fe, Mn	Si, P, K, Fe, Mn
Very low	Fe, Mn, Al, Ti, Ta, Pt, Cr, Zr, Th, REE	Al, Ti, Sn, Pt, Cr, Zr, Th, REE	Al, Ti, Sn, Te, Cr, Zr, Th, Zn, Cu, Co, Ni, Hg, Ag, Au, REE	Al, Ti, Sn, Ta, Pt, Cr, Zr, Th, REE, S, B, Mo, V, U, Se, Re, Zn, Co, Cu, Ni, Hg, Ag, Au, As, Cu, Pb, Li, Rb, Ba, Be, Bi, Sb, Ge, Cs, Tl

eventual water ingress is expected) are designed to operate deep underground where such conditions apply. Elemental mobility in oxidising conditions is very low as will initially be the case in the planned Yucca Mountain storage facility in the USA, which is located above the water table in a desert. However, as indicated in Table 3.2, if in the future the environment becomes wet and the waste packages degrade, elemental transport from Yucca Mountain would be rapid.

Soil serves as a substratum of plants and, thus, further up the food chain, of animal life. It covers land surfaces and is formed by the action of natural physical, chemical and biotic forces on the unconsolidated residue (regolith) of rocks and minerals on the Earth's surface. The most important constituent of soil is clay formed by weathering of feldspars and other silicates and leaching of bases and some silica. The two basic clay types are 1:1 clays (composed of alternating tetrahedral [silica] and octahedral [alumina] layers), which result from rapid leaching, and 2:1 clays (composed of one octahedral layer between two tetrahedral layers), which are formed by gradual leaching. Another important soil constituent is humus, which is formed by comparatively rapid decomposition of organic matter.

Further redistribution of elements is caused by living species. Different elements have varying importance and involvement in the life cycles of living organisms. Certain elements are essential for the complex processes of metabolism to take place for adequate growth and are called macroelements. Nine elements make up this group: C, H, O, N, K, Ca, Mg, P and S. Other essential mineral elements are required in smaller amounts ($\leq 0.01\%$) and are called microelements. These are Fe, Cl, Mn, B, Cu, Mo and Zn. The macroelements C, H, O and N constitute more than 96% of the dry weight of plants. The approximate quantities of chemical elements in the human body (in per cent of wet weight) are estimated to be O (65), C (18), H (10), N (3), Ca (2), P (1.1), S (0.25), K (0.20), Na (0.15), Cl (0.15), Mg (0.05), Fe (0.004), Cu (0.00015), Mg (0.00013) and I (0.00004). Also present are traces of about 20 other elements (including Zn, Co, Si, Mo, Se, Al, As, Ba, B, Br, Cd and Cr).

3.3. Hazard Potential

Excess of certain elements in the environment can cause adverse effects on individuals. Whether a substance acts as a poison depends on the dose. Values of maximum permissible concentrations (MPC) or intervention levels (IL) are used to describe this quantity for every potential contaminant including radio-nuclides. These are given in regulatory documents both for air and drinking water. The dose concept is important because according to it, even a substance

as innocuous as water is poisonous if too much is ingested. The term toxicity is used to measure the hazard of substances for a human.

Consider a certain volume of material V containing a number of radionuclides. The *ingestion* potential hazard or radiotoxicity (H_p) is defined as the volume of drinking water, in which the initial material must be diluted to obtain an allowable level of radionuclides so that concentrations are below IL_i :

$$H_p(t) = \sum_i \frac{C_i(0) \exp(-\lambda_i t)}{IL_i} V \quad (3.1)$$

where $C_i(0)$ is the initial concentration of the i th radionuclide, λ_i is the decay constant and t is time. The potential hazard is measured in units of volume $V(\text{m}^3)$. The higher the potential hazard of a given contaminant the larger the volume of water required for dilution. The potential hazard shows the maximum possible volume of contaminated drinking water when the contaminants are considered as completely dissolved in water.

The *inhalation* potential hazard or radiotoxicity is defined as the volume of air in which the initial material must be diluted to obtain a permitted content of radionuclides so that levels do not exceed IL_i .

Figure 3.2 shows the ingestion potential hazard of high-level radioactive waste (HLW) from the reprocessing of spent nuclear fuel from one year of operation of a 1 GW nuclear power plant as a function of time. Note the long timescales mean that log time is used in this and many subsequent figures. Figure 3.2 indicates that over a timescale of 100 000 years or so (5 on the log scale) many of the fission products have decayed significantly. However, ^{226}Ra production from U decay (Fig. 5.1) and the long half-life of ^{129}I (Section 11.4) are problematic.

The dimensionless index of potential hazard or radiotoxicity $I_p(t)$ is obtained by dividing the potential hazard by the initial volume of material:

$$I_p(t) = \sum_i \frac{C_i(0) \exp(-\lambda_i t)}{IL_i} \quad (3.2)$$

The index of potential hazard gives the maximum necessary dilution ratio to obtain drinking water. Dilution of contaminants to obtain non-contaminated media is the oldest and simplest disposal option. It is continuously used in nature and by humans. However, it can only be used when the total amount of contaminants is relatively low. For industrial sources of contaminants this route in many cases is unacceptable as the index of potential hazard is too high.

An index of potential hazard equal or lower than unity presumes no pollution hazard. For radioactive contaminants (unlike, e.g. heavy metals) the index of

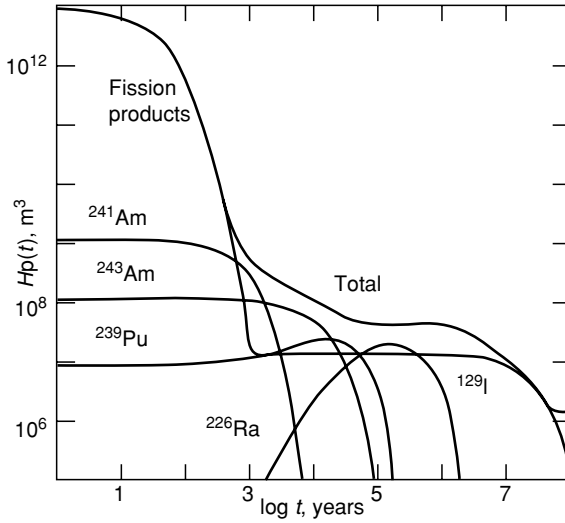


Figure 3.2: Ingestion potential hazard of HLW.

potential hazard diminishes with time. Finally, the contamination hazard vanishes when $I_p(t) < 1$.

3.4. Relative Hazard

The environment naturally contains contaminants although usually at lower concentrations compared to man-made materials. The relative radiotoxicity index as a function of time of a waste $RTI(t)$ is defined as the ratio of its potential hazard to the potential hazard of natural ore:

$$RTI(t) = \frac{H_p(\text{waste})}{H_p(\text{ore})} = \frac{I_p(\text{waste})}{I_p(\text{ore})} \quad (3.3)$$

This allows comparison of the anthropogenic to the natural contribution to the toxicity of materials. For example, the potential radiotoxicity of spent nuclear fuel can be compared to a typical 0.2% uranium ore used to produce nuclear fuel. Figure 3.3 shows the relative radiotoxicity index of spent nuclear fuel (SNF) from light water reactors (LWR) as a function of time.

The relative toxicity of radioactive waste diminishes with time. Typical pressurised water reactor (PWR) spent fuel contains ~ 9 g of actinides (mostly ^{239}Pu) and ~ 35 g of fission products per kilogram of fuel. The RTI for PWR spent fuel decreases with time and at $\sim 480\,000$ years it is the same as that of the

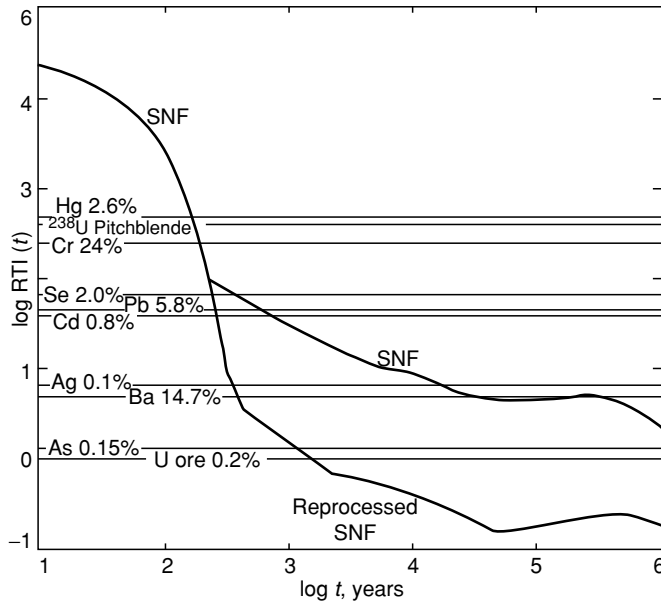


Figure 3.3: Relative toxicity of some materials as a function of time.

natural uranium ore. However, if the nuclear fuel is reprocessed and plutonium is recycled, the toxicity of the waste becomes less than that of natural uranium after ~ 2000 years. Figure 3.3 also demonstrates the RTIs of ores containing Hg, Cr, Se, Pb, Cd, Ag and As revealing that their toxicity is stable as the toxicants, unlike radionuclides do not eventually vanish with time.

3.5. Real Hazard Concept

Waste contaminants do not necessarily dissolve completely in water, so the real or residual hazard of materials $H(t)$ is much less than the potential one $H_p(t)$. Obviously if the contaminants are in the form of aqueous solutions or readily soluble salts, the real hazard will equal the potential hazard. In contrast, toxicants from durable and insoluble materials are not extracted into the water, so in practice the hazard is minimal. The real (residual) hazard of waste-forms accounting for their limited dissolution rates can be calculated from:

$$H(t) = \sum_i \frac{C_i(0) \exp(-\lambda_i t)}{\Gamma_i} \Phi_i V \quad (3.4)$$

where the dimensionless coefficient $\Phi_i \leq 1$ is equal to the released inventory fractions for each radionuclide from the given waste-form.

The dimensionless index of real (residual) hazard or radiotoxicity $I(t)$ is given by

$$I(t) = \sum_i \frac{C_i(0) \exp(-\lambda_i t)}{\text{IL}_i} \Phi_i \quad (3.5)$$

Hence the efficiency of a waste-form is characterised by the coefficient Φ_i , which accounts for the release of radionuclides from the waste-form to the environment. For an aqueous solution (liquid waste) obviously $\Phi_i = 1$, whereas durable waste-forms may hold $\Phi_i \ll 1$. The more durable a waste-form the lower the values of Φ_i .

3.6. Form Factors that Diminish the Hazard

The inverse of the coefficient Φ_i is retention coefficient or retardation waste-form factor for the given i th radionuclide. The coefficient Φ_i can be calculated from the known corrosion behaviour of a waste-form in water. Consider three waste-forms: metals, glasses and cements as immobilising matrices for short-lived radionuclides (with half-lives, $T_{1/2,i} < 30$ years).

A metallic barrier with a thickness d will be corroded after a time:

$$\tau_c = \left(\frac{d}{D_{oc}} \right)^{\frac{1}{a}} \quad (3.6)$$

where D_{oc} and a are the coefficients characterising the progress of corrosion with time: $D = D_{oc} t^a$. Hence the coefficients Φ_{mi} for a metallic case can be defined as:

$$\Phi_{mi} = \Theta(t - \tau_c) \quad (3.7)$$

where $\Theta(t)$ is the Heavyside function ($\Theta(t) = 1$ if $t > 0$ and is 0 otherwise). This shows that a metallic-encapsulated waste does not contaminate the water until time τ_c , and may contaminate it only after times exceeding τ_c .

The corrosion of vitreous waste-forms occurs through incongruent diffusion-controlled ion exchange and glass network dissolution (see Section 20.6). For a vitreous waste-form the coefficient Φ_{gi} is a function of time, but for $t \gg T_{1/2,i}$ these asymptotically tend to maximum possible values:

$$\Phi_{gi} \approx \frac{S}{V} \left(\sqrt{1.44 D_i T_{1/2,i}} + 1.44 r_c T_{1/2,i} \right) \quad (3.8)$$

where (S/V) is the waste-form surface to volume ratio (m^{-1}), D_i is the effective diffusion coefficient (m^2/s) and r_c is the glass dissolution rate (m/s).

A cement waste-form releases radionuclides via diffusion mechanisms (see Section 20.4), hence the released inventory fractions Φ_{ci} can be assessed asymptotically ($t \gg T_{1/2,i}$) by

$$\Phi_{ci} \approx \frac{S}{V} \left(\sqrt{1.44 D_i T_{1/2,i}} \right) \quad (3.9)$$

where (S/V) is the waste-form surface to volume ratio (m^{-1}), and D_i is the effective diffusion coefficient of radionuclides (m^2/s). Leaching factors L_i (cm^2/day) can be used instead of D_i for cementitious waste-forms. These can be determined through standard leaching tests, e.g. test protocol ISO 6961–1982.

The average diminishing factor of a waste-form can be defined as the ratio of real (residual) hazard to the potential hazard:

$$K_{\text{wf}} = \frac{\sum_i \left(\frac{C_i(0)}{L_i} \right) \exp(-\lambda_i t)}{\sum_i \left(\frac{C_i(0)}{L_i} \right) \exp(-\lambda_i t) \Phi_i} \quad (3.10)$$

Table 3.3 demonstrates the retention properties and hazard-diminishing factors of three types of cement matrices determined for the same radioactive waste composition. The better the retention properties of a waste-form the higher is its average hazard-diminishing factor. As a result the high alumina cement looks to be a very promising waste immobilising matrix.

For a system of immobilising barriers the overall retention capacity can be assessed by multiplying the released inventory fractions for each barrier. For example, a cemented waste-form in a metallic drum is characterised by the overall released inventory:

$$\Phi_{\Sigma i} = \Phi_{mi} \times \Phi_{ci} \quad (3.11)$$

Table 3.3: Diminishing factors of different cement matrices containing the same waste

Waste-form	Leaching factor, L (cm^2/day)	Average hazard diminishing factor, K_{wf}
Portland cement	8.5×10^{-6}	32
Portland blast furnace slag-composite cement	2.5×10^{-6}	60
High alumina cement	2.5×10^{-6}	222

Equation 3.11 demonstrates that the waste will not contaminate the water until time τ_c . For times exceeding τ_c the waste has a limited impact, which in this case is determined by diffusion-controlled leaching of radionuclides (see equation 3.9) from the cement matrix.

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Chapter 4

Heavy Metals

4.1. Metallic Contaminants

While this chapter may appear out of context in a book concerning radioactive waste we feel it is appropriate to compare problems arising from heavy metal elements to those associated with radionuclides. Unlike radioactive elements, the toxicity of stable elements does not diminish with time; they can only change form. Certain forms of some metals can be quite toxic even in relatively small amounts. Unless precautions are taken, metal contamination is likely to be with us indefinitely.

Several examples of lack of care when dealing with heavy metals, such as Pb, Cd and Hg, demonstrate the seriousness of high levels of exposure. In the 1950s, chronic Cd poisoning from rice, coupled with dietary deficiencies, caused an epidemic of kidney damage and a painful skeletal disease in Japan. A disease caused by Hg poisoning from eating fish from a polluted bay in the same country became known as Minamata disease. Severe effects on birdlife were observed in the 1950s and 1960s when many farmers laced their seeds with methyl Hg to prevent mould growth. Arsenic poisoning of water resources, while often not man-made, is currently a serious problem in many areas particularly in low-lying Bangladesh.

4.2. Biogeochemical Cycle

Metals occur in many forms, e.g. as ions dissolved in water, as vapours, or as salts or minerals in rock, sand and soil. They can also be bound to organic or inorganic molecules, or attached to particles in the air. Both natural and anthropogenic processes and sources emit metals into air and water. Sources of metals include weathering of rock and human activities, such as mining, metal processing, and burning of fossil fuels. Heavy metals in consumer goods and industrial processes

enter the environment from burning or burial of waste in landfill sites. These increase the flux of metals that can be transported by wind and water and thus find their way into plants, animals and finally to humans. Elements are continuously circulating the environment through geochemical and biogeochemical cycles. Figure 4.1 illustrates the biogeochemical circulation of elements.

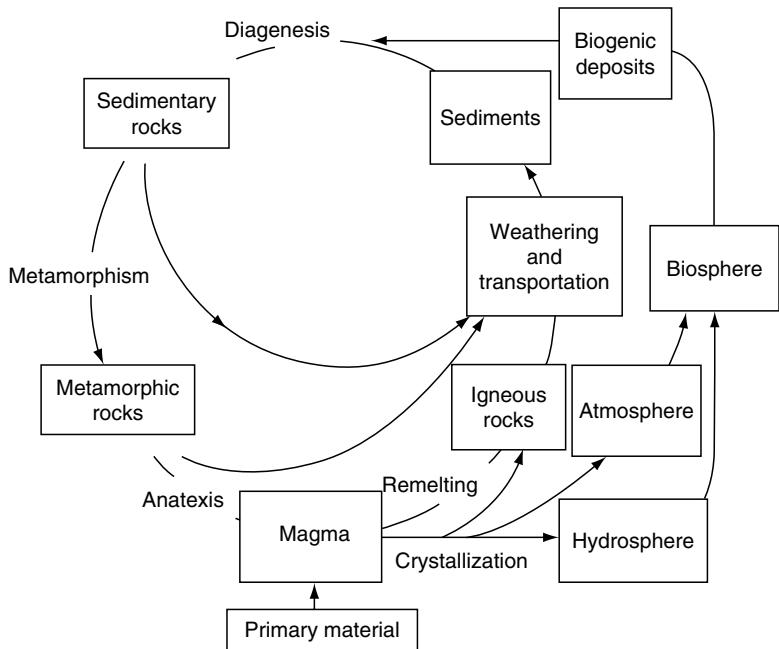


Figure 4.1: Biogeochemical cycle of elements.

The effect of metals in the environment depends, to a large extent, on whether they occur in forms that can be taken up by living species. Pb may be strongly adsorbed onto sediment particles and is therefore largely unavailable, while Cd ions can be directly absorbed by living species from water. Hg is strongly bound to sediments and organic material, but microorganisms can transform inorganic Hg into methyl mercury, which is readily taken up by both aquatic and terrestrial organisms.

Environmental variables, such as the presence of ions that may bind the metals, often play an important role in organism uptake ability. In salt water, chloride ions bind some metal ions, making them less available to living cells. Cd and Pb thus appear to be less toxic in salt water than in fresh water. Other factors that influence bioavailability are acidity, the amount of suspended matter, and the amount of organic carbon in the water.

4.3. Heavy Metals

The term heavy metal is used loosely but generally refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations, and includes Hg, Cd, As, Cr, Tl and Pb. Heavy metals, such as Pb, Cd, Hg, As, Se and Zn belong to the so-called first class of hazard. Heavy metals are natural constituents of the Earth's crust and are present in varying concentrations in all ecosystems. The main anthropogenic sources of heavy metals are various industrial sources, including present and former mining activities, foundries and smelters, and diffuse sources such as piping, combustion by-products and traffic fumes. Human activity has drastically changed the biogeochemical cycles and balance of some heavy metals in the environment (Fig. 4.2).

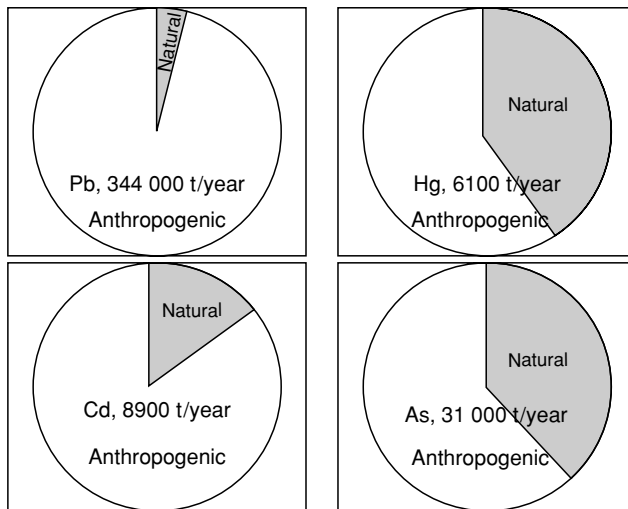


Figure 4.2: Global emissions of metals to the atmosphere in 1983.

Human activity has caused a significant increase of heavy metal concentrations in agricultural and forest soils as well as in marine and inland water sediments. Analysis of glacier samples taken in Greenland revealing the impact of human activity on the heavy metal atmospheric cycle dates back to the Roman Empire. However, it became really significant during the industrial revolution in the middle of the XIX century. From that period to the 1980s an exponential growth of heavy metal emission to the atmosphere occurred. The increase in heavy metals content is frequently observed in remote areas thousands of kilometres away from major anthropogenic sources – an observation that can only be explained by transboundary atmospheric long-range transport.

4.4. Heavy Metals in Living Species

Once absorbed, metals are distributed in the body by the circulatory system. Many metals undergo a chemical transformation in the body, which sometimes can make them less toxic but in other cases may increase their harmful potential. The most important processes for such biotransformations are the formation of inert complexes and the cleaving or building of bonds with carbon, e.g. methylation and de-methylation.

The formation of inert metal–protein complexes plays an important role in detoxifying Cd, Zn, Cu and Hg. Se can reduce the toxicity of As, Cd and Hg in a similar manner. High Se levels in the environment can thus protect against the toxicity of these metals. The creation of carbon bonds via methylation reduces the toxicity of As and Se because it allows an animal to excrete the metal. In contrast, methylation of Hg increases its toxicity because methyl mercury is more toxic than inorganic forms of Hg.

Uptake efficiency is a measure that shows in per cent how much of available metal is taken up in a particular tissue. Absorbed metal is gradually evacuated from the tissue via metabolic processes. The time necessary to evacuate a half of the absorbed metal from the organism is termed the *biological half-life*. Metals will accumulate in organisms when uptake is higher than evacuation. Table 4.1 shows how efficiently organisms are able to absorb, or evacuate, heavy metals.

Table 4.1: Uptake efficiency and biological half-life of Pb, Cd and Hg

Metal	Organism	Uptake efficiency	Half-life
Pb	Mammals	5–10% via intestines	40 days in soft tissues
		30–50% via the lungs	20 years in bone
Cd	Fish	1% via intestines 0.1% via gills	24–63 days
	Mammals	1–7% via intestines 7–50% via lungs	10–50% of life span in liver 10–30 years in kidney
Hg	Fish	Depends on chemical form, water temperature, and water hardness	323 days for organic mercury from diet, 45–61 days for inorganic mercury from water or diet
	Mammals	>95% for organic mercury via intestines, >15% for inorganic mercury	500–1000 days in seals and dolphins for methyl mercury, 52–93 days for methyl mercury and 40 days for inorganic mercury in whole body of humans

Heavy metals tend to accumulate in certain storage compartments in organisms. Cd accumulates preferentially in the kidneys, Hg in the liver and Pb in the skeleton. The accumulation can continue throughout the organism's life and is the major cause of chronic toxicity. In contrast to organic pollutants, metals accumulate in protein tissues and bone rather than fat.

4.5. Lead

Annual mining of Pb is about 2×10^6 t, up to 10% of which is released into the environment during extraction. About a half of this Pb is used to produce energy storage batteries, but only about 80% of the batteries are recycled. Pb contamination from melting may extend up to 100 km from the melting plants. Leaded gasoline is the major source of increased environmental levels on a global scale. Antiknock components in the form of lead tetramethyl or tetraethyl have been used since 1923 and were (until the 1990's) added to almost all types of petrol in concentrations of ~ 80 mg/L. From 25 to 75% of this Pb was released into the atmosphere. Other anthropogenic sources include mining and metallurgical industries, ammunition and municipal waste incineration. Both Pb and Cd are released to the atmosphere as sub- μ m aerosol particles.

Pb^{2+} ions are relatively unstable in the environment. However, Pb is accumulated in sediments in the form of sulphates and sulphites. The Pb content in drinking water can reach $2 \times 10^{-6}\%$ whereas in soil it is $1.5 \times 10^{-3}\%$ (as in the Earth's crust). The Pb content of underground waters ranges between 10^{-4} and $10^{-2}\%$. Pb being strongly absorbed by sediments and soil particles is therefore largely unavailable to plants and animals. Many of the inorganic salts of Pb (oxides and sulphides) are not readily soluble in water and are sequestered in sediments. In aquatic systems, uptake is influenced by various environmental factors such as temperature, salinity, pH and the presence of organic matter. Organic lead compounds are fat-soluble and are more toxic to animals than other forms. Animals accumulate Pb in their liver, kidneys, spleen and skeletal tissues. Pb can also accumulate in eggs and embryos. Once it has been integrated into the skeleton, it takes several years to leave the body.

Damage to the nervous system and gastrointestinal symptoms are the main signs of lead poisoning. Pb also interferes with the formation of red blood cells, leading to anaemia. Pb is especially toxic to the growing brain and can affect the behavioural development of young children, even at low concentrations. In polluted cities, fumes from cars burning leaded gasoline are known to have caused air concentrations high enough to affect children's development resulting in the recent world-wide trend to lead-free petrol.

4.6. Mercury

Annual mining of Hg is about 10^5 t. The most important anthropogenic sources of Hg are combustion of fossil fuels, particularly coal, and municipal waste incineration. Other sources are the chlorine-alkali industry and nonferrous metal production. Hg is used in thermometers, barometers, dental fillings, batteries and fluorescent lamps. About 50×10^6 t of Hg are accumulated in the oceans. Natural erosion contributes about 5×10^3 t/year and human activities another 5×10^3 t/year of Hg to ocean waters. The natural content of Hg in air is about $3\text{--}9\text{ ng/m}^3$. Hg in emissions can occur in various physico-chemical forms. Hg is primarily in the form of Hg^{2+} . Much of the Hg in the environment is strongly bound to sediments and organic matter, and thus unavailable to organisms. However, due to interaction with organics Hg is transformed into the toxic substances methyl-mercury and dimethyl-mercury. Dimethyl-mercury is stable at high pH values but dissociates into $(\text{CH}_3\text{Hg})^+$ at low pH. Methyl-mercury is readily soluble and can be taken up by plants which when eaten by humans enters the body. Hg is a nerve toxin and the main health concern is its effect on the brain, particularly in a growing organism. The phrase 'mad as a hatter' arose from the Hg poisoning of hat makers who used the metal for curing felt.

4.7. Cadmium

Cd is a by-product of Zn and Pb production. The pyrometallurgical production of Zn is the most important anthropogenic source of Cd in the environment. Annual production of Cd is about 2×10^4 t whereas that of Zn is 7×10^6 t. Zn is used to produce alloys, in galvanic processes, e.g. galvanised iron. Other major sources of Cd are fossil fuel combustion and waste incineration. Cd is used in a wide spectrum of applications including alloys, pigments, metal coatings, batteries and in the electronics industry. The Cd and Zn content of ocean water is $0.1 \times 10^{-7}\%$ and $2 \times 10^{-7}\%$ whereas their content in soils is about $4.5 \times 10^{-4}\%$ and $50 \times 10^{-4}\%$, respectively. Cd is often a contaminant in chemical fertiliser, manure, compost and sewage sludge. Cd is toxic to most life forms. It can be taken up directly from water, and to some extent from air and via food, and it has a tendency to accumulate in both plants and animals. Mushrooms, in particular, can be very rich in it. Animals accumulate Cd in their kidneys and liver, where most of it binds to a special protein that makes the metal harmless. Cd can damage the kidneys and upset metabolism of vitamin D and calcium. Concentrations of $100\text{--}200\text{ }\mu\text{g}$ in the kidneys can be a risk for mammals. Cd leaves the body extremely slowly and has a biological half-life ranging over decades.

4.8. Arsenic

Arsenic has been used since 3000 BC. In the United Kingdom, for example, it was used to extract iron from iron ore. As has also been widely used as a pesticide and in medicine.

As contamination has become a major problem in many parts of the world. Australia, Canada, Japan, Mexico, Thailand, UK and the USA have problems arising from leaching of mine tailings. Argentina, Bangladesh, Cambodia, Chile, China, Ghana, Hungary, Inner Mongolia, Mexico, Nepal, New Zealand, Philippines, Taiwan, US and Vietnam have As contamination in natural aquifers used for water supply. The As problem is extremely acute in Bangladesh, West Bengal and, to a lesser extent, Inner Mongolia, Chile, Nepal and Vietnam. These locations have in common that they are alluvial plains where As has been brought down from the surrounding hills for millennia.

As in water at 60 ppm concentration is 100% lethal. Chronic effects of As arise from prolonged low-level exposures. Skin pigmentation, keratoses and skin cancers were found in Taiwan in 1966 among people who drank from arsenic-contaminated wells. Below ~150 ppb As has no toxic effect, which might therefore be a biological threshold. The World Health Organisation (WHO) recommends a regulatory level of 50 ppb.

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Chapter 5

Naturally Occurring Radionuclides

5.1. NORM and TENORM

Naturally occurring radioactive materials (NORM) are part of the Earth. The majority of radionuclides in NORM (principally radium and radon) arise from uranium and thorium decay. Radon exposure in homes can be high, particularly those built on Rn-containing rocks such as in SW England and the Peak District in Derbyshire as the gas continuously accumulates and may achieve potentially dangerous concentrations. Human activities and technological processes such as fossil fuel burning, mineral extraction and fertiliser application often increase concentrations of radionuclides in the NORM. Industrial practices involving natural resources often concentrate radionuclides to a degree that may pose a risk to humans and the environment. Materials that contain natural radionuclides, whose levels are concentrated due to technological operations, are termed technologically enhanced naturally occurring radioactive materials (TENORM). TENORM are, in many cases, large-volume, low-activity waste streams produced by industries such as mineral mining, ore beneficiation, phosphate fertiliser manufacture, water treatment and purification, paper and pulp manufacture, oil and gas production, scrap metal recycling and waste incineration. The level of individual exposure from NORM is usually trivial. However, TENORM in some cases can be dangerous and classified as radioactive waste.

5.2. Primordial Radionuclides

Primordial radionuclides are typically long lived, with half-lives often of the order of hundreds of millions of years. Primordial radionuclides are classified as *non-series* and *series* depending on the decay pathway. Two primary *non-series* primordial radionuclides are ^{40}K and ^{87}Rb whose basic properties are given in Table 5.1.

Table 5.1: Characteristics of non-series primordial radionuclides

Nuclide	Atomic number	Half-life	Principal mode(s) of decay	Major radiation energies (MeV/dis)			Q-value		Specific activity (Ci/g)	Daughter(s)
				α	ε	γ	MeV/dis	W/Ci		
⁴⁰ K	19	1.277 × 10 ⁹ years	β (89.33%)		0.4545	0.1559	0.6104	3.62 × 10 ⁻³	6.983 × 10 ⁻⁶	⁴⁰ Ca
⁸⁷ Rb	37	4.8 × 10 ¹⁰ years	β		0.274		0.274	1.62 × 10 ⁻³	8.57 × 10 ⁻⁸	⁸⁷ Sr

^{40}K exists effectively as a constant 0.0117% fraction of stable potassium. ^{40}K is a beta (89.33%) and gamma (10.67%) emitter and contributes both internal and external exposure doses to living species. Its external dose contribution is variable, depending on its concentration in rocks and soil although its average concentration in crustal rock is about 0.6 Bq/g (17 pCi/g). ^{40}K is found in building materials such as bricks and cinder breeze blocks. ^{87}Rb is found in crustal rock in concentrations of about 0.07 Bq/g (2 pCi/g) and since it is a pure beta emitter it causes little external hazard.

Primordial radionuclides ^{238}U , ^{232}Th and ^{235}U , are the parent radionuclides for the three naturally occurring decay series commonly called the uranium, thorium and actinium series, respectively (Fig. 5.1).

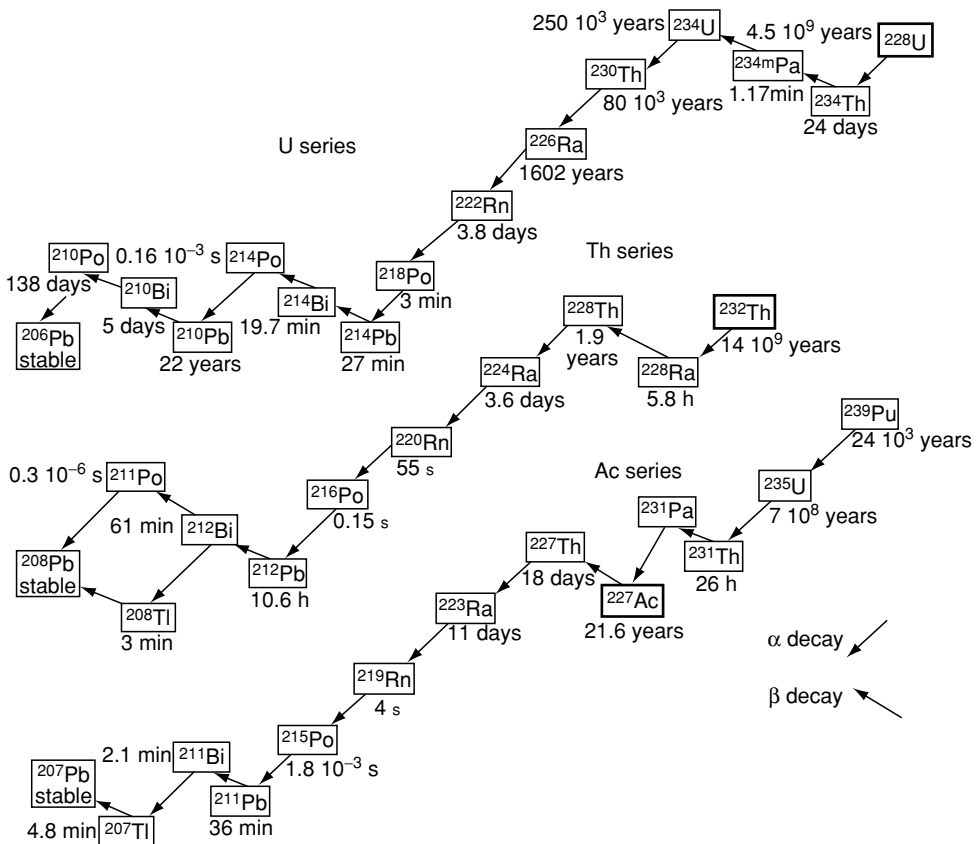


Figure 5.1: Uranium, thorium and actinium decay series.

Table 5.2 gives the basic characteristics of ^{238}U , ^{235}U and ^{232}Th . Generally, the actinium series is not significant since it is extremely rare in nature.

Table 5.2: Characteristics of ^{238}U , ^{235}U and ^{232}Th

Nuclide	Atomic number	Half-life	Principal mode(s) of decay	Major radiation energies (MeV/dis)			Q-value		Specific activity (Ci/g)	Daughter(s)
				α	ϵ	γ	MeV/dis	W/Ci		
^{238}U	92	4.468×10^9 years	α	4.1945	0.0095	0.0013	4.205	2.492×10^{-2}	3.362×10^{-7}	^{234}Th
^{235}U	92	7.037×10^8 years	α	4.3785	0.0426	0.1561	4.577	2.713×10^{-2}	2.161×10^{-6}	^{231}Th
^{232}Th	90	1.405×10^{10} years	α	4.0056		0.0002	4.006	2.375×10^{-2}	1.097×10^{-7}	^{228}Ra

5.3. Cosmogenic Radionuclides

Naturally occurring radionuclides are also produced by cosmic radiation which permeates space, arising primarily from outside of our solar system and occurs in many forms, from high speed heavy particles to high energy photons and muons. The Earth's upper atmosphere interacts with many of these cosmic radiations, and produces radioactive nuclides such as ^3H , ^7Be , ^{10}Be , ^{14}C , ^{18}F , ^{22}Na , ^{24}Na , ^{26}Al , ^{31}Si , ^{32}Si , ^{32}P , ^{33}P , $^{34\text{m}}\text{Cl}$, ^{35}S , ^{36}Cl , ^{37}Ar , ^{38}Cl , ^{38}Mg , ^{38}S , ^{39}Ar , ^{39}Cl and ^{80}Kr . The majority of cosmogenic radionuclides have very short half-lives, except ^{14}C , which is a long-lived radionuclide and ^3H , which has a half-life of 12.3 years (Table 5.3).

Table 5.3: Characteristics of some cosmogeneous radionuclides

Nuclide	Half-life	Source	Typical natural activity (Bq/kg)
^{14}C	5730 years	Cosmic ray interactions, $^{14}\text{N}(\text{n}, \text{p})^{14}\text{C}$	220 in organic materials
^3H	12.3 years	Cosmic ray interactions with N and O; spallation from cosmic rays, $^6\text{Li}(\text{n}, \alpha)^3\text{H}$	0.0012
^7Be	53.28 days	Cosmic ray interactions with N and O	0.01

5.4. Natural Radionuclides in Igneous Rocks

The original sources of primordial radionuclides in the terrestrial environment are the Earth's crust and mantle. As molten magma cools, silicate minerals are formed. In the early stages of cooling, the silicates tend to contain predominantly Fe and Mg, and are deficient in Al, Si, Na and K (mafic rocks). As cooling progresses the balance tends to reverse and rocks containing predominantly Si and Al (salic rocks) form. Neither uranium nor thorium is compatible with the crystal structure of the major silicates. In addition, they are present in such small quantities that they have little tendency to form minerals in which they are the major components. As a result the remainder of the magma cools to form a range of minor minerals containing uranium, thorium and other minor and trace elements. The last major silicates to crystallise contain most of the K and Rb. If not subjected to chemical or physical separation, each of the three

naturally occurring decay series attains a state of secular radioactive equilibrium. Crust concentrations of the parents of the three series are extremely small and as a result their decay daughters are present in extremely small concentrations (Table 5.4).

Table 5.4: Concentrations of primordial radionuclides in igneous rocks (Bq/kg)

Rock type	²³⁸ U	²³² Th	⁴⁰ K	⁸⁷ Rb
Mafic	7–10	7–10	70–400	10–50
Salic	7–10	60–80	1100–1500	170–200
Granite	40	70	>1000	170–200

Natural radionuclides may become mobile or be transported by migration of water or oil. Some organic complexes, notably humic acids, create mobile complexes of U. Moreover, U and other minor and trace elements have an affinity for crude oil.

5.5. Natural Radionuclides in Sedimentary Rocks and Soils

Mechanical (physical) and chemical weathering processes break down rock into soil. When mechanical processes dominate the breakdown, fracture usually occurs along mineral boundaries leading to separation of the major from the minor silicates containing thorium and uranium. These minor minerals include zircon and monazite, which are stable, resistant to chemical decay, and often found as small individual particles or grains. When chemical (or biological) action predominates, the thorium- and uranium-bearing minor minerals give up their radionuclides to layers of cations in clay minerals. When the host rocks erode, the clay minerals containing the adsorbed series radionuclides tend to separate from the major minerals. Therefore, if igneous rock is broken down to individual grains, the products are sands, fine-grained clay minerals and relatively small quantities of resistant, dense grains of the minor minerals containing most of the series radionuclides. Sands tend to be depleted, whereas the fine-grained clay minerals are slightly enriched, in radionuclides. K and Rb are present in water-soluble forms and so are quickly removed on contact with water. Much of the Earth’s surface soil is derived from sedimentary rock. Sedimentation processes naturally sort or classify the products of weathering and develop several major sedimentary rock types of significantly differing radionuclide concentrations such as shales, sandstones and carbonates.

Shales normally contain $\geq 35\%$ clay minerals, and a significant fraction of these contain potassium. Shales can adsorb the series radionuclides, which may also be present bound to organic matter in minor minerals or as precipitates or co-precipitates in the cementing material that binds the rock. Sandstones are usually made of grains that are primarily quartz but may contain some potassium-containing feldspar. Those sandstones that contain $>25\%$ feldspar are called arkoses, and the chief feldspars are those containing K. On the whole, sandstones are low in both the series and non-series radionuclides. However, many U deposits are found at the boundary between different layers of sandstones. Carbonate rocks are limestones or dolomites derived by chemical precipitation from water or by the build-up of shells, bones and teeth of organisms. Although the carbonate minerals themselves are relatively free of radionuclides, intergranular regions may contain elements found in the sea water from which they were deposited. K is very soluble and does not stay in the deposited matter. Th is depleted in sea water and is not metabolised by marine organisms. As a result K and Th only occur at low concentrations in carbonate rocks although U may be present because it can be fixed by reducing conditions in decaying organic matter co-deposited with the rocks. U can replace Ca or be adsorbed in the principal phosphate minerals.

Radioactivity in soil arises from weathering of the rock from which it is formed and the background radionuclide concentration is affected by many factors. It is diminished by leaching water, diluted by increased porosity and by added water and organic matter, and augmented by sorption and precipitation of radionuclides from incoming water. A summary of concentrations of radionuclides in sedimentary rocks and soil is shown in Table 5.5.

Table 5.5: Concentrations of primordial radionuclides in sedimentary rocks and soil (Bq/kg)

Rock type	^{238}U	^{232}Th	^{40}K	^{87}Rb
Shale	40	50	800	110
Carbonate	25	8	70	8
Soils	66	37	400	50

Sir Walter Marshall (ex Chairman of the UK's Central Electricity Generating Board and Chief Scientific Advisor) used to state that the top 1 metre of soil in a typical suburban garden contains 0.8 kg ^{40}K , 6 kg Th and 2 kg U!

5.6. Natural Radionuclides in Sea Water

The volume of water in the oceans is estimated as $1.3 \times 10^{18} \text{ m}^3$ including the water from the Pacific ($6.549 \times 10^{17} \text{ m}^3$) and Atlantic ($3.095 \times 10^{17} \text{ m}^3$) Oceans. Table 5.6 gives the average concentrations of primordial and cosmogenic radionuclides in the marine environment.

Table 5.6: Natural radionuclides in oceanic water

Nuclide	Approximate average concentration (Bq/L)	Total activity (Ci)		
		Pacific	Atlantic	All oceans
^{238}U	0.03	6×10^8	3×10^8	1.1×10^9
^{87}Rb	1	1.9×10^{10}	9×10^9	3.6×10^{11}
^{40}K	11	2×10^{11}	9×10^{10}	3.8×10^{11}
^{14}C	0.005	8×10^7	4×10^7	1.8×10^8
^3H	0.0006	1×10^7	5×10^6	2×10^7

5.7. Radon Emissions

^{222}Rn is a decay product of ^{226}Ra , which itself is one of the daughters of ^{238}U (see Fig. 5.1). ^{226}Ra is widespread in most rocks and soils. ^{222}Rn is an inert gas with a half-life of 3.85 days so it is short-lived and likely to decay and so damage the lungs when inhaled. In addition any radon daughter products present on dust which is breathed in, may lead to tissue damage. High levels of ^{222}Rn are associated with granite igneous rocks, shale and dirty quartz sedimentary rocks, phosphate deposits and some beach sands, which may contain high levels of U. Figure 5.2 is a map of the UK highlighting (in dark shading) regions with high natural Rn levels including Cornwall and the Peak District. The UK's population live in such areas and accept the minimal risk in so doing.

Indoor levels of ^{222}Rn are not related simply to geologic factors. The relation depends on many factors, including degree of bedrock fracture, and on the intervening pathway. ^{222}Rn mobility through soil may vary depending on soil porosity. Rock permeability is a key factor influencing ^{222}Rn availability at the surface, even in low U-content rocks such as limestone. ^{222}Rn also occurs in natural gas at up to $37\,000 \text{ Bq/m}^3$, but by the time it gets to consumers the radon has largely decayed. Another potentially important source of ^{222}Rn exposure is water. ^{222}Rn concentrations in surface waters are usually very low and aeration of municipal water supplies further diminishes ^{222}Rn levels. Deep aquifers have highly variable ^{222}Rn levels depending on the U content of the rock and the distribution of the aquifer relative to the rock. Indoor Rn concentrations are generally highest in the basement or on the ground level since the major source



Figure 5.2: Areas of high Rn potential in the UK, darker shading equals greater potential (courtesy Prof. J. Plant, Imperial College London, UK).

is influx from the soil under and around the house. First floor concentrations will be lower by about a factor of 2. Indoor Rn concentrations are typically a factor of 2–3 higher than outdoor levels. The radon concentration in the upper levels and in apartments above the first floor are usually of no concern. Radon concentrations in the air range from about 4 to 20 Bq/m³. In caves open to the public, levels of up to 25 000 Bq/m³ have been measured.

5.8. Natural Radionuclides in the Human Body

Radionuclides are naturally present in the human body. Table 5.7 shows estimated concentrations of natural radionuclides in a 70-kg adult and the average daily intake of these radionuclides.

Table 5.7: Estimated content of naturally occurring radionuclides in a human body

Nuclide	Activity	Mass	Daily intake
²³⁸ U	1.1 Bq	90 µg	1.9 µg
²³² Th	0.11 Bq	30 µg	3 µg
⁴⁰ K	4.4 kBq	17 mg	390 µg
²²⁶ Ra	1.1 Bq	31 pg	2.3 pg
¹⁴ C	3.7 kBq	22 ng	1.8 ng
³ H	23 Bq	0.06 pg	0.003 pg

Clearly the human body contains significant amounts of natural radioactivity. There have been reports that exposure to natural radiation leads to beneficial health effects (termed “radiation hormesis”), which are at least as likely as harmful effects although this is a contentious issue among researchers.

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Chapter 6

Background Radiation

6.1. Radiation is Natural

Our world is radioactive and has been since its creation. Natural radiation has been with us since the Big Bang and the appearance of the Universe. Radionuclides and radiation are constituents of the Earth and play important roles in natural processes, long-lived radionuclides, for example, maintain enhanced temperatures deep underground thereby preserving the Earth's heat balance. Living systems have adapted to, or even been stimulated by, existing levels of natural radioactivity; the soft radiation of ^{14}C (49.5 keV beta particles) is suspected of causing suitable conditions for development of life itself.

The Earth's current population receives some level of radiation from a number of natural, as well as man-made sources including cosmic rays from outer space and the Sun's surface, terrestrial radionuclides that occur in the Earth's crust, in building materials and in air, water and foods and in the human body itself. Humans contain ^{40}K and ^{14}C and hence potentially irradiate one another as the decay of ^{40}K causes emission of 1.46 MeV photons. Some of the exposure sources are fairly constant and uniform for all individuals everywhere, for example, the dose from ingestion of ^{40}K in foods. Other exposures vary widely depending on location; cosmic rays are more intense at higher altitudes. Exposures can also vary as a result of human activities and practices. In particular, the building materials of houses and the design and ventilation systems strongly influence indoor levels of ^{222}Rn and its decay products, which contribute significantly to doses through inhalation. In addition, humans collect radiation doses from artificial sources such as X-rays used in medical procedures. All of these contribute to normal or background radiation exposure.

6.2. Dose Units

Absorbed radiation in materials deposits certain amounts of energy through a variety of interactions. A measure of the energy deposited by radiation in a material is called the absorbed dose.

Absorbed dose (D) is defined as the mean amount of energy $d\bar{\epsilon}$ deposited per unit of mass (dm) as a result of the interaction of ionising radiation and matter.

$$D = \frac{d\bar{\epsilon}}{dm} \quad (6.1)$$

The unit of absorbed dose is the gray (Gy): $1 \text{ Gy} = 1 \text{ J/kg}$. An old but still used unit of absorbed dose is the rad: $1 \text{ rad} = 0.01 \text{ Gy}$.

A problem with defining absorbed dose in Gy for radiation protection purposes is that the biological effect of an absorbed dose of 1 Gy in tissue is dependent on the type and energy of the incident radiation. To overcome this difficulty a quantity called equivalent dose is used. To take account of the nature of radiation, a weighting factor called the radiation weighting factor, W_R is used.

Equivalent dose in the tissue (H_T) is given by the sum over all types and energy ranges of radiation (R):

$$H_T = \sum_R W_R D_{T,R} \quad (6.2)$$

where $D_{T,R}$ is the absorbed dose (Gy) averaged over the tissue organ due to the radiation R . The radiation weighting factors W_R adjust for the type of radiation and its energy is determined by the rate of linear energy transfer in the irradiated tissue. Numerical values for W_R have been recommended by the International Commission on Radiological Protection (ICRP) given in Table 6.1. Different tissues have different sensitivities to irradiation and hence the biological consequences of irradiation depend on the tissue type. A quantity called effective dose is used, which accounts for the relative radio-sensitivity of tissues through the tissue weighting factors W_T (Table 6.1).

Effective dose (E) is given by the sum over all irradiated tissues (T):

$$E = \sum_T W_T H_T = \sum_{R,T} W_T W_R D_{T,R} \quad (6.3)$$

The unit of equivalent and effective dose is sievert (Sv), which is the amount of absorbed dose in J/kg weighted to account for the nature of the radiation and the sensitivity of tissues. An old but still used unit of effective dose is rem: $1 \text{ rem} = 0.01 \text{ Sv}$.

Table 6.1: Radiation and tissue weighting factors

Type of radiation		W_R	Tissue or organ	W_T
Photons, all energies		1	Gonads	0.20
			Bone marrow	0.12
Electrons and muons, all energies		1	Colon	0.12
			Lung	0.12
Neutrons, energy	<10 keV	5	Stomach	0.12
	10–100 keV	10	Bladder	0.05
	100 keV–2 MeV	20	Breast	0.05
	2–20 MeV	10	Liver	0.05
	>20 MeV	5	Oesophagus	0.05
Protons other than recoil protons, energy >2 MeV		5	Thyroid	0.05
			Skin	0.01
Alpha particles, fission fragments, heavy nuclei		20	Bone surface	0.01
			Remainder	0.05

6.3. Biological Consequences of Irradiation

Radionuclides and radiation are natural components of our life; however, over-irradiation or excess of radionuclide intake can be detrimental. Biological effects of radiation vary greatly depending on such factors as the amount of exposure, rate of exposure, area of body irradiated, type of radiation and individual biological variability. Relatively large doses of radiation are required to produce short-term biological effects.

High doses: the appropriate dose quantity is absorbed dose (Gy). If enough individual cells are damaged by ionising radiation, then specific clinical symptoms will be evident. Most of these symptoms and effects can be classified as deterministic, i.e. when severity of the effect clearly depends on dose. Up to a threshold dose the deterministic effects of irradiation are negligible but above this dose severe impairment of the function of an organ or tissue occurs as a result of cell destruction by radiation. Table 6.2 gives a broad indication of the dose levels for certain short-term effects following whole body irradiation over a short period of time. If only part of the body is irradiated it would require much larger doses to produce the same effect.

Low doses: the major long-term biological effects from smaller doses received over a longer period of time are increased risk of cancer and hereditary

Table 6.2: Whole body doses for acute biological effects

Effect	Dose (Gy)
No discernible effect	0.25
Blood changes, no illness	1.0
Radiation sickness, no death	2.0
Death to 50% of irradiated people	4.5
Death to 100% of irradiated people	10.0

effects in progeny. Cancer induction is a stochastic effect, in that the probability of the resultant health effect is a function of dose. Stochastic or probabilistic effects arise from non-lethal cell modification, conventionally an alteration in the cell nucleus DNA. The shape of the dose–response function, however, is uncertain. Most likely it has a sigmoidal form, but is conservatively assumed to be linear through the origin. The linear hypothesis assumes that the demonstrated relationships between hazard and radiation dose at high levels of exposure also apply to low levels (Fig. 6.1): a deliberately conservative basis of occupational health and other radiation protection standards.

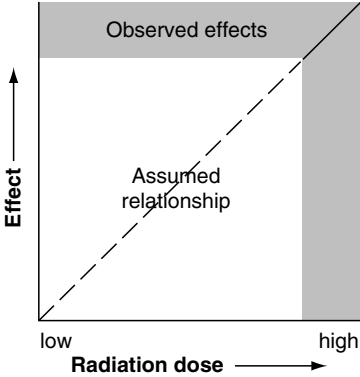


Figure 6.1: Conservative linear relationships between hazard and radiation dose.

Extensive research has not supported the linear hypothesis for low-level radiation exposure. Some evidence suggests that there may be a threshold below which no harmful effects of radiation occur. Moreover, some researchers have presented evidence showing that there may be a beneficial effect from low-level radiation possible due to an adaptive biological response (radiation hormesis).

Cancer fatality risk r_c is reasonably well known for doses over 0.1 Sv or for high dose rates from observations of the survivors of the atomic bomb attacks

Table 6.3: Probability of latent cancer fatalities

Conditions	Cancer risk r_c (per person-Sv)
High dose rates or $E > 0.1$ Sv	0.1
Lower doses, conservative linear hypothesis	0.05
Lower doses, possible actual risk	0

on Hiroshima and Nagasaki. International bodies such as the ICRP quantify this risk at about 0.1 per person-Sv, i.e. as 10 cancer events per 100 person-Sv. Presently it is assumed (following the conservative linear hypothesis) that the risk at low doses is 0.05 per person-Sv. Current opinion, however, suggests that the risk from low doses and dose rates is significantly lower than the 5% per person-Sv and may, in fact, be zero. Table 6.3 summarises the values of cancer risk (r_c) due to irradiation.

Cancer arising from radiation as a stochastic effect is described in terms of the collective dose received by the population:

$$S = NE_i \quad (6.4)$$

where E_i is the individual dose and N is the number of individuals ($N \gg 1$):

The number of fatalities is assessed from the collective dose as:

$$n_f = r_c S = r_c N E_i \quad (6.5)$$

Consider an average city with population $N = 100\,000$ with no additional irradiation above background. Statistically about 16 000 persons could eventually be expected to die from cancer induced by mechanisms other than radiation. If these people were each exposed to a total dose of $E_i = 0.01$ Sv in a short period of time, the collective dose received by this population is $S = NE_i = 1000$ person-Sv. The number of additional fatalities in years to come due to this irradiation will be $n_f = 50$, so statistically the total number of fatalities will become 16 050. Table 6.4 summarises risks associated with various not unusual activities.

Hereditary effects of radiation in humans have not been detected with a statistically significant degree of confidence in epidemiology. Nevertheless, there can be no doubt about the existence of hereditary effects in humans. Risk estimation therefore rests on genetic experimentation with a wide range of organisms and on cellular studies, with limited information available about the negative effects on humans. With this in mind, the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) estimates the risk of clinically

Table 6.4: Risks associated with different activities

Activity	Estimated days of life lost
Smoking 1 pack of cigarettes per day	2370
20% overweight	985
Home accidents	95
Occupational exposure 50 mSv per year	32
Exposure 5 mSv per year	3

important disorders appearing in first-generation offspring of exposed parents at 0.002–0.004 per Sv in that part of the population of reproductive age.

6.4. Background Radiation

Background radiation levels are not constant and vary worldwide from approximately $2\text{--}8 \times 10^3 \mu\text{Sv}/\text{year}$ (Fig. 6.2).

Some areas with sizable populations have much higher than average background radiation levels. The highest are found primarily in Brazil, India and China and are due to high concentrations of radioactive minerals in the soil. In

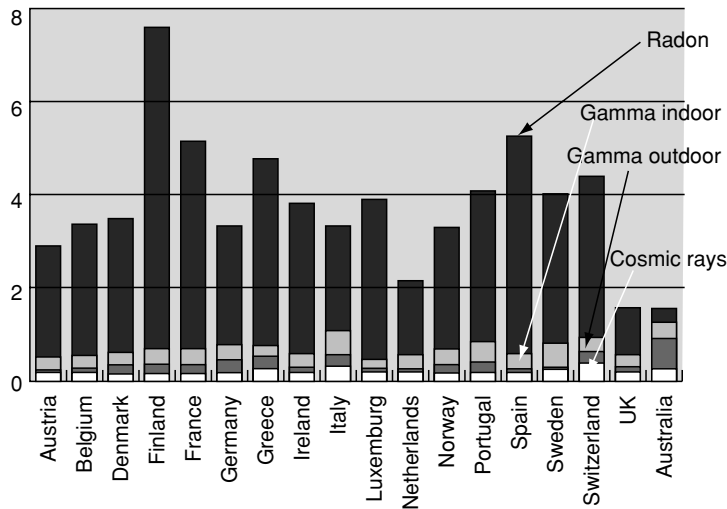


Figure 6.2: Average annual doses of radiation in mSv/year in various countries.

Brazil, for example, the monazite sand deposits along certain beaches result in external radiation levels $\sim 50 \mu\text{Gy/h}$. Natural radiation fields vary around certain average magnitudes everywhere. Temporal changes in background range also occur during short to long time frames; hours to days, months to years, and centuries or more. In addition, there are changes in background from terrestrial and cosmic sources. Table 6.5 quantifies contributions to background radiation from various sources while Fig. 6.3 shows the average annual radiation dose to the UK population from all sources. It is worth noting that 85% of the dose is from natural sources, largely associated with Rn emission from the ground. The dose arising from man-made radioactive discharges, both deliberate and accidental, is dominated by beneficial medical applications.

Table 6.5: Annual effective natural background radiation doses

Source	Dose range ($\mu\text{Sv/year}$)	Worldwide average ($\mu\text{Sv/year}$)
Cosmic rays	300–1000	400
Terrestrial gamma rays	300–600	500
Inhalation (^{222}Rn)	200–10000	1200
Ingestion (^{40}K)	200–800	300
Total	1000–10000	2400

Air travel adds about $(1.5\text{--}5.0 \mu\text{Sv/h})t$ to the average background dose where $t(\text{h})$ is the flight duration. Airline pilots are monitored for cancer due to this

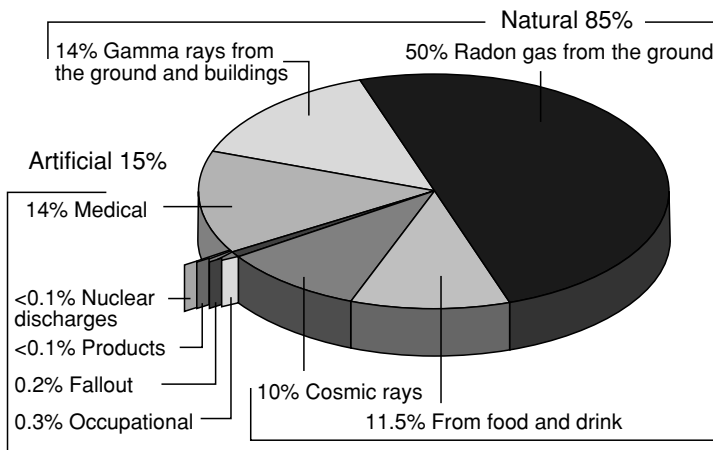


Figure 6.3: Average annual radiation dose to the UK population. Courtesy of Prof. J. Plant, Imperial College London UK.

increased risk. Exposure dose limits recommended by the ICRP are as follows: for general public 1 mSv/year, and for nuclear workers 20 mSv/year averaged over five consecutive years.

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Chapter 7

Nuclear Waste Regulations

7.1. Regulatory Organisations

The nuclear power generation industry is mature and more highly regulated than any other. Laws and regulations for the nuclear industry typically require licensing various aspects of its activities including implementation of technical and environmental standards for protecting people from radiological and other hazards. National and international bodies (Fig. 7.1) provide recommendations on radiation protection and the most influential of the latter are:

ICRP – International Commission on Radiological Protection,

ICRU – International Commission on Radiological Units and Measurements,

UNSCEAR – United Nations Scientific Committee on the Effects of Atomic Radiation and

IAEA – International Atomic Energy Agency.

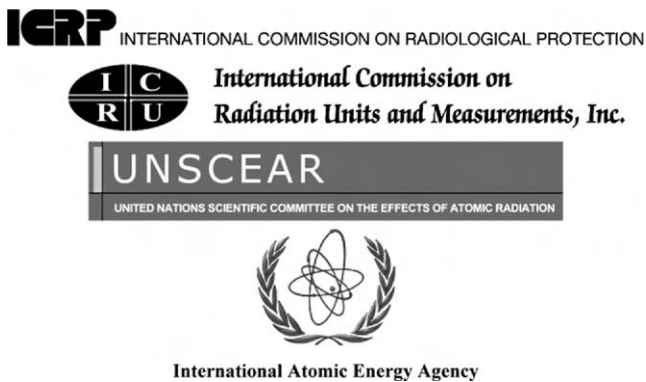


Figure 7.1: Symbols of international organisations providing recommendations on radiation protection.

Recommendations made by these organisations eventually become internationally acknowledged legal standards. Governments are responsible for enforcing national regulations through a system that includes a Regulatory Authority or similar body. Regulatory authorities such as the Environmental Protection Agency (EPA) in the USA or Gosatomnadzor in Russia establish a system of regulatory documents and define levels for radionuclides that are accepted as safe. Some international recommendations often serve as the basis for many of the regulations on radiation protection adopted by national regulatory bodies.

7.2. Protection Philosophies

Radiation and radioactive substances are natural and permanent features of the environment, and thus the risks associated with radiation exposure can only be restricted, not eliminated entirely. The acceptance by society of risks associated with radiation and radioactive materials must be conditional on the benefits to be gained from their use. Nonetheless, the risks must be minimised. The underlying philosophies of radiation protection have evolved over time. Early protection philosophies were based on individual protection from acute doses such as the tolerance dose. Nuclear weapons testing programmes and development of civil nuclear power reactors lead to broadening of these philosophies to encompass chronic exposure of populations (the collective dose, Section 6.3) notably with respect to genetic doses. Finally, regulations addressing sources of radiation were promulgated to minimise doses to people receiving exposure to them.

For regulatory purposes the term *source* means anything that causes radiation exposure, hence source includes both a radioactive material and a source of radiation. Any human activity that introduces additional sources of exposure or exposure pathways is considered as a *practice*. Three ICRP general principles of radiation protection are:

1. *Justification*. The overall effect of activities involving risks from radiological hazards should be to do more good than harm;
2. *Optimisation*. Radiological risks should be managed so that they are as low as can reasonably be achieved (ALARA);
3. *Dose and risk limits*. Individual exposure from all sources susceptible to control are subject to dose limits and some control of risk from potential exposures.

Intervention is any activity that decreases overall exposure by removing existing sources, modifying pathways or reducing the number of exposed individuals.

The intervention should do more good than harm; and the form, scale and duration of the intervention should be optimised.

7.3. Regulation of Radioactive Materials and Sources

Some radioactive materials and radiation sources are beyond human interference such as primordial radionuclides present in the human body (Sections 5.2 and 5.8) or cosmic radiation (Section 5.3) and so are excluded from regulation. *Exclusion* covers such materials and sources of radiation not amenable to control (such as ^{40}K in the human body). Items or practices that are excluded from control never enter the regulatory arena (Fig. 7.2).

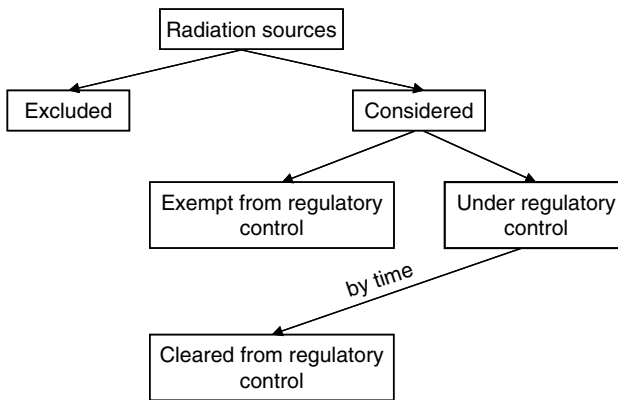


Figure 7.2: Approach to regulation of radioactive sources and materials.

All other sources are considered within the regulatory arena and are divided into exempt sources and sources under regulatory control. *Exempt* from regulatory control are sources that give rise to risks, which are so low that control would be a waste of societal resources. Sources under regulatory control may be further released from regulatory control when they do not represent any significant risk. *Clearance* refers to sources that have earlier been regulated but with time have become released from regulatory control (Fig. 7.2).

7.4. Exemption Criteria and Levels

The criteria for exemption were established by the IAEA following ICRP recommendations and principles. The criteria used to derive exemption levels for radioactive materials are:

- (a) an expected individual effective dose not higher than $10 \mu\text{Sv}/\text{year}$;
- (b) a collective effective dose not higher than $1 \text{ person-Sv}/\text{year}$.

Exemption levels were established for both concentration and total amount of radionuclides based on the individual and collective dose. These were determined for each radionuclide taking account of all possible pathways to humans including assessment of individual and collective doses. Exemption levels are published in the IAEA Basic Safety Standards (BSS), e.g. the International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources. Table 7.1 gives examples of exemption levels for some naturally occurring and waste radionuclides.

Sources of radiation are exempt from control if at a distance of 0.1 m the dose rate is below $1 \mu\text{Sv}/\text{h}$.

7.5. Clearance of Materials from Regulatory Control

Clearance levels for releasing materials and items with concentrations and total activity below specific levels are established in accordance with national legislation. Based on international approaches and exemption levels, national regulatory authorities establish the clearance or exemption levels for radionuclides. Following the exemption (clearance) approach materials are considered non-radioactive at low concentrations and low total amounts of radionuclides. It is important to note that concentration for radioactive material means activity per unit mass or volume (units Bq/g or Bq/m^3) while amount is the total activity (in Bq) for the total volume or mass of material being considered. Similarly for non-radioactive waste concentration is in g/m^3 and total amount is in g , so the same approach is used for both non-radioactive (toxic) and radioactive wastes (Fig. 7.3). The material is termed radioactive when either concentration or amount exceeds clearance levels.

Clearance levels are defined by the national regulatory authorities, however, since these take into account internationally approved recommendations, quantified clearance levels (with some exceptions) are similar in all countries.

The European Commission (EC) issued Council Directive 96/29 Euratom (OJ L159 29 June 1996) which establishes exemption levels for radionuclides similar to those recommended by the IAEA BSS. The UK regulations are codified in the Radioactive Substances Act of 1993 and the Ionizing Radiation Regulations of 1999. The Radioactive Substances (Substances of Low Activity) Exemption Order (SoLA EO), made under the Radioactive Substances Act, gives general exemption from registration and authorisation for materials containing low levels of radioactivity such as those used in household smoke

Table 7.1: Exemption levels according to IAEA BSS

Nuclide	Activity concentration (Bq/g)	Activity (Bq)
³ H	10 ⁶	10 ⁹
¹⁴ C	10 ⁴	10 ⁷
⁴⁰ K	10 ²	10 ⁶
⁶⁰ Co	10	10 ⁵
⁹⁰ Sr	10 ²	10 ⁴
⁹⁹ Tc	10 ⁴	10 ⁷
¹⁰⁶ Ru	10 ²	10 ⁵
¹²⁵ I	10 ³	10 ⁶
¹²⁹ I	10 ²	10 ⁵
¹³⁴ Cs	10	10 ⁴
¹³⁵ Cs	10 ⁴	10 ⁷
¹³⁷ Cs	10	10 ⁴
¹⁴⁴ Ce	10 ²	10 ⁵
¹⁴⁷ Pm	10 ⁴	10 ⁷
¹⁵¹ Sm	10 ⁴	10 ⁸
¹⁵⁴ Eu	10	10 ⁶
²²² Rn	10	10 ⁸
²²⁶ Ra	10 ¹	10 ⁴
²³² Th	1	10 ³
²³⁵ U	10	10 ⁴
²³⁸ U	10	10 ⁴
²³⁷ Np	1	10 ³
²³⁹ Np	10 ²	10 ⁷
²³⁸ Pu	1	10 ⁴
²³⁹ Pu	1	10 ⁴
²⁴⁰ Pu	1	10 ³
²⁴¹ Pu	10 ²	10 ⁵
²⁴² Pu	1	10 ⁴
²⁴¹ Am	1	10 ⁴
²⁴² Am	10 ³	10 ⁶
²⁴³ Am	1	10 ³
²⁴² Cm	10 ²	10 ⁵
²⁴³ Cm	1	10 ⁴
²⁴⁴ Cm	10	10 ⁴
²⁴⁵ Cm	1	10 ³
²⁴⁶ Cm	1	10 ³

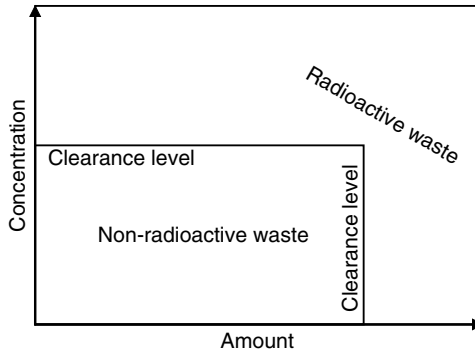


Figure 7.3: Radioactive waste contains either concentrations or amounts of radionuclides exceeding clearance levels.

alarms. The Russian Federation regulations are contained in the Norms of Radiation Safety (NRB-99).

7.6. Double Standards

Current exemption levels for the nuclear industry are based on the $10\ \mu\text{Sv}/\text{year}$ dose limit. This is an extremely small value compared to levels of background radiation, which depending on location, vary from 1000 to 10 000 $\mu\text{Sv}/\text{year}$ (see Fig. 6.2). Moreover, background radiation fluctuates with time by tens of per cent from its average in the same place. Exemption levels using the $10\ \mu\text{Sv}/\text{year}$ dose limit are highly conservative.

Application of IAEA BSS exemption levels (e.g. based on the $10\ \mu\text{Sv}/\text{year}$ dose constraint) to NORM and TENORM is impossible as it would stop many industrial activities including oil, gas and coal mining. For example, the largest TENORM waste stream is coal ash, carrying ^{238}U and all its non-gaseous decay products, as well as ^{232}Th and its progeny. Coal ash is produced globally in amounts exceeding 280 million tonnes each year. A compromise solution has led to double standards: lower levels for the nuclear industry and higher levels for non-nuclear industries. This allows, e.g. coal ash to be buried in landfill sites which it could not be if it were a waste from the nuclear industry. Another dose constraint ranging from 100 to 1000 $\mu\text{Sv}/\text{year}$ is applied to recyclable materials from the oil and gas industries. This constraint applied for TENORM is still only $\sim 10\%$ of most natural background levels and so is within the natural dose variation range with time. Moreover, this constraint is two orders of magnitude lower than that experienced naturally by many people living in areas with high

background levels of radiation (Fig. 6.2) who suffer no apparent ill effects. However, for release of materials from the nuclear industry the $10\mu\text{Sv}/\text{year}$ dose constraint is still applied. Thus double standards apply so that materials with identical levels of activity could be reused if generated as waste from non-nuclear industries but must be treated as radioactive waste if generated by the nuclear industry.

7.7. Dose Limits

The third principle of radiation protection after optimisation and justification states that individual irradiation doses are limited by certain threshold levels. In fact, as emphasised by the ICRP and IAEA, the choice of a dose limit is not, and cannot be, a matter of science and scientific judgement alone. The final decision is essentially a political and economic one that needs to be made as part of the national regulatory process. So the ICRP and IAEA BSS-recommended limits represent a professional judgement based on a complex and sophisticated multi-attribute analysis. The dose limits recommended by the ICRP (which may vary slightly from national values) are given in Table 7.2.

Table 7.2: Dose limits for individual exposure

Dose		Occupational ($\mu\text{Sv}/\text{year}$)	Public ($\mu\text{Sv}/\text{year}$)
Effective		20	1
Effective in any single year		50	–
Annual equivalent	Eye lens	150	15
	Skin	500	50
	Hands and feet	500	–

7.8. Control of Radiation Hazards

A key principle of radiation protection is the minimisation of personnel dose. The level of radiation must be assessed to diminish the occupational radiation hazard and three parameters are usually emphasised as controlling the radiation hazard: time, distance and shielding. These are based on estimates of irradiation dose received in a field of a radiation source. Radiation fields near a source of gamma radiation can be assessed by approximating it to an isotropic (uniform in all directions) point source. The dose rate of gamma radiation

P ($\mu\text{Sv/h}$) at distance r (m) from an isotropic point source of radiation of total activity Q (Bq) behind a shield with the reduction ratio k can be assessed as:

$$P = \frac{QK_\gamma}{kr^2} \tag{7.1}$$

where K_γ is the ambient dose equivalent rate ($\mu\text{Sv m}^2/\text{h/GBq}$).

The reduction ratio k for a shield of thickness d (m) can be assessed as:

$$k = 2^{d/L_{0.5}} \tag{7.2}$$

where $L_{0.5}$ (m) is the half-value thickness of shielding material for given type of radiation. For gamma radiation, dense materials such as lead and steel are the most effective, and therefore, these materials are frequently used in packaging and shielding designs. Table 7.3 gives K_γ and $L_{0.5}$ for gamma radiation arising from a number of radionuclides.

Table 7.3: Parameters of gamma radiation emitted from some radionuclides

Radionuclide	Ambient dose equivalent rate ($\mu\text{Sv m}^2/\text{h/GBq}$)	Half-value of lead (mm)
^{60}Co	380	12
^{137}Cs	92	6
^{226}Ra (in equilibrium with decay products)	283	14
^{241}Am	19	0.2

The dose D (μSv) received in a field of radiation of dose rate P ($\mu\text{Sv/h}$) is proportional to time of exposure t (h):

$$D = Pt = \frac{QK_\gamma}{kr^2} t \tag{7.3}$$

Therefore, the dose from external radiation can be reduced either by reducing the *time* spent near the source (making t smaller), or by moving a greater *distance* from the source (making r larger), or by *shielding* (making k higher). Three ways of diminishing the radiation hazard are hence time, distance and shielding. Reducing the time spent near the source of radiation will reduce the total dose that a person receives. Increasing distance from a source is a good way of reducing the radiation dose rate and hence the total doses. For small sources emitting gamma rays, the inverse square law applies. Doubling the distance will reduce the dose rate to one quarter.

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Chapter 8

Principles of Nuclear Waste Management

8.1. International Consensus

The acceptance by society of risks associated with radiation and radioactive materials is conditional on the benefits to be gained from their use. A key issue, if radiation and radionuclides are to continue to be used and accepted by the public, is the safe management of nuclear waste. There is justifiable public concern about nuclear waste management, in particular, that planned for high-level waste (HLW), which may include spent nuclear fuel and spent sealed radioactive sources. Lack of public acceptance often leads to the so-called “not in my backyard” (NIMBY) syndrome. Although this lack of acceptance has a number of roots, the central issue is that of safety and it is not only a question of achieving safety but also of convincing people that safety is achievable. Despite the technical difficulties associated with HLW disposal, it cannot be postponed and remains the responsibility of the current generation. The essence of this requirement is expressed in the internationally approved document “The Principles of Radioactive Waste Management” (IAEA, Vienna, 1995), which has involved input from many countries with experience of the nuclear industry. Moreover, the IAEA has approved procedures for the safety of un-reprocessed spent fuel as well as reprocessed high level radioactive waste management through the Joint Convention, which establishes commonly shared safety objectives and sets out specific obligations for states generating such materials. The Radioactive Waste Management Committee of the Organisation for Economic Co-Operation and Development (OECD) Nuclear Energy Agency approved the Environmental and Ethical Basis of the Geological Disposal of Long-lived Radioactive Waste. All of these efforts and publications are geared towards ensuring both safety and public acceptance of nuclear energy worldwide.

8.2. Objective of Radioactive Waste Management

The objective of radioactive waste management is to deal with radioactive waste in a manner that protects human health and the environment, now and in the future, without imposing an undue burden on future generations. National regulations and internationally recommended standards and guidelines have been developed dealing with radiation protection and radioactive waste management. It has been an exemplary feature of radioactive waste management that special attention has been given to protection of future generations. Particular consideration is given to potential radiation exposure, the possible need for surveillance or maintenance and economic consequences.

8.3. Fundamental Principles

Improperly managed radioactive waste would undoubtedly result in adverse effects to human health and the environment now and for many generations to come. Adherence to the nine accepted fundamental principles of nuclear waste management (Table 8.1) will ensure that such effects do not occur.

8.4. Comments on the Fundamental Principles



Protection of human health

Many of the hazards induced by radioactive waste are similar to those associated with toxic waste produced by industries, associated with, e.g. mining and chemical plant operations and should be controlled. However, lack of care with radioactive waste may lead to exposure to ionising radiation. An acceptable level of protection therefore needs to be provided. It is necessary to control the ways that humans might be exposed to radiation, and to ensure that such exposure is within established limits. For activities extending over extremely long time periods, e.g. radioactive waste disposal, it is necessary to consider the fact that the benefits and the exposures that might result, will affect populations separated by many generations, and that long time periods lead to increased uncertainties in the results of safety assessments.

Table 8.1: Fundamental principles of nuclear waste management

1. Protection of human health	Radioactive waste shall be managed in a way to secure an acceptable level of protection for human health.
2. Protection of the environment	Radioactive waste shall be managed in a way that provides protection of the environment.
3. Protection beyond national borders	Radioactive waste shall be managed in such a way as to assure that possible effects on human health and the environment beyond national borders will not be greater than what is acceptable within the country of origin.
4. Protection of future generations	Radioactive waste shall be managed in a way that predicted impacts on the health of future generations do not exceed relevant levels that are acceptable today.
5. Burdens on future generations	Radioactive waste shall be managed in a way that will not impose undue burdens on future generations.
6. Legal framework	Radioactive waste shall be managed within an appropriate legal framework including clear allocation of responsibilities and provision for independent regulatory functions.
7. Control of radioactive waste generation	Generation of radioactive waste shall be kept to the minimum practicable.
8. Radioactive waste generation and management interdependencies	Interdependencies among all steps in radioactive waste generation and management shall be appropriately taken into account.
9. Safety of facilities	Safety of facilities for radioactive waste management shall be appropriately assured during their lifetime.



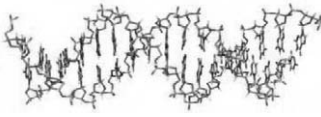
Protection of the
environment

When radionuclides are released into the environment, species other than humans can potentially be exposed to ionising radiation and the impact of such exposures must be considered. Since humans are among the most radiation-sensitive organisms, measures taken to protect individual humans from radiation hazards are, in general, considered adequate to protect other species, although these measures may not necessarily protect individual members of the species. Therefore, the presence of humans should generally be assumed when assessing the impact on the environment, particularly when assessing radioactive waste disposal. Radioactive waste disposal, like chemical waste disposal, may adversely affect future local availability or utilisation of natural resources, e.g. land, forests, surface water, ground water and raw materials, over extended periods of time. Radioactive waste management, therefore, should be conducted in such a way as to limit these effects. Possible future exploration for, or exploitation of, valuable natural resources could potentially result in adverse effects on the containment capability of a repository. Thus, possible future exploration or exploitation should be taken into account when siting and designing repositories. Radioactive waste management activities may also result in non-radiological environmental impacts, such as chemical pollution or alteration of natural habitats, which must also be considered.



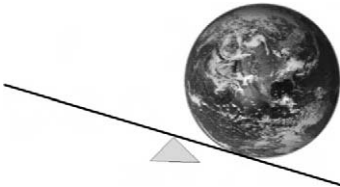
Protection beyond national
borders

This principle is based on the ethical premise that a country has a duty to behave responsibly towards its neighbours. In the case of normal release, potential release or migration of radionuclides across national borders, the country of origin and the affected countries may choose to agree to expand on this principle, e.g. through information exchange.



Protection of future generations

This principle is derived from an ethical concern for the health of future generations. While it is not possible to ensure total containment and isolation of radioactive waste over extended timescales, the intent is that there will be no significant impact on human health when radionuclides enter the environment. In implementing radioactive waste management, particularly for disposal, uncertainties in the long-term safety assessment should be taken into account, e.g. by using the multiple barrier approach (see Sections 12.3 and 19.3).

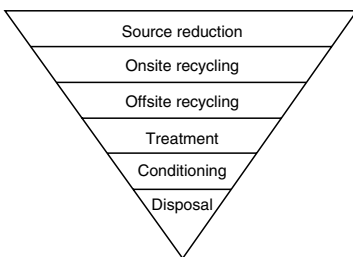


Burdens on future generations

This principle is based on the ethical consideration that the generation that produces waste should be responsible for managing it. Some activities, however, may be passed to succeeding generations, e.g. continued institutional control over a repository. The responsibility of the present generation includes developing the technology, constructing and operating the facilities, and providing a funding system and sufficient controls for the management of radioactive waste. This includes providing the means and the technology for disposal. The timing and implementation of disposal of individual radioactive waste types will depend on scientific, technical and economic factors such as the availability and development of suitable sites and the decay of radioactivity and heat during interim storage. Timing and implementation are also affected by political and public acceptance. Management of radioactive waste should not rely on long-term institutional control as a necessary safety feature, although future generations may decide, e.g. to monitor radioactive waste repositories. The identity, location and inventory of a waste disposal facility should be appropriately recorded.



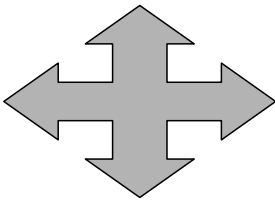
Legal framework



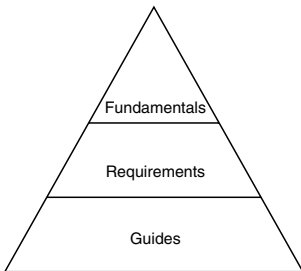
Control of radioactive waste generation

Countries in which radionuclides are produced or used should develop a national legal framework, taking into account overall strategies, and providing laws, guidelines and regulations for radioactive waste management. The responsibilities of each party or organisation involved in radioactive waste management should be clearly allocated for all waste management activities that take place in a country. Separation of the regulatory function, including enforcement, from the operating function, is required especially, to ensure safe operation of facilities. This ensures an independent review and oversight of radioactive waste management activities. The legal framework should specify the way in which separation of the functions is achieved. Since radioactive waste management can span timescales involving many human generations, appropriate consideration of present, and likely future, operations should be taken into account. Sufficiently long-lasting administration, including continuity of responsibilities, and funding requirements should also exist.

The generation of radioactive waste, both in activity and volume, must be kept to the minimum practicable by appropriate design measures and operating practices. This includes the selection and control of material, recycling and reuse of materials, and the implementation of appropriate operating procedures. Emphasis should be on segregation of different types of waste and materials to reduce the amount of radioactive waste to be managed. Safe radioactive waste management includes keeping the releases from the various waste management steps to the minimum practicable. The preferred focus of radioactive waste management should generally be on concentrating and containing radionuclides rather than dilution and dispersion in the environment.



Radioactive waste
generation and management
interdependencies



Safety of facilities

The basic steps of radioactive waste management are pre-treatment, treatment, conditioning, storage and disposal. A holistic approach is necessary as each step has some influence on the others. Decisions on radioactive waste management made at one step may foreclose alternatives for or otherwise affect a subsequent step. Such decisions should be consistent with the safety requirements for disposal. Further, there are relationships between waste management steps and operations that generate radioactive waste or recyclable materials. Those responsible for a particular waste management step or operation generating waste must adequately recognise these interactions and relationships so that safety is not compromised. This includes taking into account the implications of transporting radioactive waste. Conflicting requirements that could compromise operational and long-term safety should be avoided. Since the steps of radioactive waste management occur at different times, there are, in practice, many situations where decisions must be made before all radioactive waste management activities are established. As far as reasonably possible, the effect of future radioactive waste management activities should be taken into account at the time when any radioactive waste management activity is considered.

Siting, design, construction, operation and decommissioning of a facility or closure of a repository should be carried out giving safety and accident prevention priority. Public issues should be addressed throughout these steps. Site selection should take into account relevant features, which might affect the safety of the installation or which might be affected by the installation. Design, construction and operation should provide and maintain, where applicable, several levels of protection to limit any

possible radiological impacts. Application of the appropriate level of quality assurance and of adequate personnel training and qualification should be addressed throughout the life of radioactive waste management facilities. Appropriate assessments should be performed to evaluate the safety and environmental impact of the facilities.

8.5. Ethical Principles

The Environmental and Ethical Basis of the Geological Disposal of Long-lived Radioactive Waste formulated in 1995 by the Radioactive Waste Management Committee of the OECD Nuclear Energy Agency (OECD NEA) concluded that:

The geological disposal strategy can be designed and implemented in a manner that is sensitive and responsive to fundamental ethical and environmental considerations; both environmentally and ethically it is justified to continue development of geological repositories for those long-lived radioactive wastes which should be isolated from the biosphere for more than a few hundred years; stepwise implementation of plans for geological disposal leaves open the possibility of adaptation, in the light of scientific progress and social acceptability, over several decades, and does not exclude the possibility that other options could be developed at a later stage.

In pursuing the reduction of risk from a geological disposal, current generations should keep in perspective the resource deployment in other areas with potential for greater reduction of risks.

8.6. Joint Convention

The Joint Convention on the Safety of Spent Fuel Management and on the Safety of Radioactive Waste Management is the first international legal instrument to directly address these issues on a global scale. The Joint Convention applies to spent fuel and radioactive waste resulting from civilian nuclear reactors and applications and from military or defence programmes. It also applies to planned and controlled releases into the environment of liquid or gaseous radioactive materials from regulated nuclear facilities. The obligations with respect to the safety of spent fuel and radioactive waste management are based, to a large extent, on the fundamental principles outlined in Table 8.1.

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Chapter 9

Sources and Characteristics of Nuclear Wastes

9.1. Key Waste Characteristics

Radioactive waste is material that contains, or is contaminated with, radionuclides at concentrations or activities greater than established clearance levels, and for which no use is foreseen. The characteristics of radioactive waste have a major influence on the selection of processing methods and final disposal options. Characterisation of radioactive waste is important also for its proper classification. A number of parameters are considered in classification schemes, the most important of which are shown in Table 9.1.

9.2. Classification Schemes

Key parameters in any classification scheme are the radionuclide concentrations and half-lives. Radioactive waste is generally classified by activity level into exempt, low-level waste (LLW), intermediate-level waste (ILW) and high-level waste (HLW). Often LILW is used to mean low and intermediate level wastes. The most commonly accepted classification scheme includes radionuclide half-lives by separating waste into two classes: short lived and long lived (Fig. 9.1).

The most important classes of radioactive wastes are defined as follows:

Exempt waste. It has activity levels (concentrations and total amounts) below exemption levels. This waste is excluded from regulatory control because radiological hazards are negligible (see Chapter 7).

Low-level waste (LLW). It has activity levels above clearance levels, but does not require shielding in handling or storage. LLW with extremely low activity

Table 9.1: Important characteristics of radioactive wastes

Property	Origin	Radiological	Physical	Chemical	Biological
Parameter	Source, manufacturer	Criticality; half-life; heat generation; intensity of radiation; activity and concentration of radionuclides; surface contamination; dose factors of relevant radionuclides	Physical state (solid, liquid, gas); size, volume and weight; compressibility; dispersibility; volatility; solubility; miscibility	Potential chemical hazard; corrosion resistance; corrosiveness; organic content; combustibility; reactivity; gas generation; sorption of radionuclides	Potential hazard; decomposition rate and products

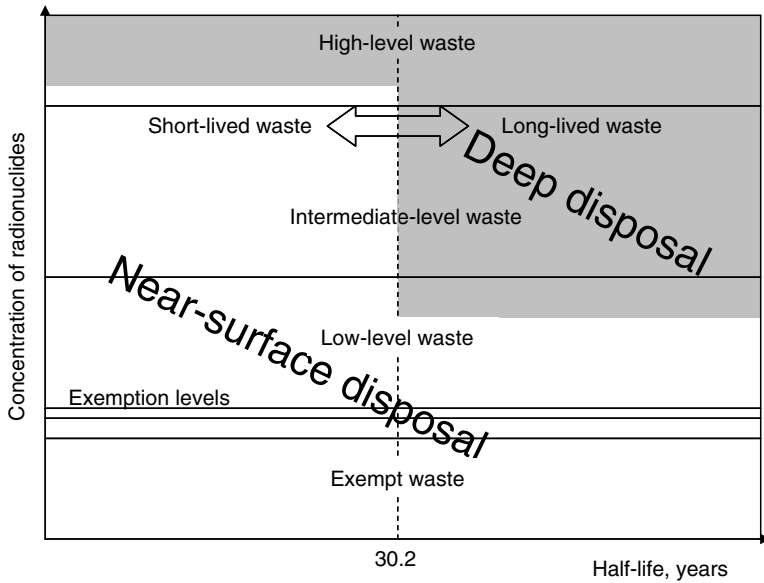


Figure 9.1: Classification of radioactive wastes.

levels can be acceptable for landfill disposal and is classified as very low-level waste (VLLW).

Intermediate-level waste (ILW). It contains higher activity levels compared to LLW and requires shielding in handling or storage. ILW with low content of long-lived radionuclides is acceptable for near-surface disposal.

High-level waste (HLW). It has substantial high activity levels and requires extensive personnel protection, shielding, remote handling and consideration of the effects of radiogenic heat generation. Typically, this waste arises from spent nuclear fuel reprocessing or is the spent fuel itself. HLW requires deep underground disposal.

Short-lived waste. It does not contain significant levels of radionuclides with half-lives greater than that of ^{137}Cs , i.e. 30.2 years. Specific levels depend on the disposal option and are determined in each case through performance assessment modelling (see Chapter 20). Concentrations are usually limited to ≤ 4000 Bq/g in an individual waste package and an overall average concentration of 400 Bq/g in all packages. Short-lived LLW and ILW are acceptable for near-surface disposal.

Long-lived waste. It contains significant levels of radionuclides with half-lives greater than 30.2 years and requires deep underground disposal.

9.3. Examples of Waste Classification

Classification of radioactive waste varies from country to country. In the UK, radioactive wastes are classified as VLLW, LLW, ILW and HLW (Table 9.2).

Russia classifies radioactive wastes as LLW, ILW and HLW (Table 9.3).

Table 9.2: Classification of radioactive waste in the UK

Class	Description
VLLW	Wastes which can be disposed of with ordinary refuse, each 0.1 m ³ of material containing less than 400 kBq of beta/gamma activity or single items containing less than 40 kBq
LLW	Containing radioactive materials other than those suitable for disposal with ordinary refuse, but not exceeding 4 GBq/t of alpha or 12 GBq/t of beta/gamma activity – that is, wastes which can be accepted for authorised disposal at Drigg, Dounreay or other landfill sites by controlled burial.
ILW	Wastes with radioactivity levels exceeding the upper boundaries for LLW, but which do not need heating to be taken into account in the design of storage or disposal facilities.
HLW	Wastes in which the temperature may rise significantly as a result of their radioactivity, so this factor has to be taken into account in designing storage or disposal facilities.

9.4. Sources of Waste

Nuclear waste arises from three main sources, the Nuclear Fuel Cycle (NFC) used for power generation and military uses, Non-NFC institutes (including non-nuclear industries, medical and research institutions) and Accidents. Schematically these are shown in Fig. 9.2 where (not to scale) the relative volume is indicated along the *x*-axis and the relative hazard along the *y*-axis.

The NFC is the main source of radioactive waste. NFC produces all types of radioactive wastes, including HLW, which are further defined as Open NFC and Closed NFC. In the Open NFC, spent nuclear fuel is disposed of without reprocessing (as HLW) whereas in the Closed NFC, spent nuclear fuel is reprocessed to extract fissile U and Pu and only the remaining HLW is disposed of (Fig. 9.3).

Unfortunately, during the early part of the nuclear era consideration was not given to disposal of radioactive waste or in design of systems with the total cycle concept in mind. As a result some NFC wastes (now termed legacy or

Table 9.3: Classification of radioactive waste in Russia

Category of waste	Specific radioactivity (Bq/g)		
	Beta radionuclides	Alpha radionuclides	Transuranic* radionuclides
Low level	Less than 10^3	Less than 10^2	Less than 10
Intermediate level	More than 10^3 but less than 10^7	More than 10^2 but less than 10^6	More than 10 but less than 10^5
High level	More than 10^7	More than 10^6	More than 10^5

*Transuranic radionuclides have atomic numbers of 93 or greater

historic wastes) are ill-characterised and stored under conditions which are far from ideal. They comprise a vast range of materials, e.g. Pu-contaminated materials (PCM) such as paper, wood and plastics, fuel cladding, damaged and corroded fuel elements, old tools and equipment and assorted test samples (Fig. 9.4) often mixed together. Sometimes these have been stored under water and have degraded over time to form complex sludges and supernatant liquids.

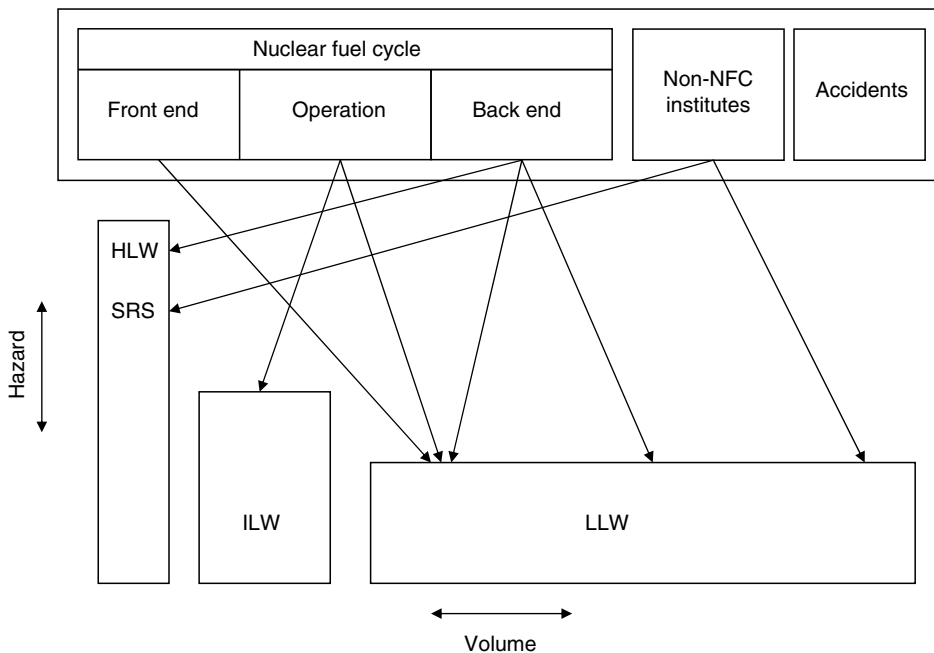


Figure 9.2: Main sources of radioactive waste. SRS are spent sealed radioactive sources.

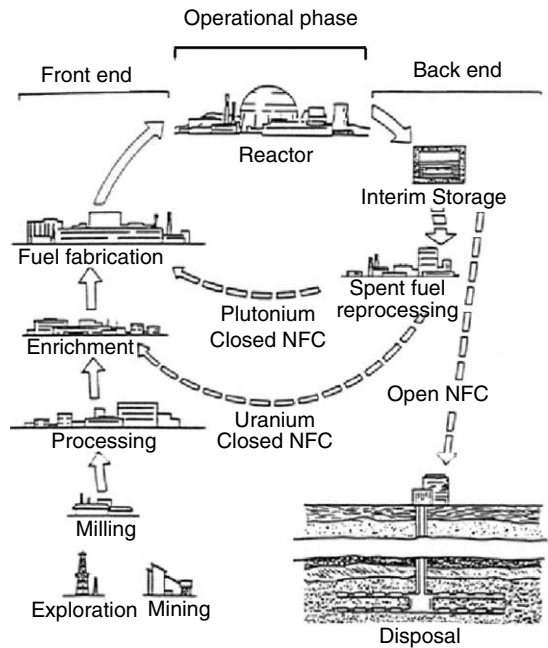


Figure 9.3: Schematic of Closed and Open NFC.



Figure 9.4: Typical legacy waste.

At the Hanford site in the USA 177 tanks each holding up to a million gallons of ill-defined radioactive material (Fig. 1.2) from the USA's military programme were built, some with single walls, which leaked their contents into the underlying soil. Overall the tank wastes are made up of pumpable liquids; a water-soluble precipitate known as salt cake and insoluble particulate material termed sludge. A costly clean-up and storage operation is underway. Similar although not as massive problem wastes are present in most of the established nuclear-generating countries. Figure 9.5 shows a disused Magnox storage pond at Sellafield, UK holding 1000 m³ of sludge. Fortunately, this tank is not leaking.

In addition, large volumes of weapons-grade Pu left over from the cold war era and the arms race between the USSR and the USA must be managed. In some countries including the UK, such Pu is not regarded as a waste but as a resource because it can be recycled in MOX fuel and used to generate electricity (see Chapter 18).

Non-NFC institutions generate lower amounts but a greater range of radioactive waste. These include many industrial users of radionuclides, research institutions including nuclear research centres (often housing research reactors),



Figure 9.5: Disused Magnox storage pond at Sellafield, UK.

medical and other small users. Non-NFC institutions generate mainly LLW. However, they may produce highly radioactive wastes such as spent sealed radioactive sources (SRS) from medical use, which are highly hazardous. Accidental nuclear waste is also termed abnormal radioactive waste and is caused by unforeseen accidents involving radioactive materials such as the reactor accidents at Three Mile Island or Chernobyl and accidents with SRS such as that at Goiania, Brazil. The nature and type of accidental wastes can be very different from the more controlled wastes generated within NFC or Non-NFC institutes.

9.5. Front end and Operational NFC Waste

The NFC comprises a number of activities starting from exploration of uranium ore and ending with disposal of wastes (Fig. 9.6).

Conventionally, the NFC is divided into three phases: Front end, Operational phase and Back end which includes decommissioning of active facilities. Since the main purpose of the NFC is to produce electricity the amounts of nuclear waste generated are usually measured per 1 GW of electricity produced per year. Tables 9.4 and 9.5 give typical waste arisings from the Front end and the

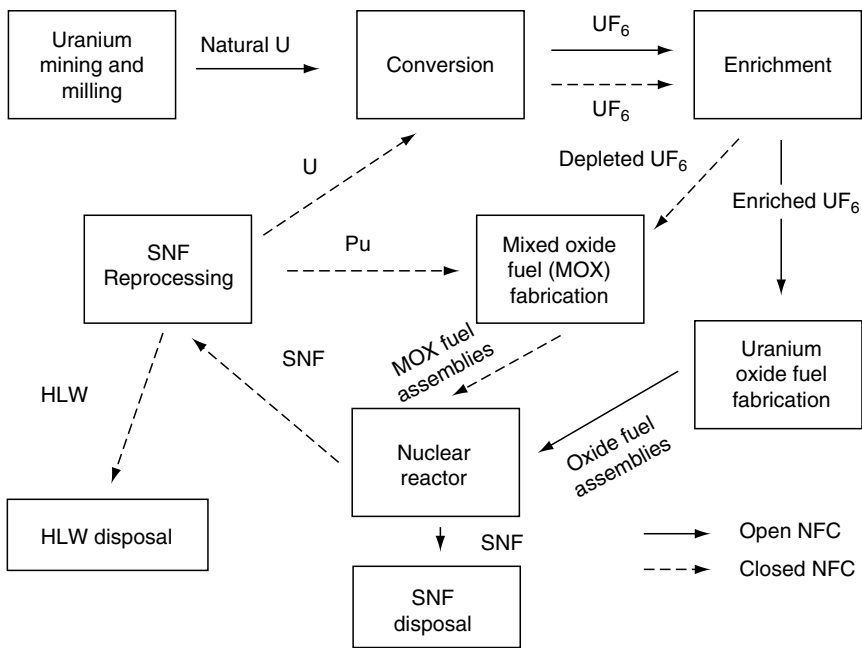


Figure 9.6: Schematic of NFC activities. SNF is Spent Nuclear Fuel.

Table 9.4: NFC Front end waste generation ($\text{m}^3/\text{GW year}$)

Stage	Waste type	Quantity
UF ₆ conversion	Liquids, solids	50
UF ₆ enrichment	Gaseous, liquids, solids	25
UO ₂ fabrication	Liquids, solids	75
MOX fabrication	Liquids	5.6

Operational phase of the NFC. Front end waste is contaminated basically with naturally occurring radionuclides (so it predominantly is TENORM) whereas operational waste also contains fission and activated products (typically LLW and to a lesser extent ILW).

The NFC Operational phase waste arises from the electricity generation process as well as from maintenance activities. Process waste is mainly generated by treatment of water from the reactor or ancillaries including spent fuel storage ponds and some decontamination operations. Standard effluent treatment technologies are based on evaporation (distillation), ion exchange, filtration or centrifuging (see Chapter 14). Typical process wastes of pressurised water reactors (PWR) are borated water concentrates, sludge or filter cartridges, and organic bead resin ion exchangers (blow-down resins) from primary and secondary circuits whereas those from boiling water reactors (BWR) are water concentrates and sludge containing different types of ion exchange or filter media as organic powdered resins, diatomaceous earth, activated carbon, cellulose and organic bead resins.

Maintenance (or technological) waste is mainly solid waste comprising spent or damaged and contaminated equipment which cannot be repaired or recycled, and items such as contaminated clothes from operators, cardboard, bags, tools and plastic sheeting from maintenance work. Maintenance waste arises also

Table 9.5: NFC Operational phase waste generation ($\text{m}^3/\text{GW year}$)

Stage	Waste type	Quantity
Evaporator concentrates	Liquids	50
Filter sludges	Liquids	10
Ion exchange resins	Solids	2
Decontamination concentrates	Liquids, solids	10
Absorber rods, neutron sources, etc.	Solids	0.1
Others	Solids	260

from dismantling the internal structures of the reactor core including the used control rods. Liquid technological wastes comprise mainly oils and small amounts of lubricants and organic solvents used for decontamination.

Typically the main radioactive contaminants in operational waste are short-lived radionuclides such as ^{60}Co , ^{90}Sr , ^{134}Cs and ^{137}Cs although long-lived radionuclides can be present in the internal elements of reactors.

9.6. Back End Open NFC Waste

Newly fabricated uranium oxide fuel contains up to 5% ^{235}U and the rest is ^{238}U . Nuclear reactions in the reactor burn up part of the uranium and produce radionuclides. Eighty per cent of ^{235}U consumed is burned by fission reactions and 20% by neutron capture to ^{236}U . ^{236}U is then burned by neutron capture to ^{237}Np , 25% of which is then converted to ^{238}Pu . 93% of the ^{238}U consumed is burned by neutron capture into ^{239}Pu and 7% by fast neutron fission. $^{239,240,241}\text{Pu}$ are all fissile. Six per cent of the ^{239}Pu produced survives as ^{242}Pu , while most of it is finally transformed by nuclear reactions into ^{243}Am and ^{244}Cm . Figure 9.7 shows the progress of nuclear reactions in a reactor as a function of time.

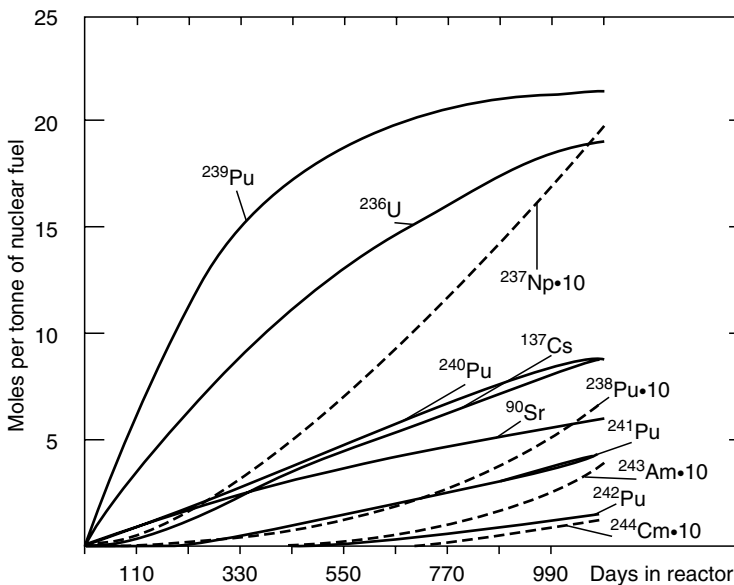


Figure 9.7: Build-up of new radionuclides as a function of time in a reactor core.

Dashed lines indicate radionuclides in which the concentrations have been multiplied by 10 to be included easily on this plot.

Table 9.6: Content of main fission products in the SNF (mol%)

Short-lived		Long-lived	
Radionuclide	Content	Radionuclide	Content
$^{106}\text{Ru}, ^{106}\text{Rh}$	0.51	^{151}Sm	0.10
^{125}Sb	0.022	^{79}Se	0.01
^{134}Cs	0.47	^{93}Zr	2.7
^{147}Pm	0.25	^{99}Tc	2.9
^{154}Eu	0.1	^{107}Pd	0.74
^{155}Eu	0.013	^{126}Sn	0.05
^{85}Kr	0.11	^{129}I	0.61
^{90}Sr	2.0	^{135}Cs	0.81
^{137}Cs	3.0	^{166m}Ho	10^{-6}

Figure 9.8a shows schematically a nuclear fuel rod and an assembly. The fuel is in the form of ceramic Pu/U oxide pellets in the metal rod. When the fuel reaches the end of its useful life, it is removed from the reactor and is considered as spent nuclear fuel (SNF). SNF contains about 95% ^{238}U , about 3% of fission products and transuranic isotopes, about 1% Pu and 1% ^{235}U . The SNF of a PWR typically contains ~ 9 g of actinides and ~ 35 g of fission products per kilogram of fuel. Actinides as can be seen from Fig. 9.5 are mostly present as ^{239}Pu . Table 9.6 gives the most important fission products but note that the actual content is a function of many parameters such as reactor type, extent of burn up and power rating.

In the Open NFC the SNF is considered as waste. SNF can serve as a final waste-form as it is a reasonably stable solid and can be encapsulated in an additional immobilising barrier such as a corrosion-resistant copper or lead container as is planned in countries such as Sweden (Fig. 9.8b). The ceramic UO_2 matrix of nuclear fuel retains the radionuclides and non-volatile fission products in its open fluorite crystal structure and its polycrystalline microstructure. The metal Zircaloy cladding of the fuel also, if intact, provides an additional barrier.

About 30 t of SNF-waste are produced per year by a typical 1 GW nuclear power plant.

9.7. Back End Closed NFC Waste

In the Closed NFC, spent nuclear fuel is reprocessed to extract useful uranium and plutonium, which are recycled for use in a nuclear reactor as mixed oxide (MOX) fuel. Several reprocessing facilities currently are in operation (Table 9.7).

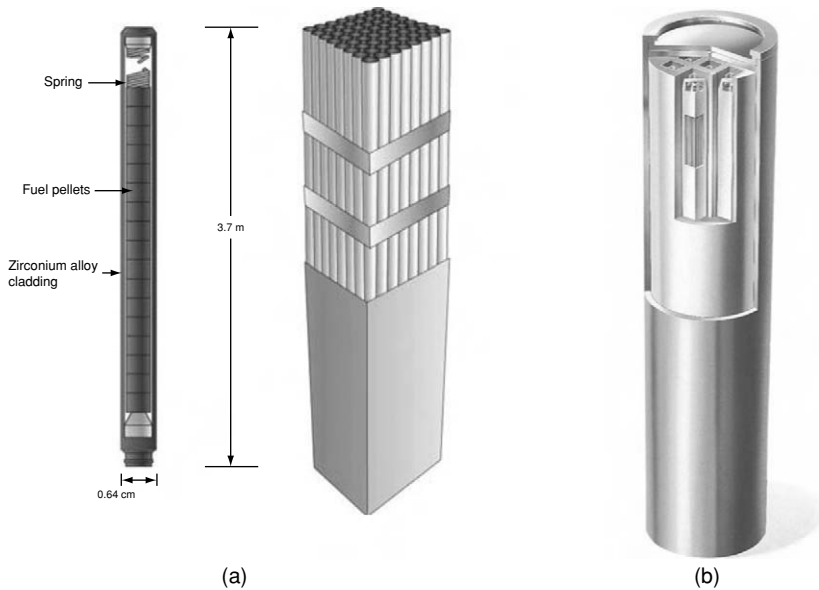


Figure 9.8: (a) Nuclear fuel rod (left) and assembly (right), (b) SNF in 5 m long copper canisters as planned for Swedish and Finnish repositories.

Reprocessing of SNF normally involves removal of the fuel rod cladding followed by dissolution of the remainder in nitric acid. This stage is then followed by chemical solvent extraction of the uranium and plutonium formed during the fuel burn-up process via the Purex (*Plutonium and Uranium Extraction*) process. The remnant solution is HLW and contains the dissolved fission products together with impurities from the cladding materials, inactive process chemicals, transuranic elements formed by neutron capture, and traces of un-separated plutonium (Fig. 9.9).

Table 9.7: SNF reprocessing facilities

Reprocessing facility	SNF reprocessed	Capacity (t)
Sellafield, UK	Light water reactors	850
Sellafield, UK	Other	1500
La Hague, France	Light water reactors	1600
Marcoule, France	Other	400
Chelyabinsk, Russia	Light water reactors	400
Japan	Light water reactors	90
India	Other	200

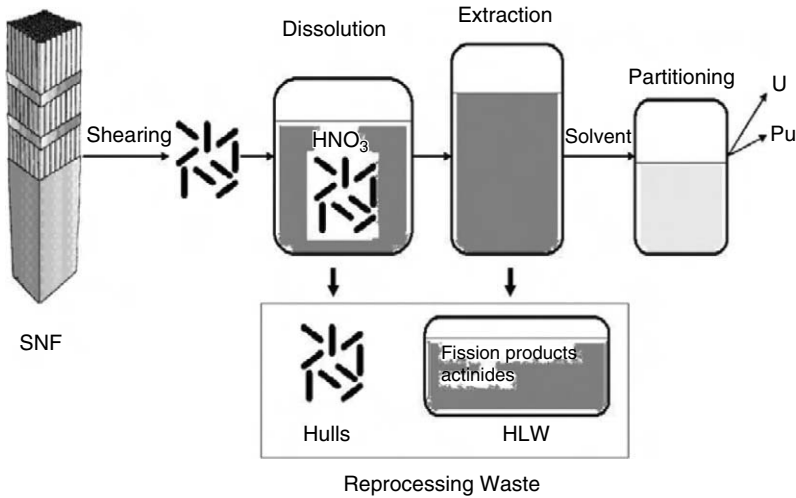


Figure 9.9: Schematic of SNF reprocessing.

HLW is concentrated by evaporation to reduce the volume and stored in aqueous nitric acid solution in stainless steel tanks. Alternatively, the solution can be neutralised by addition of an alkali. Table 9.8 gives the volumes of wastes produced by Closed NFC, not including the decommissioning stage.

HLWs contain a host of products ranging from uranium fission products to fuel alloying elements including F, Al, Si and Mo; cladding elements (Fig. 9.10) including Zr, Mo, Nb and Mg; transuranic elements including Np, Am, Cm and residual Pu. HLWs also contain some of the process chemicals including kerosene, tributyl phosphate and related organic materials. Table 9.9 gives compositions of a number of international HLW.

Table 9.8: Closed NFC Back end waste generation ($\text{m}^3/\text{GW year}$)

Stage	Waste type	Quantity
Hulls/hardware	Solids	15
Feed sludge	Solids	0.02
Tritium containing effluents	Liquids	70
HLW	Liquids	28
ILW	Liquids	25
LLW	Liquids	15
	Solids	65

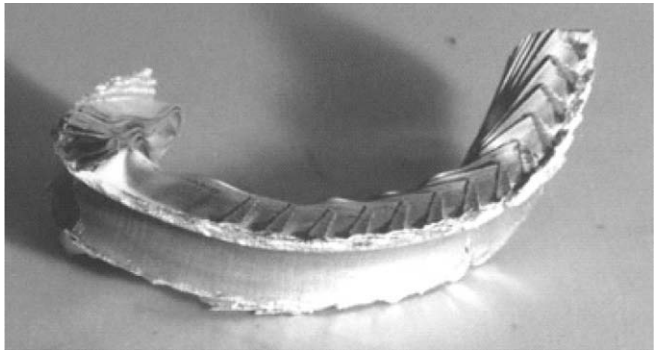


Figure 9.10: Magnox metal cladding swarf, an ILW machined from the SNF prior to its reprocessing.

Table 9.9: Composition of HLW in g/L (except for Russian waste)

Component	UK (Magnox)	France (La Hague)	Russia (mmol/L)	India (WIP)	Japan (Tokai)	USA (Hanford)
Al	26.0					1.5
Na			58.8–85.2	6.6	44.5	4.1
K			79.2–99.0	0.2		
Mg	30.0		5.6–14.0			
Fe	13.0	20.0	8.3–20.7	0.5	8.4	6.1
Ni	1.4	3.2	5.7–11.6	0.1	2.2	0.6
Cr	1.6	3.4	0.8–2.1	0.1	2.2	0.1
Mo	10.8		25.0–27.8			0.2
Zr	11.8		19.0–23.7			3.4
Hg						
Cl						0.1
SO ₄			0.01	0.5 M		0.2
NO ₃	11 M		3.5–3.8 (HNO ₃)	4.1 M		2.8
Fission products	39.1wt%	87.0	6.8–8.5 (Sr)	1.1	49.0	<2.5
Transuranic elements	2.0	5.1	<0.007	7.6	12.6	<0.1

The typical activity of HLW generated by reprocessing 1 t of SNF is about 10^{16} – 10^{17} Bq ($\sim 10^6$ – 10^7 Ci).

9.8. Back End NFC Decommissioning Waste

Decommissioning wastes are generated at the end of operation of NFC facilities including nuclear reactors. As well as waste from the radioactive ceramic fuel some structural materials become activated by elements undergoing neutron capture as discussed in Chapter 2. This will be a particular problem in projected fusion reactors generating 14 MeV neutrons (and has in fact influenced alloy design for them) but it is also important in fission reactors although it has not yet influenced selection of material for operating reactors. The high alloy steel end caps from each fuel bundle in an Advanced Gas-Cooled Reactor (AGR), for example, become so activated they are treated as HLW; as there are ~ 100 of these in each AGR assembly and a complete refuel occurs every 2 years the amount of waste is significant. The alloying elements of particular concern in steels are Co, Nb, Ni and Mo. Less activatable steels are being examined for the next generation of fission reactors (i.e. advanced LWRs, Generation IV and fast reactors) which are Co free and with substitutions of Ta for Nb, Mn for Ni and W for Mo. Neutron capture is also a problem with elements like B and Ni (again) which both produce insoluble He which forms bubbles reducing a steels toughness.

After the SNF is removed the NFC facilities must be decommissioned, demolished and eventually returned to green field or brown field use. During this process, large volumes of wastes are generated, although most is not radioactive. The amount of waste arising from decommissioning a typical nuclear power plant is 10 000–15 000 t. Much of this waste is concrete and other building material containing only small amounts of radioactivity. About a tenth of the decommissioning waste contains some radioactivity up to the intermediate level (Table 9.10).

Table 9.10: NFC Back end waste generation at decommissioning stage ($\text{m}^3/\text{GW year}$)

Stage	Waste type	Quantity
UF ₆ conversion	Solids	0.5–1
UF ₆ enrichment	Solids	5
UO ₂ fabrication	Solids	1–2
Power plant	Solids	375
Reprocessing	Solids	5

9.9. Non-NFC Wastes

Various applications of radionuclides in research, medicine and industry generate a wide spectrum of radioactive waste. The types and volumes of waste can vary extensively in radiochemical, chemical and physical content. Table 9.11 shows some waste types from Non-NFC institutions.

Research establishments such as institutes and universities are often involved in monitoring the metabolic or environmental pathways associated with materials as diverse as drugs, pesticides, fertilisers and minerals. The radionuclides most commonly employed in studying the toxicology of many chemical compounds and their associated metabolic pathways are ^{14}C and ^3H , as they can be incorporated into complex molecules with considerable uniformity. ^{125}I has proved valuable in protein labelling. A spectrum of other radionuclides is available for research. Most of the radioactive waste generated by nuclear research centres contains mainly short-lived radionuclides although long-lived radionuclides such as ^{14}C , fissile radionuclides and transuranic elements may also be present.

Medical applications of radionuclides are extremely important and continuously expanding. The main areas of applications are in radio-immunoassays, radiopharmaceuticals, diagnostic procedures and radiotherapy. The radionuclides used in hospitals for medical diagnostic procedures and treatments are very short lived, and the waste generated is usually stored for decay before further treatment as non-radioactive waste. Positron emission tomography (PET), for example, incorporates cyclotron-generated ^{11}C (20 min half-life) or ^{18}F (110 min half-life) in a molecule such as sugar, which is intravenously administered to the patient and is detected during its circulation around the

Table 9.11: Waste types from radionuclide applications

Solid	Aqueous	Organic liquids	Highly active
Metallic scrap, brickwork, sorbents including ion exchange resins, glassware, filters, cardboard, plastics, paper, swabs, tissues, protective clothes, gloves	Effluents from laboratories, hot cells, fuel storage pool, sump, decontamination, rinsing waters, mining-milling raffinates	Pump oils, scintillation liquids, extraction solvents such as tributyl phosphate (TBP), kerosene and amine	Sealed radioactive sources, radium needles, reactor-irradiated materials

Table 9.12: Some radionuclides used in medicine and biological research with half-lives longer than 100 days

Radionuclide	Half-life	Application	Typical quantity	Waste produced
^3H	12.3 years	Radio-labelling, biological research, organic synthesis	≤ 50 GBq	Solvents, solid, liquid
^{14}C	5730 years	Medical	< 1 MBq	$^{14}\text{CO}_2$
^{14}C	5730 years	Biological research, radio-labelling	≤ 50 GBq	Solid, liquid
^{14}C	5730 years	Radio-labelling	≤ 50 GBq	Solvents
^{36}Cl	3×10^5 years	Biological research	≤ 5 MBq	Gas, solid, liquid
^{57}Co	271.7 days	Clinical measurements	≤ 50 MBq	Solid, liquid
^{75}Se	119.78 days	Clinical measurements	≤ 50 MBq	Solid, liquid
^{113}Sn	155.0 days	Medical and biological research	≤ 50 GBq	Solid, liquid

body. Some radionuclides used in medical applications, however, can have longer half-lives (Table 9.12).

Medical applications of radionuclides represent the use not only of small quantities of unsealed sources and liquid solutions, but also of highly radioactive sealed radioactive sources (SRS) housed in shielded assemblies. Figure 9.11 shows the construction of a typical SRS.

Spent SRS are extremely hazardous as they may contain large quantities of radionuclides (Table 9.13).

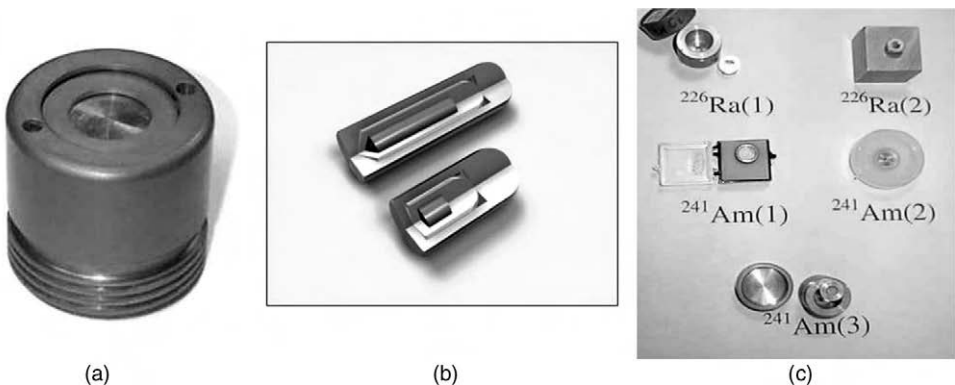


Figure 9.11: SRS: (a) ^{60}Co -teletherapy source, (b) schematic of ^{252}Cf neutron sources, (c) alpha sources.

Table 9.13: Medical applications of sealed radioactive sources (SRS)

Application	Radionuclide	Half-life	Activity of SRS	Comments
Bone densitometry	²⁴¹ Am	433.0 years	1–10 GBq	Mobile units
	¹⁵³ Gd	244.0 days	1–40 GBq	
	¹²⁵ I	60.1 days	1–10 GBq	
Manual brachytherapy	¹⁹⁸ Au	2.7 days	50–500 MBq	Small portable sources
	¹³⁷ Cs	30.02 years	30–300 MBq	
	²²⁶ Ra	1600 years	50–500 MBq	No longer used
	⁶⁰ Co	5.27 years	50–1500 MBq	
	⁹⁰ Sr	28.5 years	50–1500 MBq	
	¹⁰³ Pd	17.0 years	50–1500 MBq	
	¹²⁵ I	60.1 days	200–1500 MBq	
	¹⁹² Ir	74.0 days	5–100 MBq	
	¹⁰⁶ Ru	1.01 years	10–20 MBq	
Vascular brachytherapy	⁹⁰ Y	2.7 days	50–500 MBq	Catheterisation
	³² P	14.3 days	200 MBq	
	⁸⁹ Sr	50.6 days	150 MBq	
	¹⁹² Ir	74.0 days	0.1–1 TBq	
Remote after-loading brachytherapy	¹³⁷ Cs	30.02 years	0.03–10 MBq	Mobile units
	¹⁹² Ir	74.0 days	0.1–200 TBq	

Teletherapy	^{60}Co	5.27 years	50–1000 TBq	Fixed installations
	^{137}Cs	30.02 years	500 TBq	
Whole blood irradiation	^{137}Cs	30.02 years	2–100 TBq	Fixed installations
	^{60}Co	5.27 years	50–1000 TBq	
Research	^{60}Co	5.27 years	≤ 750 TBq	Fixed installations
	^{137}Cs	30.02 years	≤ 13 TBq	
Calibration	^{63}Ni	96 years	< 4 MBq	Fixed installations in instruments or mobile sources
	^{137}Cs	30.17 years	< 4 MBq	
	^{57}Co	271.7 days	≤ 400 MBq	
	^{226}Ra	1600 years	< 4 MBq	
	^{147}Pm	2.62 years	< 4 MBq	
	^{36}Cl	3.01×10^5 years	< 4 MBq	
Gamma radio-surgery knives	^{129}I	1.57×10^7 years	< 4 MBq	Skull cap
	^{60}Co	5.27 years	≤ 220 MBq	

Brachytherapy is a radiation therapy that allows the escalation of radiation dose while sparing normal tissues

Industrial applications of radionuclides comprise significant numbers of SRS in specialised devices for non-destructive testing and quality control as well as radioactive tracers and luminous displays (Table 9.14).

Table 9.14: Industrial applications of radionuclides

Application	Radionuclide	Half-life	Form
Thickness measurement	³ H	12.3 years	SRS
	³² P	14.28 days	
	⁶³ Ni	100.1 years	
	²⁴¹ Am	432.7 years	
Check sources	⁹⁰ Sr	28.5 years	SRS
	⁵⁷ Co	5.27 years	
	⁶⁰ Co	5.27 years	
	⁸⁵ Kr	10.72 years	
Sterilisation, irradiation	⁹⁰ Sr	28.5 years	SRS
Gauging	¹³⁷ Cs	30.02 years	SRS
Eye applicators	²²⁶ Ra(Be)	1600 years	SRS
Radiography	²²⁷ Ac(Be)	21.77 years	
Activation analysis	²¹⁰ Po(Be)	138.4 days	
	²³⁹ Pu(Be)	2.41 × 10 ⁴ years	
Smoke detectors	²⁴¹ Am	432.7 years	SRS
Water movement	³ H	12.3 years	Tracer
Luminous articles and electronic valves	³ H	12.3 years	

Spent SRS are of great concern and have been involved in several serious accidents. Figure 9.12 shows a statistical assessment of problems caused by spent SRS.

Some spent SRS such as ⁶⁰Co sources can serve as the final waste-form because they are already encapsulated in a metal capsule. However, most SRS must be reliably immobilised in an additional corrosion-resistant barrier such as copper or lead.

9.10. Accidental Wastes

Radioactive contamination and waste may arise from accidents. Accidents generate radioactive waste of volume and composition, which depend on the material involved and the magnitude of the accident. Table 9.15 shows the most significant accidents involving radioactive materials that occurred between 1945 and 1999.

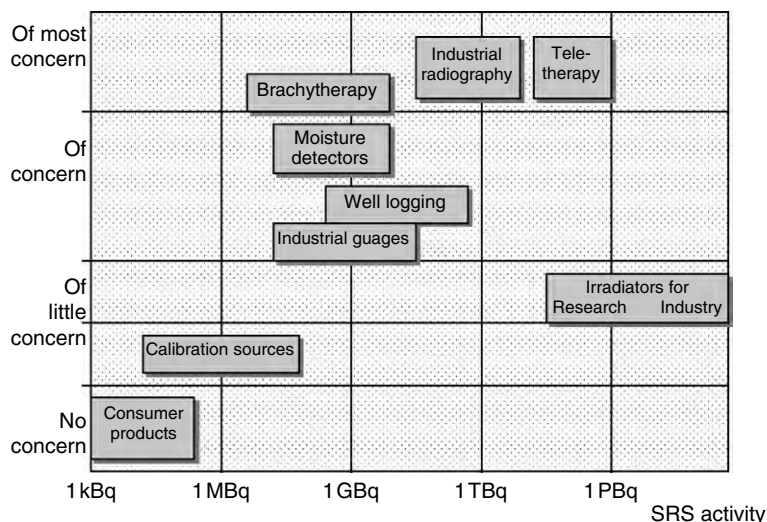


Figure 9.12: Range of spent SRS types and level of concern over their management.

Table 9.15: Severe accidents involving radioactive materials

Year	Place	Source	Dose	Overexposures/deaths
1945/1946	Los Alamos, USA	Criticality	≤ 13 Gy	10/2
1961	USSR	Submarine accident	1–50 Gy	>30/8
1961	Idaho Falls, USA	Explosion in reactor	≤ 3.5 Gy	7/3
1962	Mexico City, Mexico	^{60}Co SRS	9.9–52 Gy	5/4
1963	China	^{60}Co SRS	0.2–80 Gy	6/2
1964	Germany	^3H	10 Gy	4/1
1964	Rhode Island, USA	Criticality	0.3–46 Gy	4/1
1984	Morocco	^{192}Ir SRS	unknown	11/8
1986	Chernobyl, USSR	NPP	1–16 Gy	134/31
1987	Goiania, Brazil	^{137}Cs SRS	≤ 7 Gy	50/4
1992	China	^{60}Co SRS	>0.25–10 Gy	8/3
1996	Costa Rica	^{60}Co SRS	60% overdose	115/13
1999	Tokaimura, Japan	Enriched U		119/3

Only two major reactor accidents have occurred in over 10 000 cumulative reactor-years of commercial operation in 32 countries – Three Mile Island and Chernobyl. In 1979, a cooling malfunction caused part of the core to melt in #2 reactor at Three Mile Island in the USA and the reactor was destroyed. Some radioactive gas was released a couple of days after the accident, but not enough to cause any dose above background levels to local residents. There were no injuries or adverse health effects from the accident.

The Chernobyl accident in 1986 was due to lack of care in operation and disregard for standard safety procedures. The resulting steam explosion and fire released about 5% of the radioactive reactor core into the atmosphere. About 31 people were killed in the first few weeks after the accident, and there have since been other deaths from thyroid cancer due to the accident. An authoritative UN report in 2000 concluded that there is no scientific evidence of significant radiation-related health effects to most of the people exposed to radiation during or after the accident.

The most recent criticality accident occurred in Tokaimura, Japan in 1999. The accident was caused by bringing together too much uranium enriched to a relatively high level, causing a limited uncontrolled nuclear chain reaction, which continued intermittently for 20 h. A total of 119 people received a radiation dose over 1 mSv from the accident, with three operators receiving doses above permissible limits, two of whom have since died.

Perhaps more severe consequences have resulted from accidents involving SRS. More than 2300 cases have been reported of SRS found in scrap metal. A large number of cases have been reported of accidental melting of SRS with scrap metal in, e.g. steel and aluminium foundries. The total number of cases of melting SRS with scrap metals exceeds 60 in 18 countries. In Algeciras, Spain in 1998 radioactive gases, aerosols and particles from melting SRS with scrap were released and detected all over Europe. Concentrations up to 2000 Bq/m³ of ¹³⁷Cs in the air were detected although the incident had minor consequences. Since 1983, 30 cases of melting of SRS with scrap metal occurred in the USA, which required \$8–10 million in each case to decontaminate and restore the metallurgical facilities.

In 1987 a serious accident occurred in Goiania, Brazil with a ¹³⁷Cs SRS left within a teletherapy unit. The SRS was found by two scavengers who took the unit home, removed the source from the unit and ruptured the source capsule. This caused significant contamination of people and the surrounding environment. Four severely exposed people died and many others were seriously affected. More than 112 000 people were monitored for radiation exposure, of which nearly 300 showed ¹³⁷Cs contamination. The emergency response and clean-up effort of houses, buildings and land lasted 6 months. The amount of radioactive waste generated by this accident exceeded 3500 t.

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Chapter 10

Short-Lived Waste Radionuclides

10.1. Introduction

Short-lived waste is radioactive waste that does not contain significant levels of radionuclides with half-lives longer than 30.2 years. Short-lived radionuclides are present in both HLW and LILW. In contrast to HLW the concentration of short-lived radionuclides in LILW is relatively low. The relative weight content of radionuclides in the waste f (%) can be found from the specific content of radionuclides q (Bq/g) using:

$$f(\%) = \frac{q(\text{Bq/g})}{\text{SA}(\text{Ci/g}) \times 3.7 \times 10^{10}(\text{Bq/Ci})} \times 100\% \quad (10.1)$$

where SA is the specific activity of the radionuclide. Taking a typical maximum content of ^{137}Cs in LILW as $q \sim 10^7$ Bq/g (Table 9.3) and the specific activity of the longest lived short-lived radionuclide ^{137}Cs : $\text{SA} = 86.8$ Ci/g (Table 2.2), reveals that the relative weight content of ^{137}Cs in LILW is $\leq 0.027\%$. Hence the physical and chemical properties of LILW can potentially be affected very little by the presence of radionuclides and in practice are determined solely by the non-radioactive constituents. Important short-lived radionuclides in radioactive waste include ^3H , ^{90}Sr , ^{60}Co , ^{63}Ni , ^{106}Ru , ^{134}Cs , ^{137}Cs , ^{144}Ce , ^{147}Pm , ^{151}Sm and ^{154}Eu . These are often of radiological concern in performance assessment. Most short-lived radionuclides are formed by the fission of fissile radionuclides in the nuclear fuel although they can also form by nuclear reactions, for example, active ^{60}Co and ^{63}Ni can arise from neutron capture of inactive isotopes in structural steels (Chapter 9).

10.2. Tritium

Tritium (^3H) is the only radioactive isotope of hydrogen. The nucleus of a tritium atom consists of a proton and two neutrons. This contrasts with the

nucleus of an ordinary hydrogen atom (which consists solely of a proton) and a deuterium atom (which consists of one proton and one neutron). Deuterium comprises $\sim 0.02\%$ of all naturally occurring hydrogen. Tritium is naturally produced in very small quantities in the atmosphere, comprising $\sim 10^{-18}\%$ of natural hydrogen. Natural tritium is produced as a result of the interaction of cosmic radiation with gases in the upper atmosphere, and the natural steady-state global inventory is about 7.3 kg. About five times this amount remains from past atmospheric nuclear weapons tests. Tritium is readily incorporated into water and falls to earth as rain, thus entering the natural hydrological cycle. Figure 10.1 shows the ^3H content in atmospheric precipitates caused by global fallout. Enhanced concentrations resulted from nuclear weapons tests and in 1963, the USSR, USA and UK signed the Moscow treaty on terminating atmospheric nuclear weapons tests and tests in space and underwater. As China and France have not joined this treaty thermonuclear explosions in the atmosphere were stopped only in 1980. The Chernobyl accident had no significant effect on the annual average ^3H content in precipitation.

Tritium is produced as a fission product in nuclear weapons tests and in nuclear power reactors, with a yield of about $0.01\text{--}0.02\%$. Other sources of tritium in light water nuclear reactors are the activation of boron contained within the coolant as well as activation of boron in control rods according to



A large commercial nuclear power reactor produces about 20 000Ci ($\sim 2\text{ g}$) of tritium per year. This tritium is generally incorporated in the nuclear fuel and cladding.

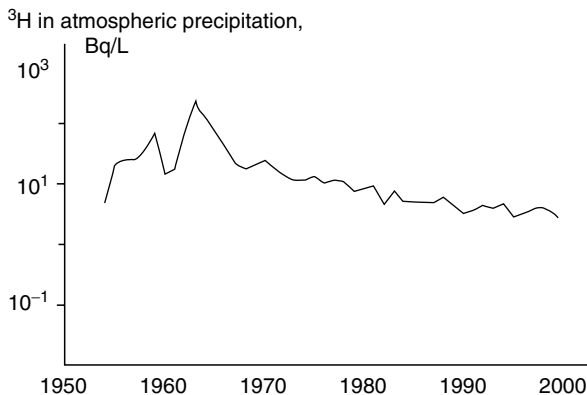


Figure 10.1: Fallout data for tritium in the USSR.

Because of its small natural concentration tritium must be synthesised for all commercial use. It can be made in nuclear reactors designed to optimise the generation of tritium and special nuclear materials such as ^{239}Pu . Tritium is produced also by neutron absorption of lithium targets according to



Tritium can also be produced in accelerators by bombarding ${}^3\text{He}$ with neutrons although this approach has not been proven on a large scale. Tritium is primarily used in industrial thickness gauges, luminous paints, unpowered self-luminous light sources, as an agent in luminous paints such as those used to make building exit signs, airport runway lights and watch dials. It is used in fusion research, thermonuclear weapons, and as a radioactive tracer in chemical, biological and environmental studies. Tritium has a half-life of 12.3 years and decays to ${}^3\text{He}$ with emission of a low-energy beta particle with maximum energy of 19 keV. It is usually considered to be one of the least hazardous radionuclides. However, since it can replace normal hydrogen in chemical compounds essential for life, tritium may be very mobile within the physical and biological environment.

Many wastes, including reactor evaporator bottoms and institutional and academic research laboratory rubbish, contain tritium. The most common forms are tritium gas (HT) and tritium oxide (HTO), also called tritiated water. The chemical properties of tritium are essentially the same as those of ordinary hydrogen. Tritium oxide (HTO) is generally indistinguishable from, and can move rapidly through the environment in the same manner as, normal H_2O . Tritium is naturally present in surface waters at about 0.4–1.2 Bq/L (10–30 pCi/L) and is extremely mobile in ground water and surface water systems. It can be taken into the body by drinking water, eating food, breathing air or via the skin although uptake by the latter even in hot humid conditions is about half that associated with inhalation. Up to 99% of inhaled tritium oxide can be taken into the body from the lungs, and circulating blood then distributes it to all tissues. Ingested tritium oxide is almost completely absorbed, moving quickly from the gastrointestinal tract to the bloodstream. Within minutes once ingested tritium is found in varying concentrations in body fluids, organs and other tissues. Tritium is uniformly distributed through all biological fluids within 1–2 h and is eliminated from the body with a biological half-life of 10 days, the same as for water. A small fraction of the tritium remains incorporated into easily exchanged hydrogen sites in organic molecules.

Since tritium decays by emitting a low-energy beta particle with no gamma radiation it poses a health hazard only once inside the body. The most likely form of uptake is as tritium oxide (or tritiated water) since the uptake of tritium gas is typically low (less than 1%). The health hazard of tritium is associated

with cell damage caused by ionising radiation that results from radioactive decay, with potential for subsequent cancer formation.

10.3. Cobalt-60

^{60}Co is produced in the structural steels and other alloys of nuclear reactor vessels and internal components from neutron activation of ^{59}Co , the only stable isotope of cobalt. ^{60}Co is not a naturally occurring radionuclide. There are nine major radioactive cobalt isotopes but only ^{57}Co and ^{60}Co have half-lives ≥ 80 days. A schematic of the nuclear decay of ^{60}Co , which has a half-life of 5.27 years, is shown in Fig. 2.6. Since ^{60}Co emits two highly energetic gamma rays of 1.17 and 1.33 MeV, ^{60}Co poses an external exposure hazard.

Because of its high-energy gamma radiation, ^{60}Co has been used extensively as a radiation source for both commercial and medical uses (Fig. 10.2). The transportation industry uses it to measure the thickness of automobile sheet steel while the metals industry uses it as a radiography source to detect flaws in welded joints and casting. The chemical and medical industries use it as a catalyst in flow studies, drug-metabolism studies and sterilisation of medical supplies. ^{60}Co is one of the principal irradiation sources for treatment of cancer in humans.

Reactor components are the primary waste materials containing ^{60}Co . In general, cobalt is easily adsorbed by soils and is not easily leached into the ground water. Gastrointestinal absorption from food or water is the principal source of internally deposited cobalt in the general population. Cobalt is an essential element found in most body tissues, with the highest concentration in



Figure 10.2: ^{60}Co commercial sealed radioactive sources used in industry and medicine.

the liver. Fifty per cent of cobalt that reaches the blood is excreted right away, mainly in urine; 5% deposits in the liver, and the remaining 45% deposits evenly in other tissues of the body. Of the cobalt that deposits in the liver and other tissues, 60% leaves the body with a biological half-life of 6 days and 20% clears with a biological half-life of 60 days; the last 20% is retained much longer, with a biological half-life of 800 days. Inside the body, cobalt presents a hazard from both beta and gamma radiation.

The main concern surrounding ^{60}Co is in limiting the exposure received by persons handling sources or associated with the decommissioning and dismantling of nuclear facilities.

10.4. Strontium-90

Sr is commonly associated as a trace impurity with Ca/Ba minerals while predominantly Sr minerals such as celestite (SrSO_4) and strontianite (SrCO_3) are quite rare. Sr comprises about 0.025% of the Earth's crust. The most prevalent form of strontium in nature is ^{88}Sr , comprising about 83% of the natural inventory. The other three stable isotopes and their relative abundance are ^{84}Sr (0.6%), ^{86}Sr (9.9%) and ^{87}Sr (7.0%). ^{90}Sr has a half-life of 29.1 years and its decay occurs by emission of a high-energy beta particle with a maximum energy of 546 keV. Almost no gamma photons are released from the ^{90}Sr decay sequence. ^{90}Sr decays to ^{90}Y , which has 64 hour half-life. ^{90}Y emits another high-energy beta particle with a maximum energy of 2.28 MeV.

The main source of ^{90}Sr is fission of ^{235}U or other fissile nuclides. When an atom of ^{235}U undergoes fission, it generally splits asymmetrically into two large fragments (fission products) with mass numbers in the range of about 90 and 140 and two or three neutrons (Fig. 2.7). ^{90}Sr is one such fission product, and it is produced with a yield of about 6%. ^{90}Sr is a major radionuclide in spent nuclear fuel (SNF), high-level radioactive wastes (HLW) resulting from SNF reprocessing and radioactive wastes associated with the operation of reactors and fuel reprocessing plants.

However, ^{90}Sr is used industrially to measure the thickness of paper, plastic, rubber and metal foils because of the high beta particle energies of ^{90}Sr and its daughter nuclide ^{90}Y . Medical applications of ^{90}Sr comprise sources for treatment of some eye and skin diseases. One of the most important applications of ^{90}Sr has been the isotopic energy source in various research applications, including radioisotope thermoelectric generators (RTG) or systems for nuclear auxiliary power (SNAP) devices to power remote weather stations, navigational buoys and satellites. Figure 10.3 shows a Russian type of RTG – called RITEG – stored in a transport container.



Figure 10.3: A view of a spent RTG in a transport container (authors' photo).

The largest source of ^{90}Sr , and the largest potential source of waste material, is commercial SNF. Most of the waste generated at nuclear power plants contains some ^{90}Sr ; however, other radionuclides (e.g. ^{137}Cs) are usually more prevalent and generally determine the waste characteristics. Wastes that contain ^{90}Sr include both wet and dry wastes such as spent ion exchange resins, filter sludge, filter cartridges, evaporator bottoms, compactable and non-compactable rubbish and irradiated components. A smaller fraction of wastes containing ^{90}Sr are generated from industrial, institutional and medical applications.

^{90}Sr is found worldwide in surface soil as a result of fallout from past atmospheric nuclear weapons tests. Average ^{90}Sr concentrations in surface soil are about 4 mBq/g (0.1 pCi/g). Figure 10.4 shows the average annual concentrations of ^{90}Sr (and ^{137}Cs) in air. These follow major nuclear events. The sharp increase in concentration in 1986 was due to Chernobyl. The $^{137}\text{Cs}/^{90}\text{Sr}$ concentration ratio is ~ 1.7 in the products of nuclear explosions and ~ 10 in the products of the Chernobyl accident.

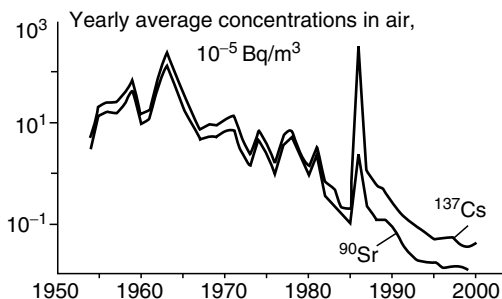


Figure 10.4: Fallout data for ^{90}Sr and ^{137}Cs in the USSR.

Strontium is highly water-soluble and is transported readily with rain and ground water deep into soils where it preferentially adheres to soil particles. The amount in sandy soil is typically about 15 times higher than that in water; concentration ratios are typically higher in clay soil. ^{90}Sr is taken up by plants through the roots and this is the principal means by which strontium gets into the food chain. From 30 to 40% of ingested strontium is absorbed into the bloodstream. Absorption is higher (about 60%) in children in their first year of life. Strontium behaves similarly to calcium and about 15% of that which enters the bloodstream is deposited in bone, the remainder going to soft tissue. The biological half-life of strontium remaining in the body is about 30 years. Once ^{90}Sr is ingested, it concentrates in bone tissue. Since these areas are near blood-producing bone marrow, one of the principal health problems with ^{90}Sr contamination is reduction in the blood platelet production. Other hazards include the possibility of bone cancer.

10.5. Caesium-137

Naturally occurring caesium is entirely non-radioactive ^{133}Cs . The natural source yielding the greatest quantity of caesium is the rare mineral pollucite. Pollucite ores, found in Maine and South Dakota, USA contain about 13% Cs_2O . Stable caesium is present to a lesser extent in soil.

There are 11 major radioactive isotopes of caesium but only three have relatively long half-lives: ^{134}Cs , ^{135}Cs and ^{137}Cs . Each of these decays by emitting a beta particle, and their half-lives range from about 2 years to 3 million years (Table 2.2) while the half-lives of the other caesium isotopes are less than two weeks. ^{134}Cs , ^{135}Cs and ^{137}Cs are produced by nuclear fission. ^{137}Cs is produced with relatively high yields of about 6.2%.

^{137}Cs has a half-life of 30.17 years and emits one to two high-energy beta particles. Figure 10.5 shows the decay of ^{137}Cs . Approximately 85% of all ^{137}Cs decays result in emission of a 0.662 MeV gamma ray.

^{137}Cs has important medical and industrial applications because of its long half-life. The gamma ray of $^{137\text{m}}\text{Ba}$ in equilibrium with ^{137}Cs , has been used to sterilise medical supplies, milk cartons and irradiate food. Industrial applications of ^{137}Cs include the production of plastic shrink tubing as irradiated plastic has the tendency to shrink after being heated; radiography to inspect metal castings and welds for flaws and material defects (such as cracks in steel pipes), radioactive measurement gauges for liquid or solid thicknesses (e.g. gauging of automobile sheet steel), treatment of sewage sludge to kill bacteria and viruses and radiotherapy to kill cancerous tissue.

The largest source of ^{137}Cs and potential waste material is from nuclear reactor operations. ^{137}Cs is a major radionuclide in SNF and HLW as well as in radioactive wastes associated with the operation of nuclear reactors and fuel reprocessing plants. A smaller quantity of ^{137}Cs -containing waste is generated in medical, academic or commercial facilities. Ion exchange resins used to purify coolant water in nuclear power plants frequently contain large amounts of ^{137}Cs . ^{137}Cs was released into the stratosphere by the testing of above-ground nuclear weapons in the late 1950s and early 1960s and deposited as fallout (see Fig. 10.4). An interesting comparison between Sr and Cs arose with the Chernobyl accident. While the fission yields and charge densities are similar their inventories in the reactor core would have been similar. However, on meltdown Cs and Sr were fractionated as Cs is more volatile while Sr is more refractory. As a result fallout a long way from the reactor (such as the UK) has lower Sr than Cs while the reactor debris has higher Sr than Cs.

Caesium is a highly electropositive and alkaline element, and thus, more easily than other elements, it loses its single valence electron and forms ionic

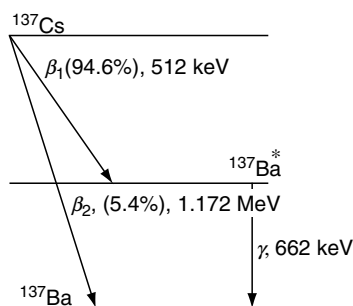


Figure 10.5: Schematic of ^{137}Cs decay.

and electrovalent bonds with nearly all inorganic and organic anions. The common chemical compounds of ^{137}Cs are water-soluble and will readily move with ground water. Nevertheless caesium is generally one of the less mobile radioactive metals in the environment. It preferentially adheres to soil, particular to clay minerals, and the concentration associated with sandy soil particles is estimated to be 280 times higher than in interstitial water, concentration ratios are much higher (about 2000 to more than 4000) in clay and loam soils.

Absorption of caesium by humans takes place primarily through the digestive tract. Caesium and potassium have similar chemical properties because both are alkali metals. One of the problems with caesium is its potential effect on the potassium levels in the body in addition to its radiation effects on the various body tissues. Essentially all caesium that is ingested is absorbed into the bloodstream through the intestines. Caesium tends to concentrate in muscles because of their relatively large mass. Like potassium, caesium is excreted from the body fairly quickly: 10% is excreted with a biological half-life of 2 days, and the rest leaves the body with a biological half-life of about 110 days. ^{137}Cs is infamous because of an accident with a spent sealed radioactive source containing it which occurred in Goiania, south-central Brazil in 1987, when a lead canister containing 1400 Ci of ^{137}Cs was opened launching the second largest nuclear accident after Chernobyl (see Table 9.15).

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Chapter 11

Long-Lived Waste Radionuclides

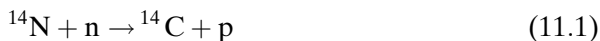
11.1. Introduction

Long-lived waste contains significant levels of radionuclides with half-lives greater than 30.2 years. Figure 11.1 illustrates the decay of radionuclides in HLW indicating that with time the activity of the long-lived radionuclides becomes dominant.

Radioactive wastes from fuel fabrication, nuclear reactor operation and decommissioning can also contain long-lived radionuclides. Among the most important long-lived radionuclides in radioactive waste are ^{14}C , ^{99}Tc , ^{129}I , $^{238,239,240,242}\text{Pu}$ and ^{237}Np .

11.2. Carbon-14

^{14}C is a naturally occurring radionuclide. Before man-made disruptions of the normal level of ^{14}C by burning of fossil fuels and atmospheric testing of nuclear weapons this radionuclide was produced in nature only by cosmic rays impinging on the atmosphere. Almost all ^{14}C in nature is produced by the reaction:



Nuclear explosions generate ^{14}C through the same reactions. Reactor fission supplies large numbers of neutrons, which induce neutron activation of reactor materials such as construction materials, coolant, moderator, fuel, gases and impurities. The inventory of natural ^{14}C on the Earth is estimated as 44.2 t with an additional 1.3 t resulting from nuclear weapons testing. As a naturally occurring radionuclide ^{14}C can be used for historical dating to determine the age of certain archaeological artefacts of biological origin up to about 50 000 years old. The ratio of stable ^{12}C to ^{14}C in the air and in all living species at any

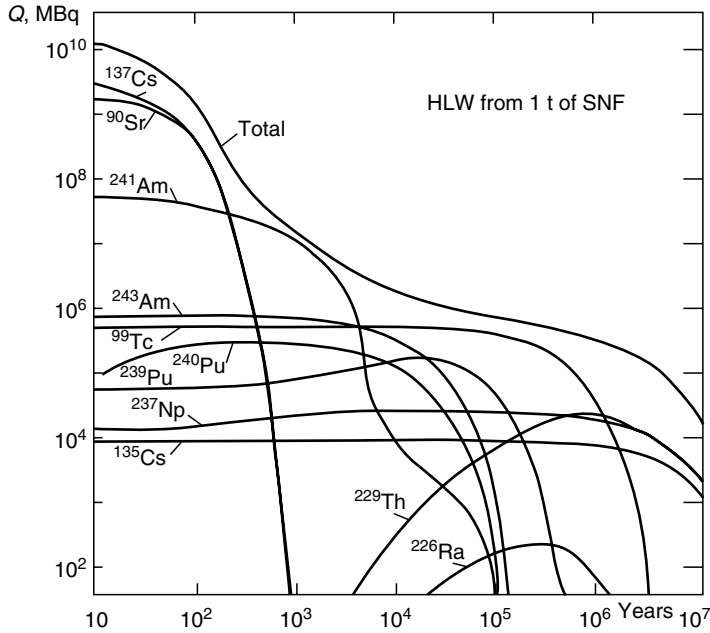


Figure 11.1: Activity of radionuclides in HLW from the reprocessing of SNF with time after reprocessing.

given time is nearly constant although recent ^{14}C production from weapons testing has complicated the situation. As soon as a living organism dies, it stops taking in new carbon and this disturbs the ratio of ^{12}C to ^{14}C . By examining the ratio of ^{12}C to ^{14}C in the dead organism and comparing it to the ratio in a living organism, it is possible to determine how old it is using

$$t = 1.44 T_{1/2} \ln \left(\frac{N_0}{N_f} \right) \quad (11.2)$$

where N_0/N_f is the ratio of ^{14}C in the sample compared to the amount in living tissue, and $T_{1/2}$ is the half-life of ^{14}C .

Disposable wastes containing ^{14}C include reactor-irradiated graphite, activated metals from reactors, sealed radioactive sources and animal carcasses from research laboratories (typical LILW). The world inventory of irradiated graphite wastes comprises 160 000 t (Fig. 11.2).

Considerable amounts of high-level graphite waste containing fragments of fuel and fission products have been accumulated during operation of uranium-graphite reactors. The UK has a large proportion of this arising from its graphite-moderated Magnox reactors and AGRs whose lifetimes are governed

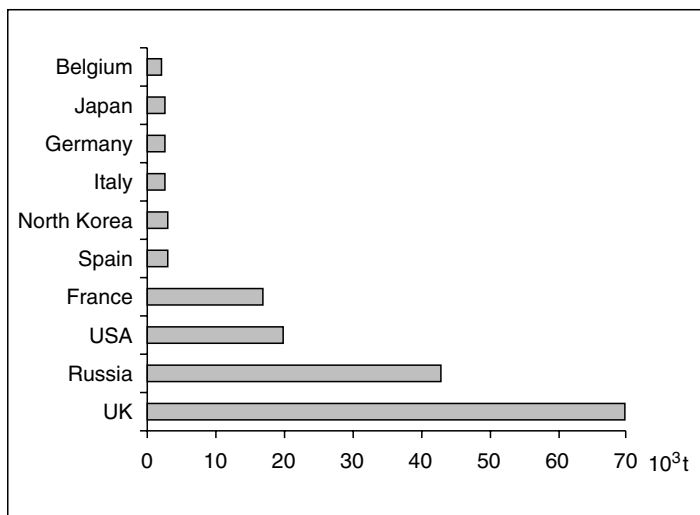


Figure 11.2: Reactor graphite in the world (in thousands of tonnes).

by aging of the graphite by fast neutron damage and radiolytic oxidation. The content of ^{14}C in reactor graphite after use can be as high as 1 wt.%, which is a problem as ^{14}C is particularly mobile in ground water systems and in the atmosphere in the form of gaseous CO_2 . As a beta emitter ^{14}C presents an internal hazard to humans and enters the human body either by inhalation or ingestion. ^{14}C decays to ^{14}N emitting a beta particle with a maximum energy of 156 keV and an average energy of 49.5 keV. Options for graphite waste management include packaging of non-conditioned graphite waste with subsequent direct disposal of the waste packages and conditioning (mostly incineration) of graphite waste with immobilisation and disposal of the conditioned incinerator ash.

11.3. Technetium-99

^{99}Tc is produced by U and Pu fission and is a key radionuclide in SNF and HLW. Small amounts of ^{99}Tc can also be present in waste generated at medical laboratories and academic institutions. Essentially all the technetium on the Earth has been created by human activities involving fissionable materials. Taking its name from the Greek word *technetos* meaning artificial, it was first produced in 1937 by bombarding molybdenum with deuterons in a cyclotron. An extremely small quantity of ^{99}Tc was created naturally in sustained underground nuclear reactions estimated to have occurred about 1.9 billion years ago

in Gabon, Africa. This phenomenon occurred because much higher concentrations of ^{235}U were present at that time. The current ^{235}U concentration (about 0.72%) is not enough to sustain nuclear fission reactions in nature.

There are no stable isotopes of technetium. Of the 10 major radioactive isotopes, three – ^{97}Tc , ^{98}Tc and ^{99}Tc – have long half-lives. The half-lives of the other isotopes are less than 90 days. Only ^{99}Tc is produced in sufficient quantities to be of concern for the environment. ^{99}Tc decays by emitting a beta particle to produce the stable isotope ^{99}Ru . The very long half-life of ^{99}Tc (2.13×10^5 years, Table 2.2) limits its radioactive hazards. The short-lived metastable radionuclide $^{99\text{m}}\text{Tc}$ (an isomeric state of ^{99}Tc) with a half-life of about 6 h is largely used in medical diagnostic procedures. $^{99\text{m}}\text{Tc}$ is a decay product of ^{99}Mo , which has a half-life of 66 h and decays by emitting a beta particle. Both ^{99}Tc and ^{99}Mo are fission products with a relatively high yield of about 6%. $^{99\text{m}}\text{Tc}$ is commonly used in nuclear medicine as a radioactive tracer. In this application, the radionuclide is chemically attached to a drug chosen for its tendency to collect in specific organs of the body, and the solution is then injected into the patient. After a short time an image is collected with a radio-sensitive detector for analysis. This technique is useful in identifying cancer metastases in locations distant from primary tumours.

Technetium occurs either as pertechnetate, TcO_4^- anions, or as a simple Tc^{4+} cation. ^{99}Tc is present in soil due to fallout from past atmospheric nuclear weapons tests. Estimated concentrations in surface soil are about 0.1 pCi/kg. ^{99}Tc is extremely mobile in the environment, especially under aerobic conditions when oxygen is present. Most technetium compounds do not bind well to soil particles. The concentration associated with sandy soil particles is estimated at 0.1 of that in interstitial water, although technetium binds more tightly to clay soils with concentration ratios 10 times higher. ^{99}Tc has been discharged into the sea by BNFL in the UK but this is now regarded as unacceptable. A new process using tetraphenylphosphonium bromide separates the ^{99}Tc from liquid wastes as TcO_4^- , which is the predominant form of ^{99}Tc at radwaste disposal facilities. Because TcO_4^- is highly mobile in ground water and because ^{99}Tc has a long half-life its disposal presents a potential long-term hazard to the public. No waste-form is currently available for the TcO_4^- .

Reduced forms of technetium are not mobile in environmental media. TcO_4^- is readily taken up from the intestines and lungs following ingestion or inhalation, with about 50–80% of the amount ingested being transferred to the bloodstream. About 4% of the TcO_4^- deposits in the thyroid where it is retained with a biological half-life of 0.5 days. The other two organs to which this isotope preferentially distributes are the stomach wall (10%) and liver (3%). The rest that enters the blood is uniformly distributed throughout all other organs and tissues with a short residence time. For the technetium

that is distributed to organs other than the thyroid, about 75% leaves the body with a biological half-life of 1.6 days, 20% clears with a half-life of 3.7 days, and 5% clears with a half-life of 22 days. Because ^{99}Tc is a beta emitter with a maximum energy of 293 keV, it has a greater internal than external hazard to humans. The main route by which ^{99}Tc enters the human body is ingestion.

11.4. Iodine-129

Iodine in nature mainly occurs as stable ^{127}I in the form of iodide ions, and in this form only, it is taken into our bodies. The long-lived radionuclide ^{129}I occurs in nature at very low concentrations. The fission yield of ^{129}I is about 1% and the yield of ^{131}I is close to 3%. ^{131}I has a short half-life (8 days) and is not generally a major isotope of concern for environment. In nature, ^{129}I is produced by spontaneous fission of uranium in the lithosphere and hydrosphere and by interactions of cosmic ray particles with xenon in the atmosphere. The total inventory is approximately 326.8 TBq. To this inventory about 0.3 TBq have been added by the atmospheric testing of nuclear weapons. The Chernobyl accident added another 7.1 MBq. ^{129}I is present in soil around the world as a result of fallout from past atmospheric nuclear weapons tests and is one of the most mobile radionuclides.

^{129}I decays by emitting a beta particle. It has a half-life of about 15.7 million years (Table 2.2); the half-lives of all other iodine radionuclides are less than 60 days. The long half-life of ^{129}I combined with the low energy of its beta particle and minimal gamma radiation limit its radiological hazard. ^{131}I is used for a number of medical procedures, including monitoring and tracing the flow of thyroxin from the thyroid. With its short half-life of 8 days, it is essentially gone in less than 3 months. ^{129}I has no important commercial uses. Iodine is present in nature in various materials, with soil, rock and all living organisms containing low concentrations. Iodine is assimilated by seaweeds and sponges and is found in Chilean saltpeter, caliche and brine associated with salt deposits. The ratio of stable ^{127}I to radioactive ^{129}I in the environment is more than 10^7 to 1. The human body contains 10–20 mg of iodine, of which more than 90% is contained in the thyroid gland.

Because ^{129}I is primarily a beta emitter with a maximum energy of 0.150 MeV, it represents a greater internal than external hazard to humans. The main route by which ^{129}I enters the human body is ingestion. Whether inhaled or ingested, most radioiodine dissolves in body fluids, travelling to and concentrating in, the thyroid. Clearance from the thyroid is age dependent, with biological half-lives ranging from 11 days in infants to 23 days in a 5-year-old child and 80 days in

adults. The low-energy beta particle may irradiate the thyroid to the point of inducing cancerous thyroid nodules. Iodine is a difficult radionuclide to immobilise as it is not amenable to conventional technologies. It has low solubility in vitreous waste-forms and is volatile at the processing temperatures used in vitrification (see Chapter 17). All halide anions are highly soluble in cement pore water leading to poor durability of any cemented waste-form containing them. Furthermore, I is highly soluble and mobile in ground water.

11.5. Plutonium

All the plutonium presently on Earth has been created within the past six decades by human activities involving fissionable materials. Several plutonium isotopes exist, all of which are radioactive. As is common in the actinide series Pu has a variable oxidation state and occurs in complex variable geometries in crystal structures. Except for ^{241}Pu , the plutonium isotopes decay by emitting an alpha particle. ^{241}Pu decays by emitting a low-energy beta particle to produce ^{241}Am , an alpha-emitting radionuclide with a half-life of 430 years that is much more radiotoxic than its plutonium parent. The maximum activity of ^{241}Am , which occurs 73 years later, is about 3% of the initial activity of ^{241}Pu .

Plutonium was first produced in large quantities to create atomic bombs, and this production continued at a high level throughout the cold war. Plutonium is formed when the nucleus of a uranium atom captures one or more neutrons. This process occurs in nuclear reactors and mainly involves transforming ^{238}U into plutonium. Extremely small quantities of plutonium were created naturally in sustained underground nuclear reactions estimated to have occurred about 1.9 billion years ago in Gabon, Africa.

^{239}Pu is used in nuclear weapons and nuclear power generation. The fission of ^{235}U in the reactor of a nuclear power plant produces two to three neutrons, and these neutrons can be absorbed by ^{238}U to produce ^{239}Pu and other isotopes. ^{239}Pu can also absorb neutrons and fission along with the ^{235}U . Plutonium fission provides about one-third of the total energy produced in a typical commercial nuclear power plant. ^{238}Pu is used as a material for sealed radioactive sources (SRS). SRS are used in many applications including many sites operated by small users. ^{238}Pu is also used as a heat source (Fig. 11.3) and in radioactive thermal generators (RTG, SNAP) to produce electricity for unmanned spacecraft and interplanetary probes.

The USA recovered or acquired about 110 000 kg of plutonium between 1944 and 1994, and about 100 000 kg remains in inventory. Of this amount, over 80% is in the form of weapons-grade plutonium, primarily ^{239}Pu .

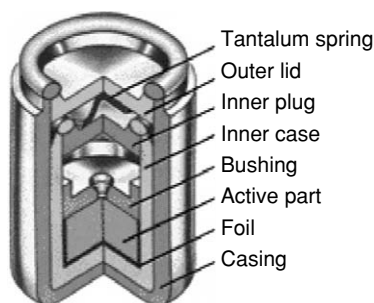


Figure 11.3: Radioactive thermal generator containing ^{238}Pu .

Atmospheric testing of nuclear weapons, which was ceased worldwide by 1980, generated most of the environmental plutonium. About 10 000 kg were released to the atmosphere during these tests. Average plutonium levels in surface soil from fallout range from about 0.01 to 0.1 pCi/g. Accidents and other releases from weapons production facilities have caused greater localised contamination.

The most common form of plutonium in the environment is plutonium oxide and it is in the form of oxide powder that most Pu from reprocessing or military production is stored. Plutonium is typically very insoluble. It adheres tightly to soil particles and tends to remain in the top few centimetres of soil as the oxide. In aquatic systems, plutonium tends to settle out and adhere strongly to sediments, again remaining in the upper layers. Typically one part of plutonium will remain in solution for every 2000 parts in sediment or soil. A small fraction of plutonium in soil can become soluble through chemical or biological processes, depending on its chemical form.

When plutonium is inhaled, a significant fraction can move from the lungs through the blood to other organs, depending on the solubility of the compound. A small fraction ($\sim 0.05\%$) is absorbed from the gastrointestinal tract after ingestion but little is absorbed through the skin following dermal contact. After leaving the intestine or lung, about 10% clears the body; the rest enters the bloodstream and deposits about equally in the liver and skeleton where it remains for long periods, with biological retention half-lives of about 20 and 50 years, respectively. The amount deposited in the liver and skeleton depends on the age of the individual, with fractional uptake in the liver increasing with age. Plutonium in the skeleton deposits on the surfaces of bones and slowly redistributes throughout the volume of mineral bone with time. Plutonium poses a health hazard only if it is taken into the body because all isotopes but ^{241}Pu decay by emitting an alpha particle, and the beta particle emitted by ^{241}Pu is of low energy. Inhaling airborne plutonium is the primary concern for all

isotopes, and cancer resulting from the ionising radiation is the health effect of concern. The ingestion hazard associated with common forms of plutonium is much lower than the inhalation hazard because absorption into the body after ingestion is quite low.

Options for military Pu left over from The Cold War of which there are many hundreds of tonnes concentrated predominantly in the USA, Russia and the UK include its reuse in MOX or inert matrix fuels or, especially where it is contaminated with other materials, immobilisation in various crystalline ceramic hosts (Chapter 18).

11.6. Neptunium-237

^{237}Np is principally a man-made nuclide, although trace amounts of it do exist in nature (as is true for Tc and Pu), caused by the irradiation of uranium ore by naturally occurring neutrons. This is the longest lived of the isotopes of neptunium, all of which are radioactive. ^{237}Np decays by alpha particle emission to ^{233}Pa , which is also a radioactive nuclide. The stable nuclide ^{205}Ti is formed after several additional decays. When ^{237}Np decays it emits moderately high-energy alpha particles, low-energy gamma rays, and low-energy electrons. The total particle and photon spectrum is complex due to the complex decay scheme of ^{237}Np . Because of the long half-life of ^{237}Np (over 2 million years, Table 2.2) its presence in waste can be significant in assessing the long-term performance of a site due to the quantity, radiotoxicity and mobility of its daughter products, which include an isotope of radium.

Neptunium, as an actinide, is reactive and forms compounds with many other elements, such as the halides, oxygen and hydrogen. Unlike most of the other actinides, there is no member of the lanthanide series that has a similar chemical behaviour so simulating its presence in inactive experiments is difficult. The ability of soil to adsorb ^{237}Np out of ground water depends on a number of factors, including pH and the type of soil. Neptunium is soluble and tends to remain in the ground water unlike other actinides, such as plutonium and americium, which are adsorbed by the soil.

The principal radiological hazard associated with ^{237}Np is due to its relatively high-energy alpha particles. External exposure to ^{237}Np does not pose a high risk. The principal risk is due to either inhalation or ingestion. Inhalation can occur as a result of suspension of neptunium-laden aerosols. Ingestion can occur when the ^{237}Np is introduced into the food chain by plant uptake. When ^{237}Np is either ingested or inhaled, it is removed from the body with a biological half-life of several years, depending on which organ has become contaminated by the nuclide. ^{237}Np tends to concentrate in bones.

11.7. Nuclear Criticality

Large amounts of long-lived fissile radionuclides can, in principle, create a critical mass and cause an uncontrolled chain reaction. This possibility is always considered when examining options for safe storage and disposal of fissile radionuclides. Table 11.1 gives minimal critical masses although the local distribution of radionuclides in a host or waste and environmental conditions are also important when analysing criticality.

Table 11.1: Minimal critical masses of fissile radionuclides

Radionuclide	²³² U	²³⁵ U	²³⁸ Pu	²³⁹ Pu	²⁴² Am	²⁴⁵ Cm	²⁵¹ Cf
Minimal critical mass (g)	570	790	4500	510	36	17	13

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Chapter 12

Management and Characterisation of Radioactive Wastes

12.1. Management Roadmaps

Radioactive waste management approaches vary from country to country and even within a country may differ depending on local factors. Figure 12.1 shows a system for radioactive waste collection and processing at a centralised radioactive waste facility. While a large number of technological options are available (to be described in later chapters), Fig. 12.1 illustrates specific approaches to safe long-term storage of various waste streams.

Another approach to managing radioactive wastes (Fig. 12.2) reveals that all activities concerned with radioactive waste are conventionally divided into predisposal and disposal stages.

Disposal is the final step in managing radioactive wastes whereas predisposal includes activities such as decommissioning, pre-treatment, treatment, conditioning, immobilisation, storage and transport. While various disposal options are available it is most likely that immobilised wastes will be disposed of in geological repositories of one sort or another (Chapter 19). Confusion often arises over the use of the term “repository”. A clear distinction must be drawn between “storage” where, by definition, the waste must be retrievable and “disposal”, which is intended to be permanent. It is probably no accident that “repository” is often used loosely in the context of nuclear waste to imply a place of temporary storage but one that might become permanent.

12.2. Predisposal

Predisposal includes all activities carried out prior to waste disposal. Unfortunately, this is often the only procedure used, as disposal facilities are not

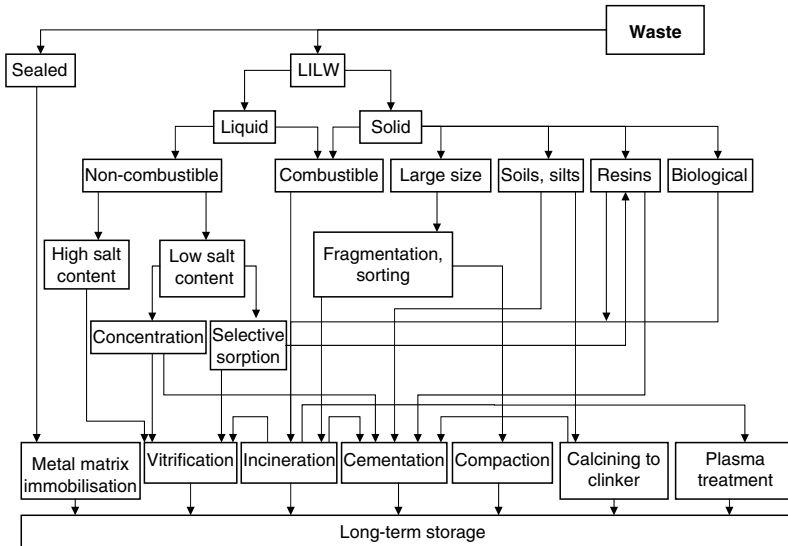


Figure 12.1: Block diagram of radioactive waste management steps at a centralised facility.

yet available for most HLW, SNF, powerful and long-lived SRS and some ILW. Predisposal comprises a number of key activities important for preparing radioactive wastes for disposal and facilitating handling procedures. Decisions made at one step may limit or rule out alternatives at another step, so careful waste management must take into account the interdependencies among all steps during the planning, design, construction, operation and decommissioning of a facility (see Chapter 8) – a holistic approach is needed.

Predisposal comprises, in most cases, the following steps: pre-treatment, treatment, conditioning, immobilisation, transportation and storage. Decommissioning of nuclear facilities is also a predisposal activity.

Pre-treatment of radioactive waste is the initial step in waste management that occurs after waste generation. Pre-treatment of radioactive wastes comprises:

- collection;
- segregation;
- chemical adjustment and
- decontamination.

Collected wastes can be stored for an interim period. This interim storage period often provides the best opportunity to segregate radioactive waste

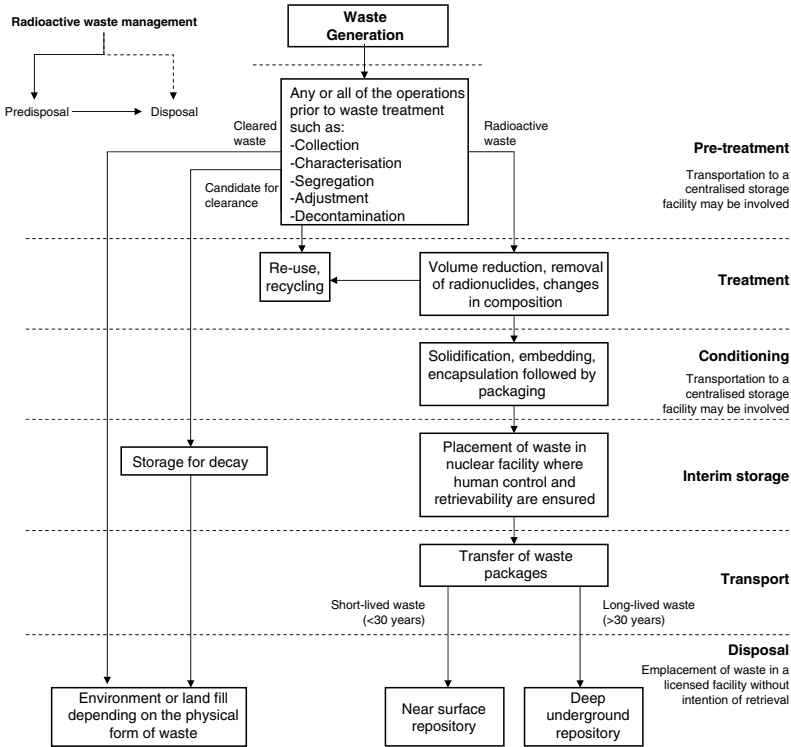


Figure 12.2: Schematic of radioactive waste management activities.

streams. It can be used to select materials for treatment or for disposal as non-radioactive waste when the quantities of radioactive materials they contain are exempt from regulatory controls. It is also used to segregate waste for near-surface or geological disposal. Segregation is separating wastes or keeping them separate according to radiological, chemical and/or physical properties, which may facilitate waste handling and/or processing. Chemical adjustment is used to facilitate interim storage, transportation and treatment of wastes, whereas decontamination may result in significant reduction of waste volume for further treatment.

Treatment of radioactive waste includes all operations intended to improve safety or economy by changing the radioactive waste characteristics. The basic treatment objectives are:

- volume reduction;
- radionuclide removal from waste and
- change of physical and chemical composition.

Examples of treatment processes include incineration of combustible waste, compaction of dry solid waste (volume reduction); evaporation, filtration or ion exchange of liquid waste streams (radionuclide removal); and neutralisation, precipitation or flocculation of chemical species (change of composition). Often several of these processes are combined to provide effective decontamination of a liquid waste stream. Treatment may result in several types of secondary radioactive waste, which need to be managed, e.g. in contaminated filters, spent ion exchangers and sludges.

Conditioning transforms the radioactive waste into a form suitable for handling, transportation, storage and disposal. Conditioning as a rule includes immobilisation of radionuclides, placing the waste into containers and providing additional packaging. Immobilisation in contrast to conditioning comprises the conversion of a waste into a waste-form by solidification, embedding or encapsulation. Common immobilisation methods include solidification of low and intermediate level liquid radioactive waste, e.g. in cement, bitumen or glass, and vitrification of high-level liquid radioactive waste in a glass matrix or embedding into a metal matrix. These, in turn, may be packaged in containers ranging from common 200-L steel drums to highly engineered thick-walled containers depending on the nature and level of radioactivity.

In many instances, treatment and conditioning take place in close conjunction with one another. Packing is the preparation of radioactive waste for safe handling, transportation, storage and disposal by means of enclosing it in a suitable container. An over-pack is a secondary or outer container for one or more waste packages, used for handling, transportation, storage or disposal.

Storage of radioactive waste involves maintaining the radioactive waste in conditions where it is subjected to isolation, environmental protection and monitoring. In some cases, storage may be practised for primarily technical considerations, such as, storage of radioactive waste containing mainly short-lived radionuclides while they decay prior to subsequent clearance from regulatory control. Storage of HLW provides a cooling period to alleviate some of the radiogenic heating prior to geological disposal. In other cases, storage may be practised for reasons of economics or policy.

Transportation of conditioned radioactive wastes precedes its disposal. It may also be necessary between the radioactive waste management steps. Special containers or vehicles can be used for transportation of radioactive wastes. Figure 12.3a shows a vehicle used for road transportation of solid radioactive wastes and spent and disused SRS in Russia while Fig. 12.3b shows a ship for transporting spent nuclear fuel from reactor site to interim storage in Sweden. The spent fuel is held on board in protective containers (Fig. 12.3c).

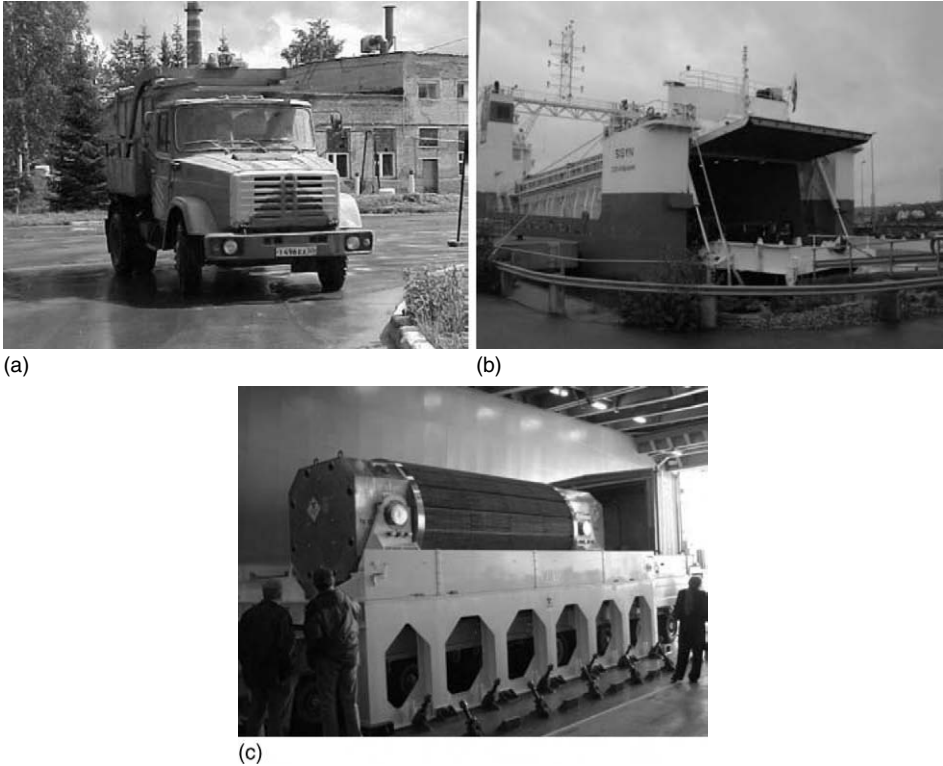


Figure 12.3: Vehicles for transportation of radioactive waste: (a) road vehicle for LILW and SRS in Russia (courtesy of I.A. Sobolev, SIA RADON) and (b) ship for SNF in Sweden along with (c) the on-board SNF containers (courtesy of J.W. Roberts, ISL Sheffield).

12.3. Disposal

Disposal is the final step in the radioactive waste management system. It consists of placing radioactive waste in a repository, or other location, so that it is safe from unintentional disturbance in a manner which also prevents escape of any of the waste material for many hundreds of thousands, if not millions, of years. This must be carried out in such a way that the waste is beyond institutional control; it is assumed that at some point in the future, society will change so much that knowledge of the waste and its location will be lost. There must be no reliance on surveillance and maintenance so that no burden is left for future generations (see Section 8.3). Disposal may also include the discharge of effluents (e.g. liquid and gaseous waste) into the environment (e.g. sea, rivers,

natural water basins and atmosphere), with subsequent dispersion. This is always done within very limited and pre-authorised limits. Disposal by discharging is an irreversible action and is considered suitable only for limited amounts of specific radioactive waste of a limited and predictable hazard.

The key issue with any disposal option is safety, which is mainly achieved by concentration and containment involving the isolation of suitably conditioned radioactive waste in a disposal facility. Containment uses many barriers around the radioactive waste to restrict the release of radionuclides into the environment. The restricting barriers can be either natural or engineered. A containment system as a rule consists of a number of barriers. Such an approach is termed the multi-barrier concept and is often called “matreshka” after a popular Russian doll (Fig. 12.4), which has smaller dolls inside larger ones, so that the total number of dolls is large.

A system of multiple barriers ensures that waste radionuclides decay below exemption levels before there is any possibility of their release. The first barrier is the waste-form in which the radionuclides are held which may be as simple as the ceramic matrix of SNF or a carefully designed vitreous or cementitious system. Next is usually a metallic package or container, which provides absolute containment but for limited periods of time compared to the half-lives of some of the long-lived nuclides. Careful design of backfill materials and the host rock

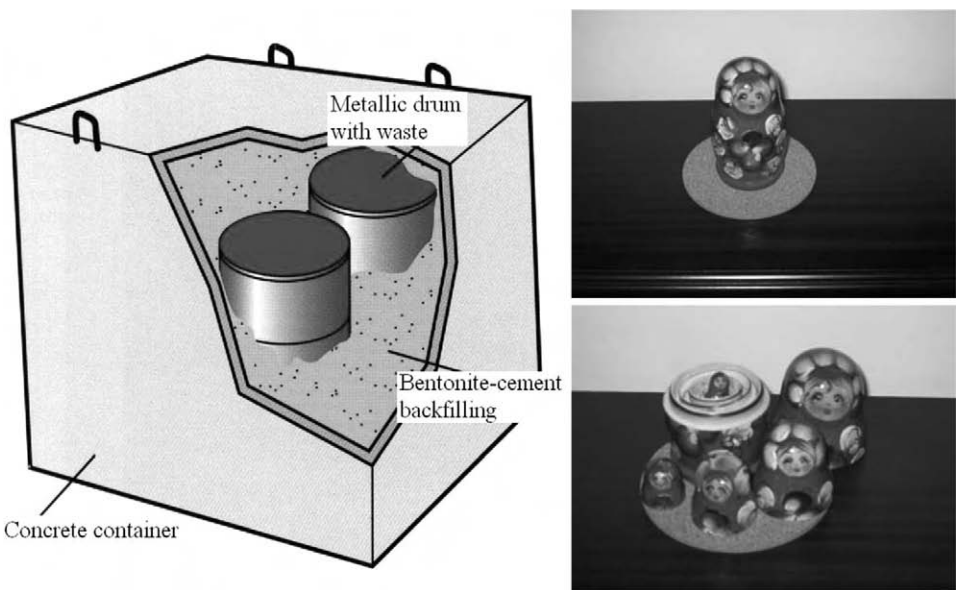


Figure 12.4: Multi-barrier isolation of radioactive waste (left) and a matreshka doll – a symbol of the multi-barrier concept.

of the repository which ideally should have high radionuclide sorption capability, retard the release of radioactive materials to the environment and biosphere. The role of the engineering barriers is dominant in near-surface disposal facilities because in this case natural barriers have limited ability to confine radionuclides. Multi-barrier systems are designed depending on the disposal option (near surface, deep underground) and the engineering barrier system used (see section 19.3).

12.4. Characterisation

The nature and composition of the waste must be thoroughly characterised and understood for predisposal and disposal. The characterisation of radioactive wastes is carried out to determine important waste parameters (Table 9.1) and to enable segregation of radioactive waste for exemption, reuse and choice of disposal option, e.g. near-surface or deep geological facility. Characterisation of radioactive waste must account for ionising radiation and any potential for escape and hence contamination of the surrounding environment. Characterisation equipment usually includes:

- sampling tools;
- radiological and spectrometric (spectroscopic) measuring devices;
- physical/chemical analysis and separation devices.

Sampling of water and gaseous effluents is carried out using dedicated devices such as those shown in Fig. 12.5.

Universal radiometers–dosimeters are used to characterise γ , β and α radiation fields. Surface contamination is characterised by taking surface smears over a 100 cm² surface (Fig. 12.6) followed by radiometric and spectrometric analyses.

Detailed information on radionuclide content in radioactive waste is obtained by analysing representative samples using γ -, β - and α -spectrometers. Materials containing low concentrations of radionuclides are the most difficult to analyse. High-purity germanium (HPG) detectors are used for highly sensitive γ -spectrometry of such materials. These detect the electrical current induced by electron–hole pairs created by γ -rays in the depletion regions of reverse-biased p–n junctions. β - and α -spectrometers may use either the scintillation phenomenon, which converts energy lost by ionising radiation into pulses of light in either solid or liquid materials, or electron–hole production in semiconductor devices. The most sensitive liquid scintillation analysis (LSA) involves dissolving samples in solvents containing scintillating additives and analysis of light emission caused by ionising β - or α -particles emitted by sample radionuclides. Processing of the resulting spectra enables both qualitative

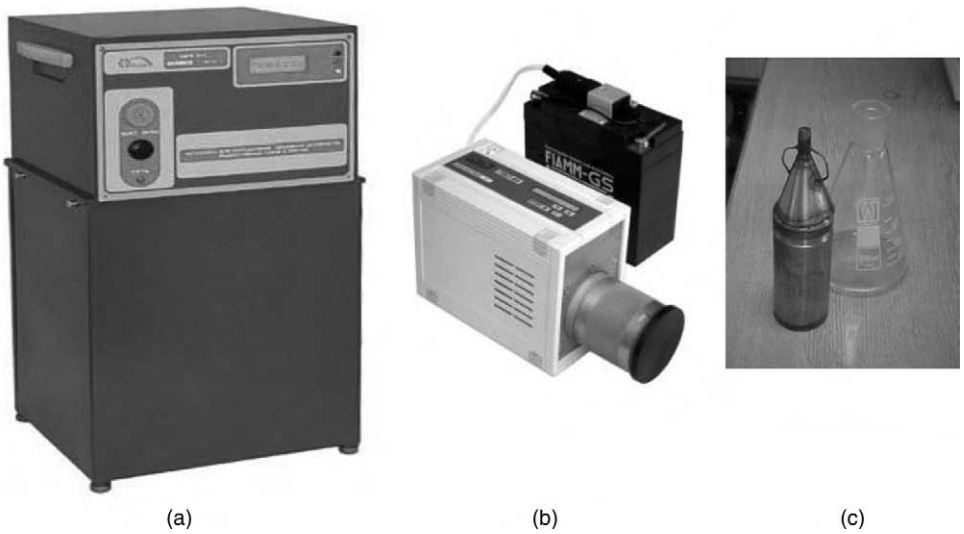


Figure 12.5: Sampling-analysing systems for radioactive materials: (a) gaseous stream radiometric system; (b) air iodine and radioactive aerosol analyser; (c) depth sampler for water solutions. Courtesy of A. Arustamov, Gamma Alliance, Russia.



Figure 12.6: Smear test kit for repository loading channels. Authors' photo.

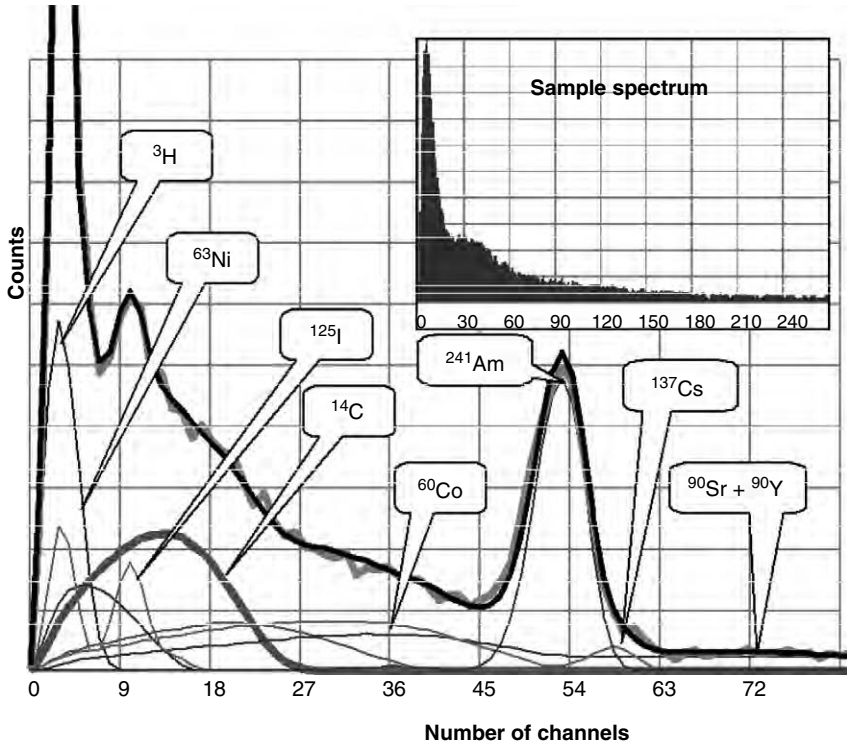


Figure 12.7: LSA sample spectrum of a low-level 1.6 Bq sample and its radionuclide composition. Courtesy of A. Sobolev, SIA RADON, Russia.

identification of separate radionuclides and quantitative determination of their content in the analysed materials (Fig. 12.7).

Thermoluminescence dosimeters (TLD) are most often used for personnel dosimetry. A TLD uses the radio-thermoluminescence effect of irradiated crystals such as CaF_2 or LiF that emit a number of light photons proportional to irradiation dose when heated. TLD are also used for environmental monitoring.

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Chapter 13

Pre-Treatment of Radioactive Wastes

13.1. Pre-Treatment Definition

Pre-treatment is a key part of any decommissioning programme and involves a variety of processes applied to liquid and solid radioactive waste. It is defined as any or all of the operations preceding waste treatment. Pre-treatment comprises such operations as collection, segregation, adjustment and decontamination. The main objectives of pre-treatment are:

- to segregate waste into active and non-active streams;
- to facilitate transport, treatment, conditioning and packaging by separating active streams into components or converting the waste into a form suitable for such operations;
- to recover products for recycling.

A number of factors need to be considered when selecting a pre-treatment method including:

- radiological protection standards and objectives;
- waste minimisation;
- availability of pre-treatment technologies;
- economic aspects;
- requirements for the further treatment, conditioning, storage, off-site transport and final disposal of the waste.

Pre-treatment results in improved safety, lowered radiation exposure and significantly lower costs in subsequent waste management operations. These benefits need to be balanced with radiation exposure and pre-treatment costs.

13.2. Collection and Segregation

Collection involves the receipt of waste from the waste-generating processes. Collection and segregation lead to additional exposure for personnel. Segregation is where waste or materials (radioactive or inactive) are separated or are kept separate according to radiological, chemical, biological and/or physical properties, which facilitate waste handling and/or processing. The main factors considered in segregation are:

- physical and chemical characteristics of the waste;
- type and half-lives of radionuclides;
- concentration of radionuclides;
- specifications or requirements to be fulfilled for further waste processing.

Segregation should be carried out at the location of waste generation to minimise personnel exposure and to avoid potential mixing of waste streams that make subsequent treatment more difficult or expensive. In practice, however, proper separation of waste streams is not always achieved at the point of generation. In this case collection is followed by a separate segregation phase.

The chemical composition of liquid waste, for example, may affect collection and segregation through its influence on:

- corrosion of storage tanks or equipment used for further waste processing;
- potential for evaporation;
- efficiency of ion exchange processes;
- toxic nature of the waste;
- safety of treatment or conditioning processes (e.g. prevention of violent reactions between organic materials and nitric acid);
- blockages in transfer pipes due to high solids content.

Usually further waste processing is considered when choosing the segregation procedure. For example, the amount of combustible material when incinerating, or separation of liquid and solid waste-forms when using compaction.

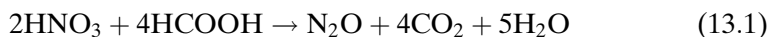
Plants and procedures for segregation of wastes are generally custom-designed to specific requirements but all the necessary technology, tools for waste handling and packaging equipment are commercially available.

13.3. Adjustment

Chemical adjustment is often required to correct the waste composition to fit the requirements of subsequent interim storage, treatment or immobilisation processes. The most common procedures of adjustment are:

- acid or alkaline adjustment (e.g. for interim storage, evaporation, ion exchange or disposal);
- removal of certain components (e.g. of ammonia by alkaline distillation prior to bituminisation);
- destruction of unwanted components (e.g. oxalates in decontamination solutions);
- use of alkaline earth ions to modify the behaviour of conditioned waste;
- neutralisation of nitric acid;
- electrolytic destruction of organic acids, such as oxalic, to reduce corrosion before treatment, e.g. evaporation.

Effluents containing nitrites and iodides may require prior neutralisation to prevent emission of toxic or radioactive gases. Chemical adjustment is required to prevent local precipitation in thin film evaporators or to prevent corrosion and to ensure efficient operation of ion exchange devices. A typical example is utilisation of chemical adjustment of nitric acid concentrates via



which results in emission of gaseous products and reduces acid concentration without salt formation.

Physical adjustment can also be used as some wastes such as process effluents may contain entrained organic solvents or other materials such as lubricating oil. Organics forming a separate phase may become subsequently attached to oleophylic debris (e.g. plastics and string) in the effluent or attract fine active solids.

13.4. Size Reduction

Size reduction techniques are used either to facilitate economic packaging for transportation or to prepare solid waste for subsequent treatment. Tables 13.1 and 13.2 give an overview of available cutting techniques used for size reduction in radioactive waste pre-treatment.

Typical pre-treatment methods include dismantling and shredding. Dismantling involves operations normally used for construction or demolition, with additional constraints for controlling radioactive contamination. Dismantling techniques include mechanical and high-temperature size reduction methods. Size reduction (fragmentation) is usually done where waste is generated. At waste-processing facilities size reduction is used to improve the performance of later treatments such as incineration and compaction.

Circular saws, compass saws and abrasive cutting wheels are used to reduce the size of large concrete blocks. Shredding of solid waste is either a prelude to

Table 13.1: Mechanical size reduction techniques

Technique	Material cut	Working environment
Shears	Metals	Air/water
Power nibblers	Mild steel, stainless steel	Air/water
Mechanical saws	Metals	Air/water
Orbital cutters	Metals	Air/water
Abrasive cutters (wheels, blades, wires, core drills)	Metals, concrete	Air/water
Milling	Metals	Air/water
Wrecking ball, slab	Concrete	Air
Paving breaker, chipping hammer	Concrete	Air/water
Abrasive water jet	Metals, concrete	Air/water
Expansive grout	Concrete	Air
Rock splitter	Concrete	Air/water
Explosives	Metals, concrete	Air/water

incineration or cementation, or a size reduction method for non-combustible waste. Shredders utilise rotating coaxial durable metallic cutters, which shatter and cut materials regardless of initial size and shape so that complex form and composition items are fragmented.

Table 13.2: Thermal cutting techniques

Technique	Material cut	Working environment
Plasma arc	Metals	Air/water
Flame	Mild steel	Air/water
Powder injection flame	Metals, concrete	Air/water
Thermic lance	Metals, concrete	Air/water
Electrodischarge machining	Metals	Air/water
Metal disintegration machining	Metals	Air/water
Consumable electrode	Mild steel	Air/water
Contact arc	Metals	Air/water
Arc saw	Metals	Air/water
Liquefied gas	All materials	Air
Lasers	Metals, concrete	Air/water
Shape memory alloys	Concrete	Air
Electrical resistance	Concrete	Air

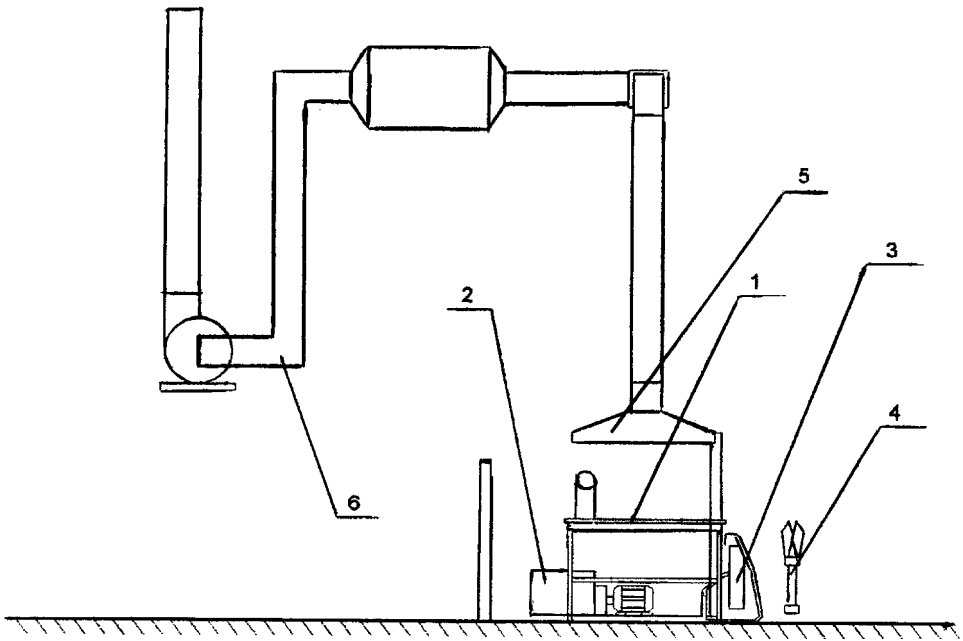


Figure 13.1: Schematic size reduction unit. 1 – operation desk, 2 – pump station, 3 – hosepipe reel, 4 – hydraulic shear, 5 – hood, 6 – extraction ventilator with HEPA filters.

13.5. Packaging

Packaging of solid radioactive waste by the waste generator for handling, transportation and further waste processing is an important pre-treatment operation. It has to comply with transport regulations (if transportation is involved), acceptance criteria or waste specifications for further waste processing and general occupational radiation protection standards.

Combustible low-level solid waste is normally collected at the point of generation in transparent plastic bags (polyethylene or PVC) with sheet thickness between 0.1 and 0.2 mm and volumes of 15–50 L, and is marked with the radiation symbol. This primary package is generally adapted to the collection system, which may be pedal bins for laboratories and other small waste generators or larger bins at nuclear facilities. After filling, the plastic bags are removed from the bins and closed with adhesive tape. Non-combustible small-size LILWs are usually collected as compressible and non-compressible materials in metal or cardboard boxes of 20–50 L for small generators and metal drums of 100–200 L for larger generators. Standard HEPA (high efficiency particulate air or high efficiency particles arrestor) filters are often packed in

welded plastic bags especially when alpha contamination is present. Cardboard boxes may be used as an over-pack.

13.6. Decontamination

Decontamination is a pre-treatment procedure. It allows removal with a decontaminating agent of the most contaminated part of a material or structure so that the remaining part can be reused or discharged as non-radioactive waste. Decontamination processes as a rule produce secondary waste streams, which also need to be treated and conditioned. Decontamination is beneficial if the value of the recovered object or advantage gained is greater than the cost of the decontamination process and also of the treatment, conditioning, transport and disposal of the secondary waste produced. The exposure of operators involved in decontamination operations must also be taken into account.

Decontamination of solid waste, such as spent tools, instruments and plant items is most commonly employed with the objective of reuse. However, it may also be employed to reduce contamination to levels acceptable for disposal as non-radioactive waste, to minimise personnel exposure during subsequent waste treatment operations or for product recovery.

The decontamination efficiency of a material is given by the decontamination coefficient K , which is calculated from

$$K = \frac{A_0 - A_f}{A_0} \times 100\% \quad (13.2)$$

where A_0 is the radioactivity of the material surface before decontamination and A_f is that after decontamination.

Table 13.3 gives simple decontaminating agents for removing weakly bound contamination from different materials. The technology of decontamination has been widely studied and a large variety of methods are well established. A range of commercial chemical and mechanical decontamination techniques is given in Tables 13.4 and 13.5.

Scarifying/scabbling/planing are used to abrade the surface of concrete structures to remove contamination. Scabblers consist of several pneumatically operated piston heads, which simultaneously strike the concrete. Needle guns are used on both concrete and steel surfaces. A needle gun consists of uniform sets of several millimetres long needles, which are pneumatically driven.

Novel decontamination technologies have been developed for different materials over the last decade as decontamination activities evolve (Table 13.6). Ultrasonic methods use solutions of formic acid with complexing agents and corrosion inhibitors at concentrations of 3–4 wt.% and temperatures of

Table 13.3: Decontaminating agents for surface-contaminated materials

Contaminated material	Decontaminating agents
Protective clothing	Detergents
Glassware	Soap or detergent and water, chromic acid solution, concentrated nitric acid, oxalic acid (5%), versene (e.g. ethylenediaminetetraacetic acid (EDTA) 5%), NH_4OH (3%), HCl (10%)
Ceramics	Mineral acids, ammonium citrate, trisodium phosphate
Linoleum	CCl_4 , kerosene, ammonium citrate, dilute mineral acids
Metal	Dilute nitric acid, 10% solution of sodium citrate or ammonium bifluoride, abrasion
Plastics	Ammonium citrates, dilute acids, organic solvents
Paint	CCl_4 , HCl (10%)
Brick and concrete	HCl (32%)

Table 13.4: Chemical decontamination techniques

Contaminated material	Technique
Stainless steel, carbon steel	Nitric acid, sulphuric acid, oxalic peroxide, citric acid, complexing agents, alkaline permanganate followed either by ammonium citrate or EDTA, or citric acid, or sulphuric acid, oxalic acid, REDOX [™] , LOMI [™] , CORD/POP [™] , nitric acid, pastes, chemical fog, CORPLEX [™] , CAN-DECON [™] , EMMA [™] , DECOFOR [™] , DECOPAINT [™] , AP Citrox 20/20 [™] , NP Citrox 21 [™] , chemical gels, foam techniques
Aluminium	Oxalic acid, oxalic peroxide, chemical gels, foam techniques
Lead	TechXtract [™] , chemical gels, foam technique
Metallic oxides	Fluoroboric acid, fluoronitric acid, formic acid
Organic materials from metals	Bleaches, detergents and surfactants, organic solvents
Organic materials from plastic, concrete	Detergents and surfactants, organic solvents
Plastic surfaces	Detergents and surfactants, organic solvents, organic acids, CORPEX [™] , chemical gels, foam techniques
Concrete	Organic solvents, detergents and surfactants, TechXtract [™] , DECONCRETE [™] , chemical gels, foam techniques
Porous surfaces	Foam techniques, chemical gels

Table 13.5: Mechanical decontamination techniques

Technique	Application area
Flushing with water	Large areas
Dusting, vacuuming, wiping, scrubbing	Concrete and other surfaces
Strippable coatings	Large nonporous surfaces
Steam cleaning	Complex shapes, large surfaces
Abrasive cleaning	Metal and concrete surfaces, hand tools
Sponge blasting	Paints, protective coatings, rust, metal surfaces
CO ₂ blasting	Plastics, ceramics, composites, steel, concrete, paints
High pressure liquid nitrogen blasting	Metals, concrete
Freon jetting	Discrete parts inside a glove-box
Wet ice blasting	Coatings, concrete surfaces
High pressure and ultra-high pressure water jet	Inaccessible surfaces, structural steel, cell interiors
Grinding, shaving	Floors, walls
Scarifying, scabbling, planning	Concrete, metal surfaces
Milling	Large number of similarly shaped items
Drilling and spalling	Concrete
Expansive grout	Thick layers of concrete
Paving breaker and chipping hammer	Floors, walls

30–35° C. The decontamination process is accelerated by ultrasound operating at intensities of 0.4–0.5 W/cm² near the contaminated surface. This process allows rapid (within 1–2 h) and effective reduction of surface contamination as well as removal of thick oxide layers (up to several tens of millimetres) from mild steels. Figure 13.2 shows a chemical ultrasonic bath. Its design is optimised to achieve maximum decontamination efficiency. Electrochemical methods (Fig. 13.3) include dry electrolysis, electrochemical etching and electropolishing.

Dry electrolysis uses anodic dissolution of contaminated surface layers of the treated metal and is utilised for flat metal shapes. It uses oxalic acid as the electrolyte and current densities ~ 100 mA/cm². Electrochemical decontamination uses electrolyte solutions based on citric acid (concentrations ~ 100 g/L) and nitric acid (~ 20 g/L) and NH₄NO₃ (~ 50 g/L) with current densities ~ 100 – 200 mA/cm² and electrolyte temperatures 25–50° C. The duration of a decontamination cycle is ~ 30 min. Best results are achieved by combining the electrolysis step with a mechanical treatment using ultrasound.

Table 13.6: Novel decontamination techniques

Technique	Application area	Applications
Ultrasonic	Small objects with weakly bonded contaminants	Commercially available, not suitable for concrete, solvent-absorbing materials and materials which absorb ultrasonic energy
Melting	Metals	Commercially available, contaminants are concentrated in slags, not suitable for activated steel
Electrochemical	Conducting surfaces	Commercially available, uses a range of electrodes
Thermochemical	Metals, concrete, asphalt, coatings on noncombustible materials	Commercially available, uses powder metal fuels (PMF)
Electrokinetics	Soils, concrete, ground water	Commercially available, utilises ionic electromigration, particular efficient for removal of heavy metals and transuranic elements
Laser ablation	Epoxy paints, adhesives, corrosion products, concrete	Emerging technology
Microwave scabbling	Surface layers of concrete	Emerging technology
Thermal degradation	Organic coatings on noncombustible materials	Emerging technology
Microbial degradation	Walls and floors with hazardous residues	Emerging technology
Supercritical fluid extraction	Contaminated surfaces, soils	Emerging technology

Another powerful decontamination technique is electrochemical polishing which uses mobile polishing cells. The cathode is in an insulated cell filled with the circulating electrolyte and an electrical current up to 1 A/cm^2 . The special mobile cell can be used in horizontal or vertical positions on flat surfaces and in corners. This technique removes about $2\text{--}5 \mu\text{m}$ of the stainless steel within approximately a minute.



Figure 13.2: Chemical ultrasonic bath. Courtesy M. Prazska, All Deco, Slovakia.

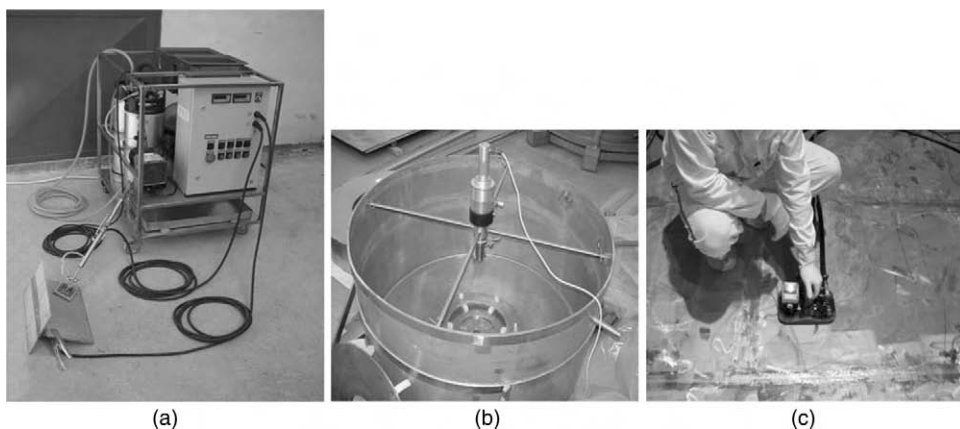


Figure 13.3: Electrochemical techniques: (a) dry electrolysis machine, (b) electrochemical bath and (c) electro-polishing device. Courtesy M. Prazska, All Deco, Slovakia.

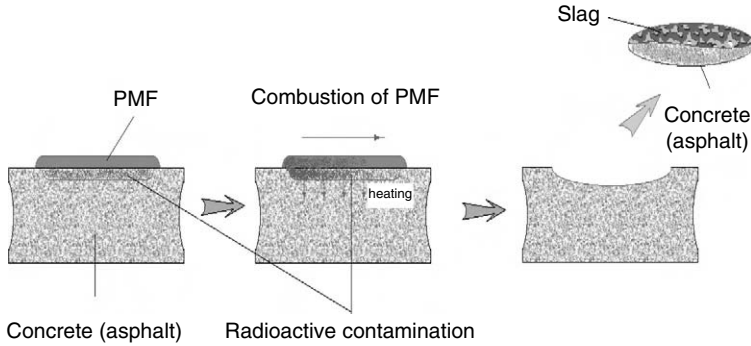


Figure 13.4: Schematic of thermochemical decontamination technique.

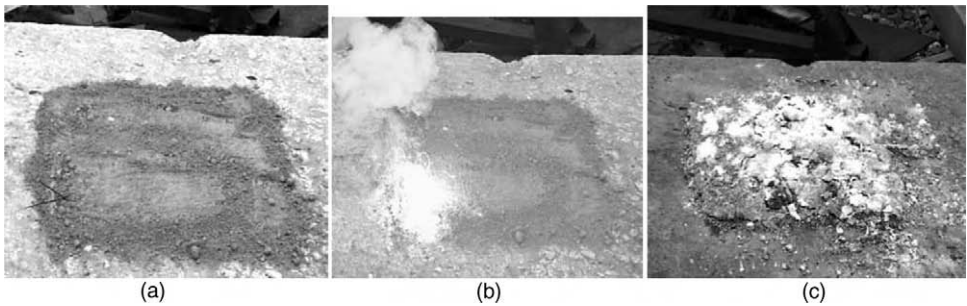


Figure 13.5: Thermochemical decontamination of concrete: (a) $\sim 1\text{ m} \times 1\text{ m}$ contaminated surface is covered by a layer of PMF, (b) ignition of PMF, (c) spallation of concrete upper layers, which are fixed to vitreous PMF combustion products.

Thermochemical decontamination uses thermal volatilisation of radionuclides due to the heat generated when a layer of powder metal fuel (PMF) burns flamelessly on the contaminated material surface (Fig. 13.4). Figure 13.5 shows application of the thermochemical technique to decontaminate deeply (several millimetres) contaminated concrete slabs.

The PMF composition is tailored to heat the surface sufficiently to volatilise the radionuclides, but simultaneously to fix them chemically in the combustion products. The slag formed during the combustion of PMF serves as a radionuclide filter confining practically all of the volatilised radionuclides in its structure. Finally, concrete and slag chips are removed for disposal. In practice thermochemical decontamination is carried out under a mobile fume hood. Decontamination using the thermochemical technique is applied remotely and can be used in limited-access areas without an auxiliary energy supply. Table 13.7 illustrates the efficiency of thermochemical decontamination.

Table 13.7: Decontamination efficiency of the thermochemical technique

Decontaminated material	Depth of material removal (mm)	Process duration (min)	Maximum process temperature (°C)	Carryover of radionuclides (%)	Efficiency K (%)
Metal	0.10–0.15	20	1100	0.1–0.5	95–99
Asphalt	25–35	15	400	0.1–0.5	99.9
Concrete	4–7	20	1300	0.1–0.5	95–99

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Chapter 14

Treatment of Radioactive Wastes

14.1. Treatment Objectives

Treatment of primary radioactive waste includes operations intended to benefit safety and economy by changing the waste characteristics. Three basic treatment objectives are:

- volume reduction;
- removal of radionuclides;
- change of physical state and chemical composition.

Examples of such operations are incineration of combustible waste or compaction of dry solid waste (volume reduction); evaporation, filtration or ion exchange of liquid waste streams (radionuclide removal); and neutralisation, precipitation or flocculation of chemical species (change of composition). Often several of these processes are used in combination to provide effective decontamination of a liquid waste stream.

The waste volume reduction factor VRF of a treatment process is defined as the ratio of initial volume of the treated waste V_0 to the final volume after treatment V_f :

$$\text{VRF} = \frac{V_0}{V_f} \quad (14.1)$$

The higher the VRF the more efficient is the treatment process. However, volume reduction inevitably leads to concentration of radionuclides which may impact on the safety and economics of the process.

Treatment may lead to several types of secondary radioactive waste, such as, contaminated filters, spent resins and sludges. After treatment, depending on the radionuclide content in the waste, it may or may not require immobilisation.

14.2. Treatment of Aqueous Wastes

In most cases treatment of aqueous waste aims to split it into two fractions: a small volume of concentrate containing most of the radionuclides and a large volume whose level of contamination is sufficiently low to permit its discharge to the environment (Fig. 14.1).

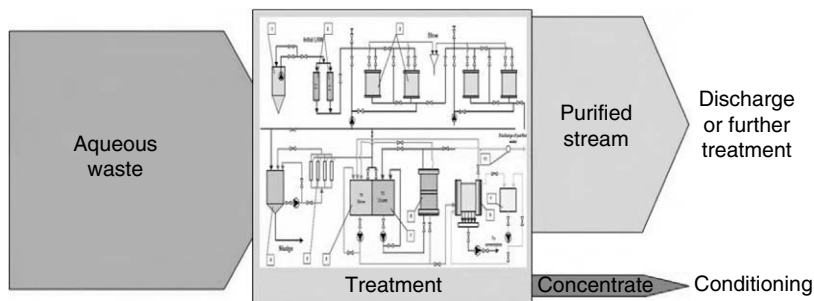


Figure 14.1: Schematic of aqueous waste treatment.

The decontamination factor (DF) achieved via an aqueous treatment process is defined as the ratio of initial concentration of radionuclides in the waste A_0 to the final concentration in the largest waste stream (e.g. purified water) after treatment A_f :

$$DF = \frac{A_0}{A_f} \quad (14.2)$$

A variety of chemical and radiochemical compositions of aqueous waste exists so that a considerable number of treatment technologies have been developed to purify radioactive liquid waste. The most developed aqueous waste treatment methods are evaporation, chemical precipitation, sorption and ion exchange, micro-filtration, reverse osmosis, electrodialysis, coagulation and ultra-filtration. Table 14.1 illustrates the DFs achieved for a number of common aqueous treatment technologies.

In practice several methods are normally used in combination, e.g. evaporation followed by ion exchange.

14.2.1. Evaporation

Evaporation is a proven method for the treatment of liquid radioactive waste providing both high decontamination factors and good concentration of salts

Table 14.1: Aqueous treatment techniques

Technique	Application	DF
Evaporation	Large volumes	$\sim 10^4 - 10^6$
Chemical precipitation (coagulation, flocculation, separation, electro-coagulation)	High salt content >1 g/L	$\sim 10 - 10^2$ for β and γ , $\sim 10 - 10^3$ for α
Ion exchange		
Organic exchangers	Low salt content <1 g/L	$\sim 10 - 10^3$
Inorganic exchangers	Selective sorption	$\sim 10 - 10^4$
Reverse osmosis	Large volumes	$\sim 10^2 - 10^3$
Electrodialysis	Low and high salt content	$\sim 10^2 - 10^3$
Ultra-filtration	In combination with other methods	$> 10^2$ (removes particulates and colloids)
Micro-filtration	Pre-treatment technique	Removes particulates

and radionuclides in bottom residues. Clean water is removed as vapour leaving behind non-volatile components such as salts and most radionuclides. The presence of volatile nuclides such as tritium and some forms of iodine and ruthenium, particularly at a high nitric acid concentration, reduces the overall high decontamination factor for evaporation.

Evaporation of liquid radioactive waste with low salt content (1–5 g/L) is normally carried out in two stages. Decontamination is performed in the first stage and concentration in the second stage. For liquid radioactive wastes with high salt content (up to 400 g/L) the evaporation process is usually carried out in one stage. Radioactive waste evaporators are generally kept simple to reduce maintenance problems at the expense of loss in thermal efficiency. Some wastes do, however, require more complex design and scraped film evaporators have been used (Fig. 14.2). Evaporation apparatus usually operates hydrothermally with hot steam at ~ 0.5 MPa and $\sim 150^\circ\text{C}$ with $\sim 380\text{ m}^3$ of steam generated per 1 m^3 of aqueous purified waste. The evaporator produces a clean condensate, which can generally be discharged directly to the environment and a concentrate, which may be encapsulated in cement or other media

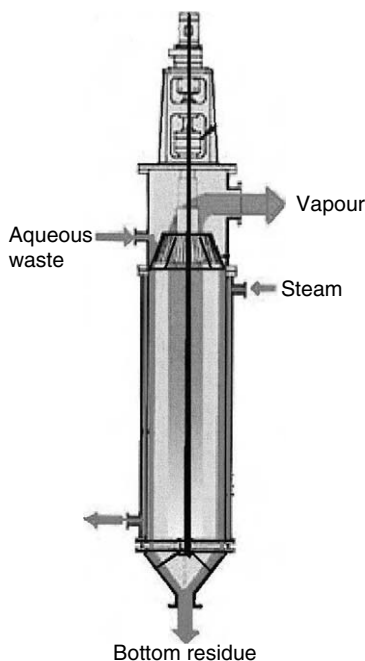


Figure 14.2: Schematic of a thin film evaporator.

for long-term storage or disposal. The main disadvantages of evaporation are high capital, energy and maintenance costs, large size of apparatus, enhanced temperatures, corrosion problems and scaling or foaming. Evaporation is one of the best techniques for relatively high salt content waste and for nitric-acid-containing effluents, when high decontamination factors (e.g. 10^4 – 10^6) are required. However, it is expensive in energy terms – typical energy consumption is $\sim 2.7 \text{ GJ/m}^3$ of purified water.

14.2.2. Chemical Precipitation

Chemical precipitation or reagent coagulation, precipitates impurities from purified water via change of pH, electro-oxidising potential or co-precipitation using precipitating agents (coagulants) such as ferrous or aluminium sulphates. Reagent oxidation is a special case of reagent coagulation in which oxidising reagents, for example, potassium permanganate or bichromate, are added in purified solution to destroy organic impurities or to change the valence of

multivalent ions following precipitation. Electro-coagulation is a process of impurity precipitation using ions passing into purified water from a dissolving anode via application of an electric current. Typical anode materials for electro-coagulation are iron or aluminium. Electro-oxidation uses decomposition of organic impurities under the action of hypo-chlorites, formed on anodes when an electric current is passed between electrodes in a solution containing chloride ions. Ozonation is applied to decompose organic impurities by ozone-enriched purified water. A typical chemical precipitation method involves four stages:

- addition of reagents, adjustment of pH to form the precipitate;
- flocculation;
- sedimentation;
- solid–liquid separation.

Table 14.2 shows typical chemical reagents used in precipitation processes.

Chemical precipitation invariably forms a sludge and thus has always to be connected to physical methods to separate the sludge and supernatant liquid. Sedimentation involves holding the waste in a tank to separate suspended solid particles from the solution under gravity at a rate determined by Stokes' Law. The radionuclides present in a liquid waste stream are concentrated into a smaller volume of wet solids that can be separated from the bulk liquid. Depending on the levels of radioactivity in the primary waste and on the concentration factors achieved, the sludge produced by a chemical treatment may be significantly more radioactive than the initial waste.

Waste volume reduction and decontamination factors (VRF and DF) achieved with a precipitation process depend strongly on the method of solid–liquid separation used. Typical techniques include sedimentation and decantation, filtration or centrifugation. A key difficulty is that most iron-bearing precipitates are notoriously difficult to filter because of their gelatinous nature so that expensive filtration plant may be needed. However, provided that the final filtrate is pure enough for discharge without further treatment, filtration is much cheaper than evaporation.

Chemical precipitation processes are well established for removal of radioactivity from LILW and are in regular use at spent fuel reprocessing facilities, research establishments and nuclear power stations. Chemical precipitation is normally used to treat high volume, low-level waste streams or if more efficient treatments, such as concentration by thermal evaporation or ion exchange, are not feasible. Alternatively, a precipitation process can precede another treatment technique such as evaporation or ion exchange.

Table 14.2: DF of radionuclide removal via chemical precipitation processes

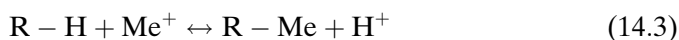
Radionuclide	Process reagent	pH	DF
Pu, Am	Hydroxides (e.g. ferric)	7–12	$>10^3$
	Oxalates	1	$>10^3$
Cr	Ferrous hydroxide	≥ 8.5	$>10^2$
Mn	Manganese hydroxide	≥ 8.5	$>10^2$
	Manganese dioxide	≥ 8.5	$>10^2$
Co, Fe	Ferrous or ferric hydroxides	≥ 8.5	$>10^2$
Sr	Ferrous hydroxides	7–13	Depends on pH
	Calcium or iron phosphate	>11	$>10^2$
	Calcium carbonate	10.5	$>10^2$
	Manganese dioxide	>11	$>10^2$
	Barium sulphate	≥ 8.5	$>10^2$
	Polyantimonic acid	1	$>10^2$
Zr, Nb, Ce	Hydroxides (e.g. ferric)	>8.5	10^2 – 10^3
Sb	Ferrous hydroxides	5–8.5	5–10
	Titanium hydroxide	5–8.5	10 – 10^2
	Polyantimonic acid and manganese dioxide	1	20–40
	Diuranate	8.5–10.5	20–30
Ru	Ferrous hydroxide	6–10	$>10^2$
	Copper + ferrous hydroxides	8.5	10–25
	Cobalt sulphide	1–8.5	30–150
	Sodium borohydride	8.5	50
Cs	Ferrocyanide	6–10	$>10^2$
	Zeolite	7–11	10
	Tetraphenylborate	1–13	10^2 – 10^3
	Phosphotungstic acid	1	$>10^2$
	Ammonium phosphomolybdate	0–9.5	>10

Chemical precipitation may be affected by the presence in the waste stream of complexants, trace organics or particulates. In these cases, pre-treatment using filtration, micro-filtration and ultra-filtration may be needed. Filtration is a water purification process occurring when water is pumped through a layer of granulated load such as sand or crushed claydite (expanded clay) or a macro-porous material such as woven textile or filter paper with pore sizes up to several tens of micrometres. Suspended particles and emulsions do not pass due to physical blocking or adhesive interaction with the filter material.

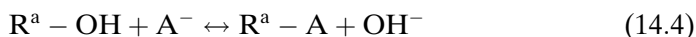
14.2.3. Sorption and Ion Exchange

Sorption is a water purification process occurring when water is pumped through a layer of granulated load material such as activated charcoals or zeolites. It works in much the same way as a home drinking water filter system. Impurities in the water (such as dissolved organic molecules, ions and surface-active particles) are extracted via the process of sorption as a result of their physical and chemical interaction with the load material. Ion exchange is a special case of sorption, when ions in solution exchange with ions in the matrix of the granulated load. Granulates used include ion exchange resins (Fig. 14.3) and natural or synthetic inorganic sorbents such as hexacyanoferrate or zeolites.

To remove both positively and negatively charged ions from solution, a mixture of cation and anion resins in a mixed bed system is often used. For example, the hydrogen form of a cation exchanger releases its hydrogen ion into solution and picks up a cation Me^+ from the waste-containing solution:



where R is the insoluble part of the cationite. Alternatively, an anion exchanger releases its hydroxide ion into solution and picks up an anion A^- from the solution:



where R^{a} is the insoluble part of the anionite. Since H_2O is only weakly dissociated, ion exchange reactions are driven to the right hand side of the



Figure 14.3: Granulates of organic ion exchange resins used in water treatment systems.

equations thereby removing the charged anions/cations. The efficiency of ion exchange purification depends on the ion exchange isotherm, distribution coefficient, separation factor and selectivity coefficient. Other important parameters of ion exchangers are ion exchange capacity, and chemical/mechanical durability.

The ion exchange sorption isotherm gives the concentration of a sorbed species in the ion exchanger, expressed as a function of its concentration in the external solution under specified conditions and at constant temperature. The total available exchange capacity of an ion exchanger is described by the number of functional groups on it. This value is constant for a given ion exchange material and is generally given as milli-equivalents per gram (meq/g), based on the dry weight of material in a given form. The ion exchange capacity K (meq/g) is determined by:

$$K = (C_0 - C_e) \frac{V}{M} \quad (14.5)$$

where C_0 is the initial and C_e is the equilibrium concentration of ions in the solution (meq/mL), V is the volume of solution (mL) and M is the weight of sorbent (g). To characterise ion exchangers, two capacity parameters are commonly used – the total static exchange capacity determined under static conditions and the dynamic exchange capacity determined by passing a solution through the exchanger bed. The exchange capacity depends on the number of functional groups per gram of exchanger. The extent of the use of the total exchange capacity depends on the level of ionisation of the functional groups of the exchanger and on the chemical and physical conditions of the process.

The distribution coefficient K_d (mL/g) characterises the capability of an ion exchanger of mass M (g) to absorb the ions from a water solution of volume V (mL):

$$K_d = \frac{(C_0 - C_e)}{C_e} \frac{V}{M} \quad (14.6)$$

where C_0 is the initial and C_e is the equilibrium concentration of ions in solution.

Under dynamic conditions, in which the ion exchange medium is used in a packed bed or in a column with a mass M_{bed} (g), the distribution coefficient can be used to calculate the theoretical maximum capacity of the ion exchange bed to purify a volume V_{tot} (mL) of waste solution:

$$V_{\text{tot}} = K_d M_{\text{bed}} \quad (14.7)$$

The value of V_{tot} is, in practice, never achieved as the process is always stopped due to diminution of the DF to breakthrough values at which the concentrated liquid passes straight through the column.

The selectivity of a sorbent $K^{M1/M2}$ for an ion M1 in relation to another M2 is determined by the ratio of distribution coefficients:

$$K^{M1/M2} = \frac{K_d(M1)}{K_d(M2)} \quad (14.8)$$

where $K_d(M1)$ and $K_d(M2)$ are the distribution coefficients for ions M1 and M2, respectively. Table 14.3 illustrates the selectivity of sorbents to Cs compared to Na ions in solution at various concentrations. Depending on the desired aim various ion exchangers can be selected; for example hexacyanoferrate has the highest selectivity in separating Cs from Na-containing solutions.

The hydro-mechanical durability of ion exchangers is their ability to withstand mechanical impact caused by water flow. Mechanical attrition of ion exchangers may lead to loss of fine particles into the waste water. Organic ion exchange resins typically have the highest hydro-mechanical durability.

A sorbent's chemical stability is determined both by its chemical nature and by the waste solution composition in which it is used. Organic ion exchange resins are the most chemically stable over a wide pH range. Inorganic sorbents based on phosphates and oxyhydrates of nonferrous metals as well as synthetic and natural zeolites, are unstable in acid media at $\text{pH} < 3$. Inorganic sorbents based on transition metal ferrocyanides are unstable in alkaline media at $\text{pH} > 10$. A large number of proven ion exchangers are currently available for the treatment of aqueous radioactive wastes. These include various organic ion exchange resins and bio-sorbents based on processed wood, lignin, turf and chitin. Inorganic ion exchangers include natural clinoptilolite, synthetic zeolites (with higher silica content, which generally gives greater hydrothermal stability, stronger-acid catalytic activity, and greater hydrophobicity) such as Na-Y

Table 14.3: Selectivity of sorbents to Cs^+ compared to Na^+

Sorbent	C_{Na} (mol/L)	$K^{\text{Cs/Na}}$
Strong acid resins*	1.0	<10
Cs-selective resin**	6.0	11400
Zeolite (mordenite)	0.1	450
Crystalline silicotitanate (CST)***	5.7	18000
Na-Ni-hexacyanoferrate	5.0	1500000

*See below for description of acidic and basic resins.

**See below for description of resin affinity.

***For example the commercial exchanger IONSIV IE-911 is a CST.

zeolite, aluminosilicate and silica gels, transition metal ferrocyanides, oxyhydrates and phosphates of titanium or zirconium in spherical granules, natural pyrolusite, modified manganese dioxide and activated charcoals. Organic ion exchange resins are widely used in water purification systems and virtually all nuclear reactors use organic ion exchangers. Depending on the type of functional group, ion exchangers can be divided into several types – strongly acidic, strongly basic, weakly acidic and weakly basic. Organic ion exchangers containing sulpho- and phospho-acidic groups are strongly acidic while those containing tetra-ammonium basic groups are strongly basic. Those containing phenolic and primary amino groups are weakly acidic and weakly basic exchangers, respectively. Exchangers with carboxy groups and tertiary amino groups are intermediate between strongly and weakly acidic and basic exchangers, respectively. Figure 14.4 shows the chemical formula of a typical organic ion exchanger, which has a SO_3H functional group.

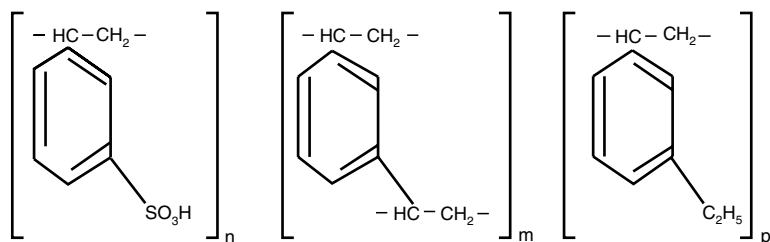
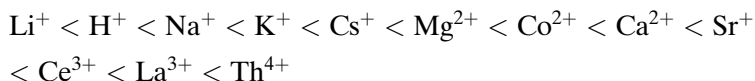
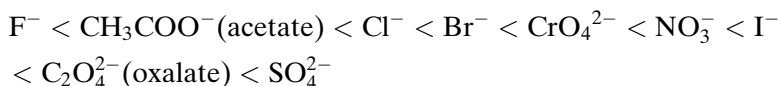


Figure 14.4: Chemical formula of an organic ion exchanger (KU-2-8).

For organic ion exchange resins at low concentrations and temperatures the affinity for cations typically increases following the series:



and for anions:



In the nuclear industry in general, and waste treatment in particular, advantage is not normally taken of the reversibility of ion exchange, e.g. on the possibility of regenerating ion exchangers. Once the ion exchange load is saturated it is removed from service and treated as radioactive waste. Inorganic ion exchangers are preferred over organic due to their longer durability and simpler immobilisation. They can be incorporated into cement, bitumen and

glasses as well as ceramic waste-forms ensuring a higher degree of radionuclide retention. Table 14.4 gives the main parameters of an inorganic ion exchanger based on natural clinoptilolite.

Table 14.4: Sorption parameters of a natural clinoptilolite sorbent

Parameter	Level		
Ion exchange capacity	>1.0 meq/g Cs ⁺ , Rb ⁺ , K ⁺ , NH ₄ ⁺ , Sr ²⁺ , Ba ²⁺ , Ag ⁺ , Tl ⁺ , Pb ²⁺ , Hg ⁺	0.5–1.0 meq/g Mn ²⁺ , Cu ²⁺ , Zn ²⁺ , Cd ²⁺	<0.5 meq/g Fe ³⁺ , Cr ³⁺ , Ce ³⁺ , Ru ³⁺ , Zr ⁴⁺ , Nb ⁴⁺ , Co ²⁺
Distribution coefficient, K_d	10 ³ –10 ⁴ ¹³⁷ Cs, ^{110m} Ag, ²⁰⁴ Tl, ²²⁶ Ra, ¹³³ Ba	10 ² –10 ³ ⁹⁰ Sr, ⁶⁰ Co, ⁵⁴ Mn, ⁵⁶ Fe, ⁶⁵ Zn, ^{115m} Cd	< 10 ² ¹⁴⁴ Ce, ¹⁰⁶ Ru, ⁹⁵ Zr, ⁹⁵ Nb
Selectivity in presence of Na, Mg, Ca	High ¹³⁷ Cs, ^{110m} Ag, ²⁰⁴ Tl, ²¹⁰ Pb, ⁹⁰ Sr, ²²⁶ Ra, ¹³³ Ba	Satisfactory ⁶⁰ Co, ⁵⁴ Mn, ⁵⁶ Fe, ⁶⁵ Zn, ^{115m} Cd	Low ¹⁴⁴ Ce, ¹⁰⁶ Ru, ⁹⁵ Zr
Optimal pH	5–9		

14.2.4. Membrane Methods

Membrane methods comprise (but are not limited to) micro- and ultra-filtration, and reverse osmosis. Figure 14.5 illustrates the size ranges of impurities that are removed from aqueous media using some of these methods.

Micro-filtration involves pumping water through a micro-mesh membrane (diaphragm) with pore sizes from 0.1 to several μm at working pressure up to 0.1 MPa. Ultra-filtration involves pumping water through a membrane with pore sizes from 0.01 to 1 μm at pressures up to 0.5 MPa, removing colloidal particles, emulsions, most large molecules and bacteria in the process. Reverse osmosis uses membranes with pore sizes from 0.001 to 0.01 μm and working pressures up to 10 MPa and removes practically all impurities from water. Electrodialysis is a membrane separation process in which an electric potential is applied across a membrane. In a typical electrodialysis cell, anion and cation

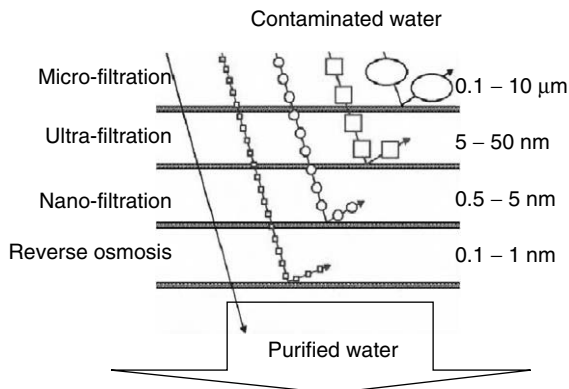


Figure 14.5: Membrane purification processes.

exchange membranes are arranged alternately in a stack. An electrical field, sufficient to force current through the stack, is applied between two electrodes placed at each end of the stack. Ions are transported through the membrane due to current flow from the diluted to the concentrated stream. Electrodialysis is used for water desalination as well as for treatment of aqueous radioactive waste.

14.2.5. Combined Methods

In variable mixed aqueous waste streams several treatments are frequently necessary to achieve the best overall decontamination factor for total alpha and/or total beta–gamma activity of the liquid waste. Figure 14.6 illustrates a typical aqueous radioactive waste treatment facility involving a combination of methods and purification equipment.

Water-purifying facilities can be either stationary or mobile. Stationary facilities are best for constant aqueous waste streams characterised by a stable chemical and radionuclide composition. Mobile module type facilities are characterised by a high degree of flexibility and hence allow more efficient purification of variable wastes (Fig. 14.7).

14.3. Treatment of Organic Liquid Wastes

The volume of organic waste is small compared to that of aqueous radioactive waste although the risk associated with its improper management may be high.

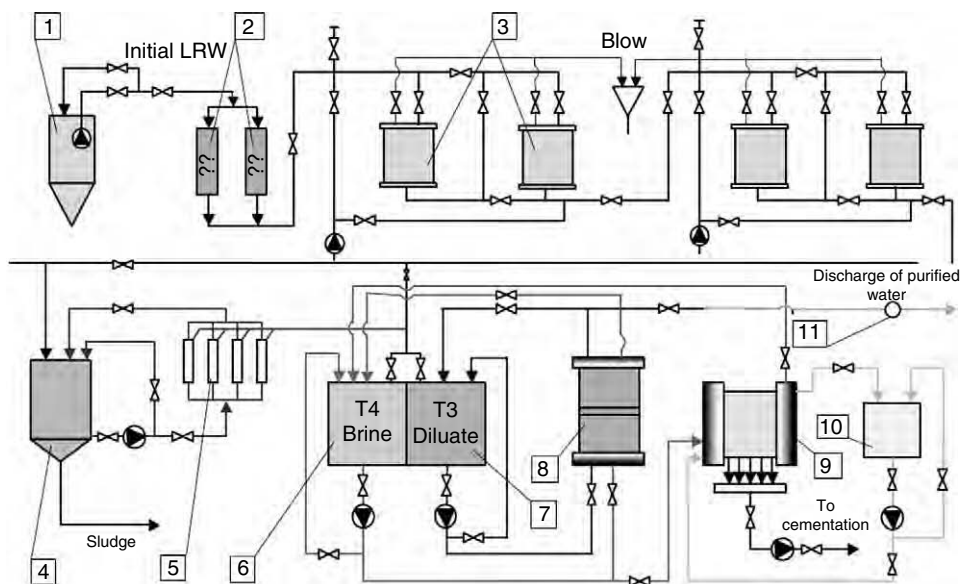


Figure 14.6: Flow diagram of a typical aqueous waste treatment facility: 1. Tank with initial liquid radioactive waste (LRW); 2. Filter-container; 3. Filter; 4. Ultra-filtration tank; 5. Ultra-filtration module; 6. Brine tank; 7. Diluate tank; 8. Electro-dialyzer (EDMS); 9. Electro-dialyzer-concentrator (EKDSO); 10. Tank for washing solution; 11. Counter for purified water.



Figure 14.7: A typical modular mobile aqueous treatment facility.
Courtesy Y. Karlin, SIA RADON, Russia.

Aqueous waste may be discharged to the environment after the radioactivity has decayed or been removed by treatment. By contrast, organic radioactive waste requires management steps that not only take account of its radioactivity, but also of the chemical organic content since this can also have detrimental effects on the environment. The “dilute and disperse” option applied for some aqueous and gaseous waste is inappropriate for organic liquid wastes. Treatment of large amounts of radioactive liquid organics is technology intensive as well as costly.

The objectives of organic liquid waste treatment may be:

- conversion to a solid form;
- conversion to an inorganic form to facilitate conditioning;
- volume reduction;
- decontamination for reuse;
- conversion to an organic form compatible with cementation.

The main organic waste treatment methods are:

- incineration;
- emulsification to facilitate encapsulation into cement;
- absorption into a matrix;
- distillation;
- wet oxidation.

Incineration is an attractive technique for treating organic liquids because they are readily combustible, and high volume reduction factors can be achieved. Ensuring complete combustion of the waste and maintaining stack emissions within acceptable limits are the main technical difficulties. In addition to containing volatile radionuclides and radioactive particulates, the off-gas system must control the release of chemically toxic or noxious effluents such as HCl, SO₂ and NO_x. Improperly controlled combustion can produce toxic compounds such as dioxins. Thermochemical treatment using powder metal fuels (PMFs) has a significant advantage in treating organic liquids as it completely destroys organics, does not generate chemical toxins and confines both volatile and non-volatile radionuclides to the combustion ash-slag residue.

A simple on-site treatment for organic liquid radioactive waste is to convert the liquid to a solid form with absorbents. As long as there is excess absorbent there is no need even for mixing; the liquid waste can be added to the absorbent in a suitable container and eventually all the liquid will be taken up. This technique has been routinely used for solidification of radioactive turbine and pump oil. Typical absorbents are:

- natural fibre (sawdust, cotton);
- synthetic fibre (polypropylene);
- vermiculite (mica);
- clays;
- diatomaceous earth.

The absorption efficiency of the different absorbents can vary by a factor of 2–3, and the waste volume increase can be up to 300%.

14.4. Treatment of Solid Wastes

The essential purpose of solid waste treatment is to reduce the volume. The fire hazard of waste is reduced by converting the waste from burnable to non-burnable form. Available solid waste treatment options include methods such as:

- compaction and super-compaction;
- incineration, pyrolysis;
- melting;
- chemical, thermochemical, biochemical decomposition.

The waste concentrates arising from volume reduction are then conditioned to give the final package for interim storage or disposal.

14.4.1. Compaction and Super-Compaction

Compaction involves compressing solid waste into containers or boxes to reduce the volume. Different types and designs of relatively simple compactors with compressive forces between 100 and 500 kN are available offering varying volume reduction possibilities. These have a typical volume reduction factor VRF \sim 2–5. In-drum compactors press waste inside packing drums, drum crushers apply higher forces and compact waste directly in drums so diminishing aerosol emissions (Fig. 14.8).

The highest volume reduction factor is achieved with super-compactors applying forces >12 – 15 MN. Application of greater force does not lead to further volume reduction (Fig. 14.9). Super-compactors compact waste directly in drums. Figure 14.10 shows a super-compactor and compacted drums produced via this process. Depending on the waste type VRFs of super-compactors can be as high as 100. The status of super-compacting facilities currently available worldwide is shown in Table 14.5.

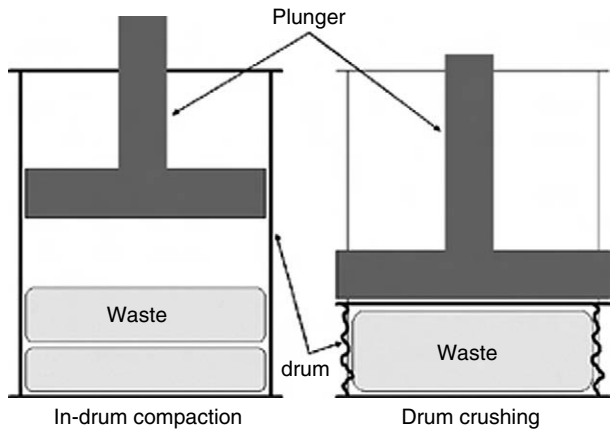


Figure 14.8: Schematic of radioactive waste compaction.

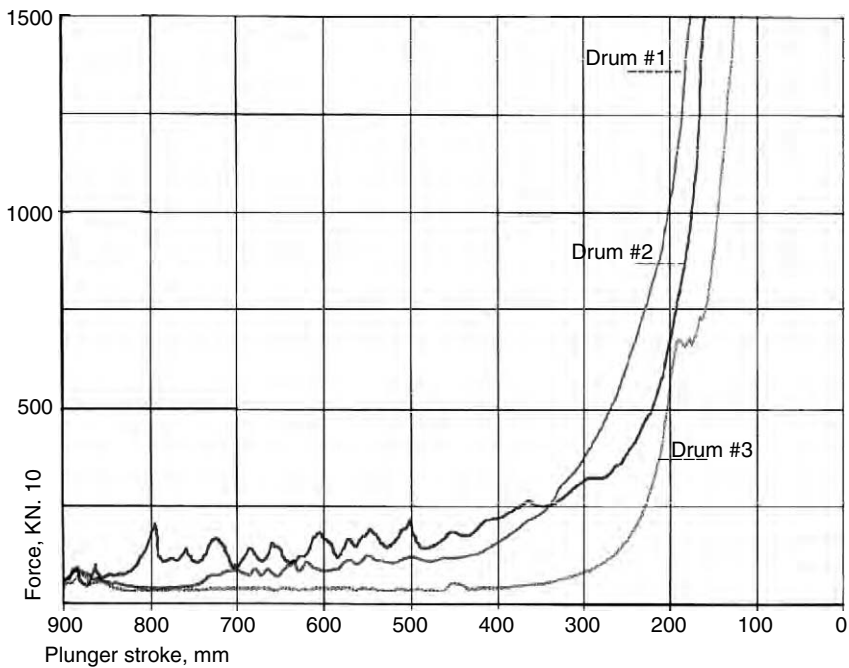


Figure 14.9: The stroke of a super-compactor plunger as a function of applied force for three different waste drums. Courtesy of Fontijne, Netherlands.



Figure 14.10: Super-compacting of radioactive waste drums. Courtesy of F.A. Lifanov, SIA RADON, Russia.

14.4.2. Incineration

Incineration is a thermal method involving oxidation of burnable components of waste, which has been successfully applied to radioactive waste for many decades. The excess air coefficient, α , of an incineration process is defined as the ratio of amount of supplied air M_{air} (oxygen) to the stoichiometric amount of air M_{stoich} (oxygen) required to achieve complete oxidation of the waste components:

$$\alpha = \frac{M_{\text{air}}}{M_{\text{stoich}}} \quad (14.9)$$

Incineration can be carried out with excess air or oxygen such that $\alpha > 1$, controlled supply of oxidiser ($\alpha = 1$), or deficit supply ($\alpha < 1$) when the process of pyrolysis occurs and burnable gases are burnt in a separate post-combustion chamber or afterburner. The combustion efficiency E_c (%) is determined by measuring the carbon dioxide $[\text{CO}_2]$ and carbon monoxide $[\text{CO}]$ concentrations in the incinerator exhaust gas:

$$E_c = \frac{[\text{CO}_2] - [\text{CO}]}{[\text{CO}_2]} \times 100\% \quad (14.10)$$

Table 14.5: Solid radioactive waste super-compacting facilities

Country	Facility, site	Start of operation	Applied force, MN	Comment
Austria	Seibersdorf	1955	20	
Belgium	Mol, Belgoprocess	1993	20	
China	China Institute of Atomic Energy	2000	20	
France	La Hague, Cogema	1986	15	ILW Mobile facility
		1997	25	
	EdF Bugey	1990	20	
	Soulanes	1991	15	
	Framatome	1999	15	
Germany	Brunsbüttel	1983	20	Scrapped in 2001
	Forschungszentrum Karlsruhe	1984	15	
		1997	20	
		2001	15	Operated by AEA Technology
	Amersham Buchler		20	
	Philippsburg	1994	20	
	Juelich	1996	15	
	Wurgassen	1997	20	
	Dortmund, GNS		20	
	Lubmin, Energie Nord		20	
	Gundremmingen, KRB		20	Fakir 7
	KWU-Karlstein	1988	16	
Italy	ENEA, Casaccia	1988	20	Mobile system
Japan	Tokyo Electric Power		20	
Netherlands	COVRA, Vlissingen	1993	15	
Republic of Korea	KEPCO	1992	20	Mobile system
Russia	Balakovo, NPP	2001	20	
	Sergiev Posad, Radon	1997	15	
Slovakia	Bihunice	1998	20	
Spain	El Cabril	1992	20	Fakir 3
UK	Dounreay, UKAEA	1990	20	Mobile system 2 units
	Sellafield, BNFL	2000	20	

USA	WTC	1996	20	Used for plutonium-containing waste
	UKAEA	1986	20	
	BWX Technologies, B&W	1986	15	Operational at naval fuel plant
	INEEL	2001	20	
	GTS Duratek	1987	15	
		1990	50	
	Savannah, SRS	1986	10	Former West Valley
	Hanford, ATG	1992	15	
	Hanford, WRAP Race	1996	20	2 units
	Rocky Flats, DOE	1989	20	Never operational
	Chem Nuclear Chicago		12	Fakir 2
	Northern States Power	1985	20	Mobile system
Taiwan, China	Taipower, Kuosheng plant	1990	20	
Ukraine	Chmelnitsky NPP	2001	20	
	South Ukraine NPP	2001	20	

Ideal combustion of organics is achieved when no CO is measured in the off gas. Incineration normally achieves the highest volume reduction and converts the waste to a form which is suitable for subsequent immobilisation and disposal. Besides off gas, incineration produces ash residue, soot and condensate from the off-gas purification systems (Fig. 14.11).

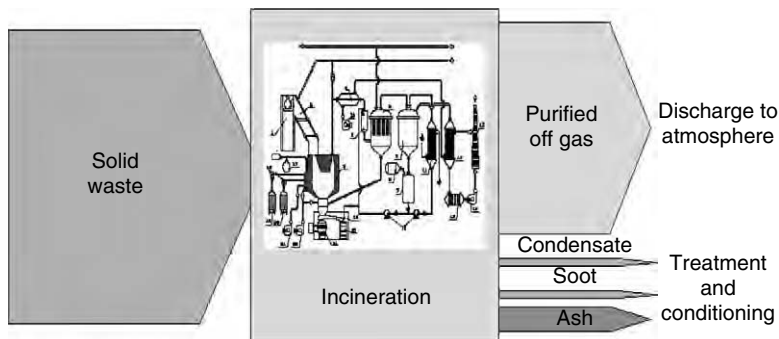


Figure 14.11: Schematic of incineration.

The VRF for an incineration process is usually defined as the ratio of the initial waste volume V_{waste} to the volume of ash residue V_{ash} :

$$\text{VRF} = \frac{V_{\text{waste}}}{V_{\text{ash}}} \quad (14.11)$$

Typical incineration VRFs range between 50 and 100 for solid radioactive waste and between 500 and 1000 for liquid waste. Typical ash contains 90–95% of the waste radionuclides with 1–5% in the soot and 0.1–2% in the condensate. The radionuclide content in waste acceptable for incineration is usually limited to a beta activity of 10^{-4} Ci/kg, and an alpha activity of 10^{-5} Ci/kg. Incineration of combustible waste containing larger quantities of radionuclides requires special off-gas purification and maintenance systems, which require high investment and operation costs. Incineration of waste occurs in a combustion chamber on fire grates and after combustion is completed the ash is discharged via downward sloping floors. Complete combustion of volatilised components is achieved in the post-combustion chamber. These are often filled with refractory materials such as silicon carbide to assist complete disintegration of the organics and their combustion (Fig. 14.12). Typical temperatures in the combustion chamber are 900–950° C although they may be higher in the post-combustion chamber.

Figure 14.13 shows a flow diagram of an excess air supply (e.g. $\alpha > 1$) radioactive waste incineration plant. Such plants can incinerate 50–200 kg of waste per hour. The specific consumption of liquid fuel is about 0.25 kg/kg of waste. A significant part of an incineration facility is the off-gas purification system, which removes radioactive and chemical toxins ensuring that the off-gas discharges are below permitted levels. An incinerator's gas purification system typically provides a reduction factor of specific radioactivity in off gases above 1000.

Advanced incineration systems may use plasma treatment of the waste, so that the ash residue can be melted into a mineral-like or glass composite



Figure 14.12: Inside view of a radioactive waste incinerator: (a) fire grates, (b) post-combustion chamber filled with silicon carbide (authors' photos).

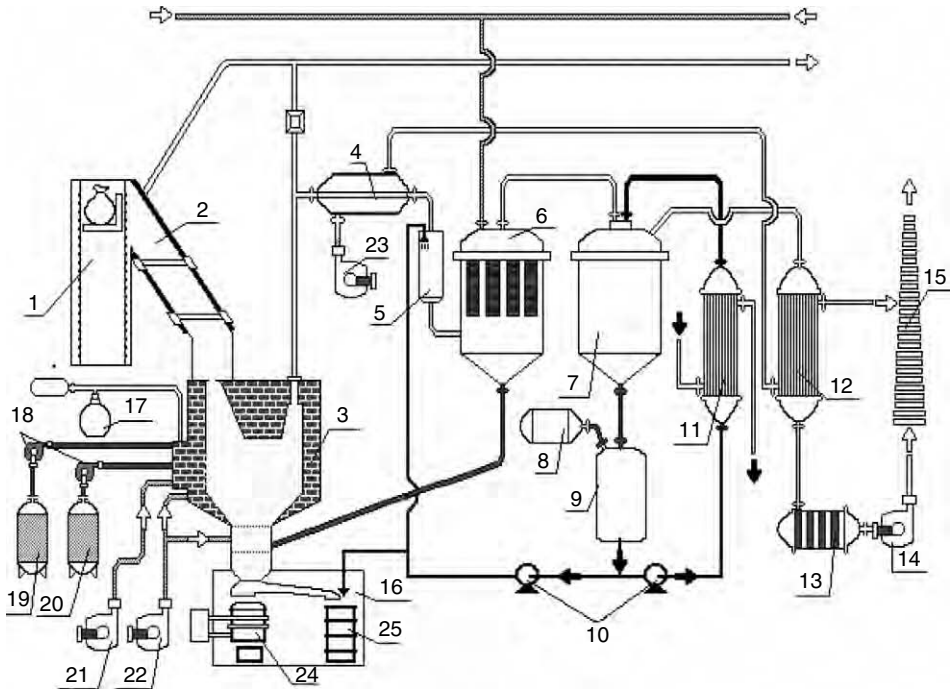


Figure 14.13: Schematic of a radioactive waste incineration plant. 1 – lift; 2 – loading unit; 3 – furnace, comprising combustion and postcombustion chambers; 4, 11, 12 – heat exchangers; 14, 21–23 – extraction fans; 5 – evaporating heat exchanger; 6 – high-temperature filter; 7 – scrubber; 8 – neutralisation vessel; 9 – scrubber solution vessel; 10, 18 – pump; 13 – HEPA filter; 15 – stack; 16 – unit of ash removal; 17 – ignition system; 19 – fuel tank; 20 – liquid radioactive waste tank; 24 – ash vitrification unit; 25 – ash cementation unit.

material (Section 17.11). Shaft furnaces supplied by plasma burners are particularly efficient and able to treat both organic and inorganic wastes such as glass, ceramics, construction materials, garbage and metal reinforcement without pre-treatment. Carryover of volatilised radionuclides in shaft furnaces is minimised by filtration of released gases through the waste in the furnace shaft (Fig. 14.14).

Temperatures of 1400–1600°C are achieved in shaft furnaces with plasma burners (plasmatrons) which melt the ash residue. Plasma slagging furnaces generate a liquid slag, which cools to a solid, chemically durable material suitable for long-term storage and final disposal. Incineration is a serious option for the large volumes of contaminated graphite remaining from graphite-moderated reactors (Section 11.2) although there are difficulties associated

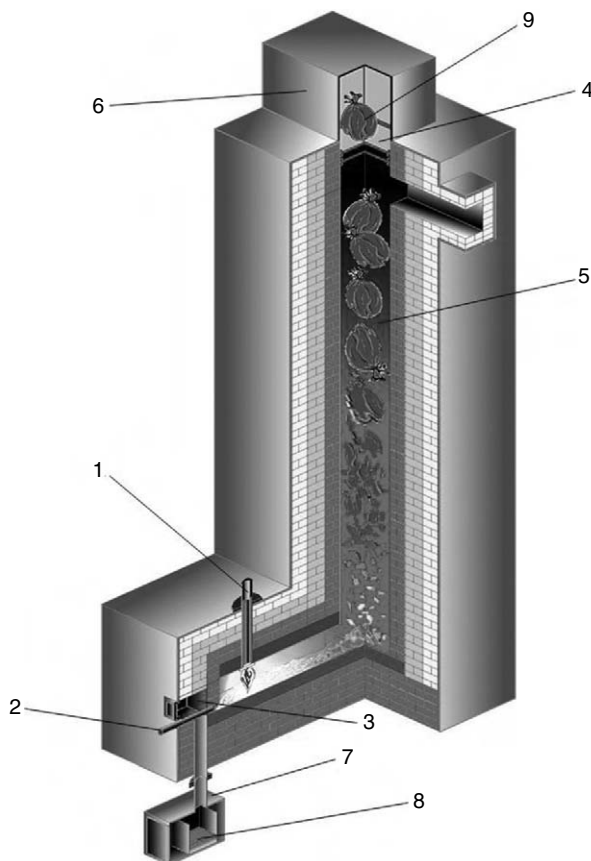


Figure 14.14: Schematic of a shaft type plasma incineration facility. 1 – plasmatron, 2 – pouring unit, 3 – window, 4 – gate, 5 – shaft, 6 – feeder, 7 – discharge unit, 8 – container, 9 – waste package.

with crushing and burning very pure graphite, potential release of radioactive gases and immobilisation of the residual ash.

The status of incineration facilities currently available worldwide is shown in Table 14.6.

14.4.3. Chemical and Thermochemical Decomposition

Chemical decomposition involves acid digestion of organics and has the advantage of avoiding high temperatures although it achieves little waste volume reduction.

Table 14.6: Solid radioactive waste incineration facilities

Country	Facility, site	Start of operation	Capacity	Comment
Austria	Seibersdorf, NRC	1983	40 kg/h	Solid waste
Belgium	Mol, Belgoprocess	1995	61 kg/h liquid, 79 kg/h solid	Solids, liquids, ion exchange resins
Canada	Ontario Power Generation Western Waste Management Facility	1976	17 m ³ /day solid, 9 L/h liquid	Batch loaded system, shut down in 2001
		2002	2 t/day solid, 45 L/h liquid	Continuous feed, starved air system
France	Cadarache Socodei Centraco	1988	20 kg/h	Commercial LLW
		1998	3500 t/annum solid, 1500 t/annum liquid	
	Melox	1994	20 kg/h	Solid alpha waste
	Valduc, IRIS	1996	7 kg/h	Solid alpha waste
	Grenoble		20 kg/h	
Germany	Karlsruhe	1980s	50 kg/h solid, 40 kg/h liquid	Solids, including plastics, rubber; liquids including oils, solvents, emulsions
India	Narora NPP	1990s		Used in short campaigns
Japan	Tokai Mura, PNC	1991	50 kg/h solid	
Netherlands	Vlissingen Oost, COVRA	1994	60 kg/h solid	Solids including animal carcasses

(continued)

Table 14.6: Continued

Country	Facility, site	Start of operation	Capacity	Comment
Russia	Sergiev Posad, Radon	1994	40 kg/h liquid	Plasma torch shaft furnace
		1991	100 kg/h solid, 20 L/h liquid	
		2002	250 kg/h solid	
Slovakia	Jaslovske Bohunice NPP, VUJE	2001	50 kg/h solid, 10 kg/h liquid	Used in campaigns for LLW
	Jaslovske Bohunice Waste Processing Facility, BSC	2001	50 kg/h solid, 10 kg/h liquid	Used in campaigns for LLW
Spain	El Cabril, ENRESA	1992	50 kg/h (solid + liquid)	
Switzerland	Wurenlingen, PSI	1974	25 kg/h	Shut down in 2003
UK	Hinkley Point NPP			
USA	Oak Ridge, TOSCA Incinerator Los Alamos	1991	700 kg/h solid + organic liquids	Shut down in 2000
	Savannah River Incineration Facility	1997	400 kg/h solid, 450 kg/h liquid	For PUREX reprocessing solvents, LLW and mixed waste
	Oak Ridge, Duratek	1989	~200 kg/h	2 units, Commercial LLW

Thermochemical decomposition was developed to process spent ion exchange resins, mixed, polymer and chlorine-containing (e.g. PVC) wastes and biological objects, which are difficult to incinerate in conventional incinerators. These are incinerated using powder metal fuels (PMFs) whose composition is

designed (taking account of the waste's chemical composition) to provide simultaneously both complete decomposition of organic matter in the waste and to confine hazardous radioactive and chemical species in the ash-slag residue. Figure 14.15 shows a schematic of a thermochemical treatment process.

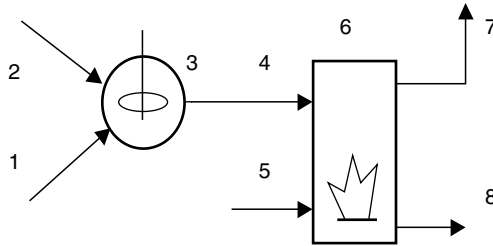


Figure 14.15: Schematic of thermochemical treatment process.

1 – waste feed, 2 – PMF feed, 3 – mixer, 4 – mixture feed,
5 – air supply, 6 – reactor (furnace), 7 – off gases, 8 – ash-slag residue.

In this process materials such as wet ion exchange resins and PMF are mixed in the appropriate ratio and the mixture is fed into the furnace where exothermic reaction occurs releasing large amounts of heat leading to evaporation and gasification of the organic waste. Air is supplied ($\alpha > 1$) to the combustion chamber to burn out the products of waste gasification and hydrogen resulting from reaction of PMF with water. The process in the furnace is controlled so that radionuclides contained in the waste are converted into low-volatility compounds in the ash residue. Typical process temperatures range between 800 and 1000° C.

14.5. Treatment of Gaseous and Airborne Effluents

Operations involving radioactive material handling may generate airborne radioactive contamination. The basic difference between airborne effluents and radioactive waste in condensed (i.e. liquid or solid) phases is that airborne material has no definite volume and its dispersion in the environment is rapid. Special technologies and equipment are therefore used for the localisation, collection and treatment of airborne effluents. Figure 14.16 shows typical atmospheric airborne particulates and equipment generally used to remove them from air.

Ventilation and air cleaning systems are a vital part of the general design of any nuclear facility including those of radioactive waste processing. The combination of a well-designed ventilation system with thorough cleaning of exhaust air prevents radioactive contamination of the air in working areas and in the surrounding atmosphere. In nuclear facilities, in general, air streams from

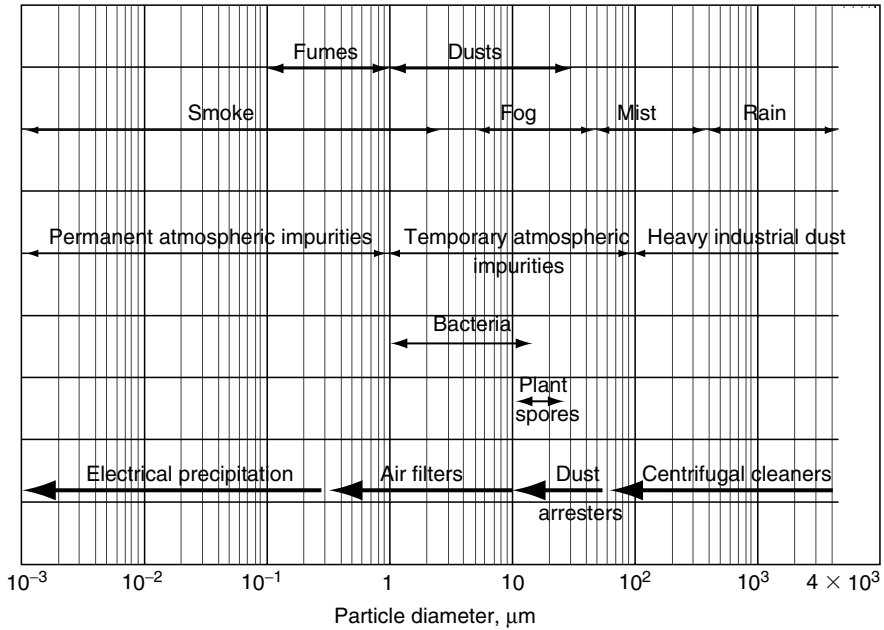


Figure 14.16: Size distribution of airborne particulates and the most suitable purifying equipment.

highly contaminated areas such as hot cells and process vessels are called off-gas streams. These may contain higher concentrations of airborne radionuclides than the room ventilation air streams contaminated only from equipment or leakage from a hermetically-sealed area. Off-gas streams must therefore be treated prior to mixing with the ventilation air for occupational and environmental safety reasons.

The general purposes of ventilation and air cleaning systems are:

- to control airborne contamination within safe working levels;
- to filter and monitor the air supply on a once-through basis;
- to maintain directional flow from the point of least contamination to the point of greatest contamination;
- to clean the exhaust air before discharge to the atmosphere;
- to monitor contaminants in the working areas and releases to the environment.

In Non-NFC institutes and facilities the ventilation and air cleaning system is usually designed to serve for both normal and accidental conditions. The exhaust air is filtered by HEPA filters and, where appropriate, absorbers.

Typical containment and ventilation system components include fume hoods, fume cupboards, glove boxes, fans and dampers. Enclosures such as glove boxes and fume cupboards are maintained at negative pressure to avoid dispersion of radionuclides in the environment.

Treating off gases from operating waste treatment systems is complex and expensive (Fig. 14.13). The filtering system of a waste treatment facility must ensure safe levels of both radioactive and noxious chemical contaminants including heavy metals, and dioxins. It consists of several filtering devices, which remove both aerosols and gaseous contaminants. Table 14.7 illustrates the purification efficiency of aerosol-removing equipment.

For gaseous contaminants (e.g. ^{14}C oxides, iodine and noble gases) absorbers

Table 14.7: Operational characteristics of gas purification equipment

Type	Particle size range (μm)	Gas velocity (m/min)	Pressure loss (mm of water column)	Efficiency (%)
Wet filters	0.1–25	30	25–125	90–99
HEPA (cellulose asbestos)	<1	1.5	25–50	99.95–99.98
HEPA (all-glass web)	<1	1.5	25–50	99.95–99.99
Single-stage electrostatic precipitators	<1	60–120	4–12	90–99

and scrubbing equipment are used. Filtering systems include several filters, some of which work at high temperatures (dry filters) as shown in Fig. 14.17. Others (wet) filters operate with aqueous solutions. Scrubbers and catalytic reactors are used to remove sulphur and nitrogen oxides from gases.

Coolers as well as dilution are used to decrease the temperature of off gases and to facilitate removal of contaminants from gaseous streams. The final step of gas cleaning involves HEPA filters (also termed absolute filters).

14.6. Partitioning and Transmutation

Partitioning is the separation of long-lived radionuclides from wastes usually by chemical means. Partitioning is being used in nuclear waste treatment facilities, for example in the Russian Federation at PO “Mayak” to extract long-lived radionuclides from HLW.

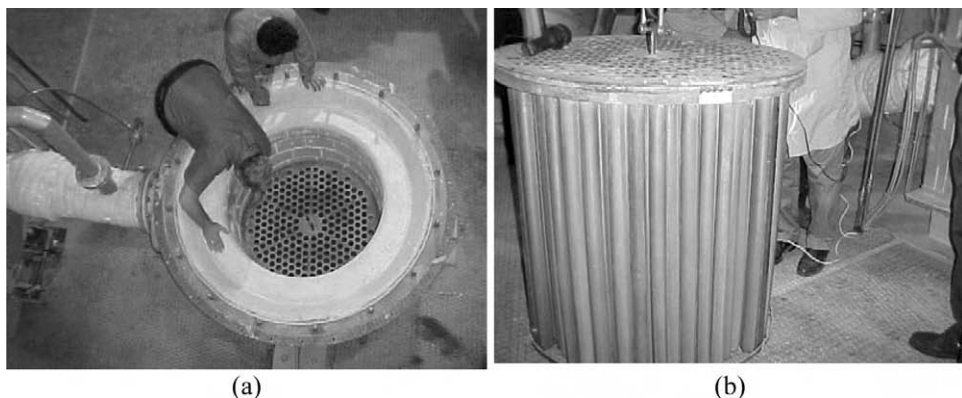


Figure 14.17: A high-temperature filter from a radioactive waste incinerator: (a) a view of filter assemblage, (b) filtering candles. Authors' photo.

Transmutation is the transformation via nuclear reactions (Chapter 2) of long-lived and/or radiotoxic radionuclides into shorter lived or stable radionuclides in reactors or by using particle accelerators. Partitioning and transmutation (P&T) is a potential option for reducing the inventory of long-lived and radiotoxic nuclides such as Tc, I, Np and Am so that the waste needs isolation for only ~ 1000 years rather than 10^5 or 10^6 years. Only a limited number of radionuclides are both easy to partition and are amenable to transmutation. Hence, most long-lived radionuclides will require an alternative treatment option. Transmutation technology is still only under development for radionuclides, which are amenable to transmutation and it will be many years before feasibility can be demonstrated on an industrial scale. The European Union, Japan, the Russian Federation and the USA have programmes to investigate partitioning and transmutation. These could reduce the amounts of waste requiring geological disposal and the times for which it is needed although it will not be feasible to apply this technique to all types of radioactive waste. There is as yet no clear indication when partitioning and transmutation might become a practical option.

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Chapter 15

Immobilisation of Radioactive Wastes in Cement

15.1. Waste Immobilisation

Waste immobilisation converts raw waste, usually containing mobile contaminants, into a solid and stable form termed a waste-form. The properties of the waste-form enable it to be handled, stored and disposed of safely and conveniently, significantly reducing potential release of radionuclides into the environment. As shown in Sections 3.5 and 3.6 this reduction can be quantified using average diminishing factors:

$$K_{\text{wf}} = \left(\sum_i (C_i(0)/IL_i) \exp(-\lambda_i t) / \sum_i (C_i(0)/IL_i) \exp(-\lambda_i t) \Phi_i \right) \quad (15.1)$$

where the coefficient Φ_i represents release fractions of radionuclides from the waste-form to the environment. The more durable the waste-form, the lower the values of Φ_i and the greater the reduction of potential release of radionuclides K_{wf} . For cemented aqueous radioactive waste K_{wf} can be from several tens to many hundreds.

For long-term storage and disposal, waste immobilisation should be an irreversible process, which avoids release of contaminants from the matrix during storage and disposal. Estimating the rate of leaching from a matrix during disposal is a key consideration in assessing an immobilisation method. Low matrix solubility ($\Phi_i \ll 1$) means reduced likelihood of radionuclide release.

15.2. Waste-Form Leaching Behaviour

The leaching behaviour of waste-forms containing different amounts of waste radionuclides is compared using the normalised leaching rates NR_i for each i th

nuclide expressed in g/cm² day and the normalised mass losses NL_{*i*}, expressed in g/cm². These are determined using a range of approved tests (such as the IAEA test protocol ISO 6961–1982) measuring concentrations *c_i* (g/L) or activities *a_i* (Bq/L) of nuclides in the water solution in contact with the waste-form after a time interval Δ*t* expressed in days. The mass fraction of a given nuclide *i* in a waste-form is defined as

$$f_i = \frac{w_i}{w_0} \quad (15.2)$$

where *w_i* is the mass of nuclide in the waste-form (g) and *w₀* is the mass of the waste-form (g). The specific activity of a given radionuclide in a waste-form *q_i* (Bq/g) is defined as

$$q_i = \frac{A_i}{w_0} \quad (15.3)$$

where *A_i* is the radioactivity of radionuclides in the waste-form (Bq). The normalised leaching rate of non-radioactive nuclides NR_{*i*} (g/cm² day) is calculated using the expression:

$$NR_i = \frac{c_i V}{f_i S \Delta t} \quad (15.4)$$

where *S* is the surface area of the waste-form in contact with the water (cm²), *V* is the solution volume (L) and Δ*t* is the test duration in days. The normalised leach rate of radioactive nuclides NR_{*i*} (g/cm² day) is calculated using the expression:

$$NR_i = \frac{a_i V}{q_i S \Delta t} \quad (15.5)$$

where *a_i* (Bq/L) is the specific radioactivity of solution. Normalised mass losses NL_{*i*} (g/cm² day) are determined for non-radioactive and radioactive nuclides, respectively, from

$$NL_i = \frac{c_i V}{f_i S} \quad (15.6)$$

and

$$NL_i = \frac{a_i V}{q_i S} \quad (15.7)$$

The typical leaching behaviour of various waste-forms is illustrated in Fig. 15.1.

Radionuclide leaching rates *r_i* can be determined by multiplying normalised leaching rates NR_{*i*} by the specific radionuclide content *q_i* (Bq/g):

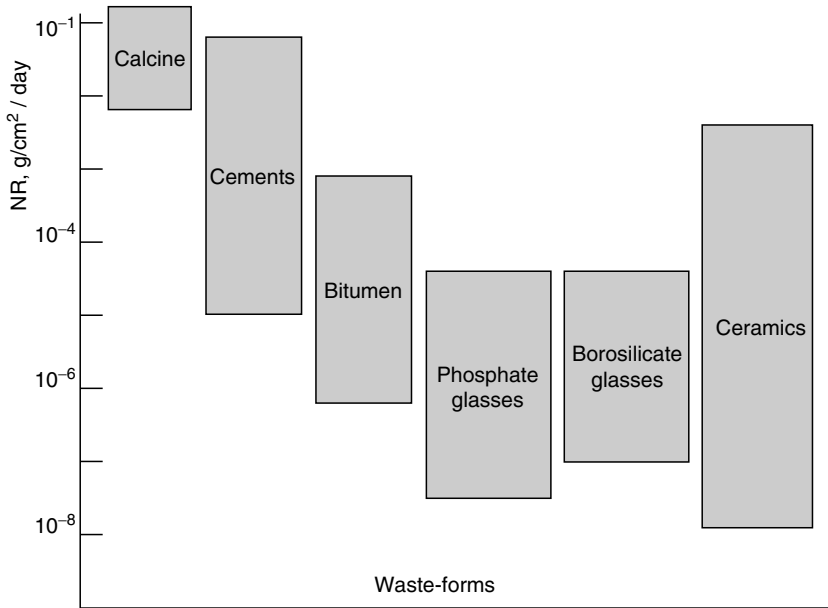


Figure 15.1: Water leaching of various waste-forms. Calcine is the powder product of heating high activity liquor from spent fuel reprocessing at high temperatures.

$$r_i = \text{NR}_i q_i \quad (15.8)$$

The higher the normalised leach rate NR_i and specific radioactivity of waste q_i the higher the leaching rates r_i . Higher q_i waste requires either a more durable waste-form or an additional package to diminish the overall coefficients Φ_i (see Chapter 3).

15.3. Immobilisation Techniques

Choosing a suitable waste-form for nuclear waste immobilisation is difficult and durability is not the sole criterion. In any immobilisation process where radioactive materials are used, the process and operational conditions can become complicated, particularly if operated remotely and equipment maintenance is required. Therefore priority is given to reliable, simple, rugged technologies and equipment, which may have advantages over complex or sensitive equipment.

A variety of matrix materials and techniques is available for immobilisation. The choice of the immobilisation technology depends on the physical and chemical nature of the waste and the acceptance criteria for the long-term storage and disposal facility to which the waste will be consigned. A host of

regulatory process and product requirements has led to the investigation and adoption of a variety of matrices and technologies for waste immobilisation. The main immobilisation technologies that are available commercially and have been demonstrated to be viable are *cementation*, *bituminisation* and *vitrification*. This chapter considers waste cementation, which is based on the use of hydraulic cements. Bituminisation is considered in Chapter 16, vitrification in Chapter 17 and other hosts including ceramics in Chapter 18.

15.4. Immobilisation in Hydraulic Cements

Hydraulic cements are inorganic materials that have the ability to react with water under ambient conditions to form a hardened and water-resistant product. The most common cements are those based on calcium silicates, such as the Portland cements. Cementation of radioactive waste has been practised for many years basically for immobilisation of low and intermediate level waste. The main advantages of immobilisation by physical encapsulation in cement are:

- inexpensive and readily available cements;
- simple and low-cost processing at ambient temperature;
- cement matrix acts as a diffusion barrier and provides sorption and reaction sites;
- suitable for sludge, liquors, emulsified organic liquids and dry solids;
- good thermal, chemical and physical stability of waste-form;
- alkaline chemistry which ensures low solubility for many key radionuclides;
- non-flammability of waste-form;
- good waste-form compressive strength which facilitates handling;
- easily processed remotely;
- flexible, can be modified for particular waste-form.

Ordinary Portland cement (OPC) is the most common type of cement used for immobilising liquid and wet solid wastes worldwide. Several OPC based mixtures are currently used to improve the characteristics of waste-forms and overcome the incompatibility problems associated with the chemical composition of certain types of radioactive waste. Composite cement systems (Section 15.9) may use additional powders as well as OPC such as blast furnace slag (BFS) and pulverised fuel ash (PFA). These offer cost reduction, energy saving and potentially superior long-term performance. As well as the waste-form matrix, OPCs will be used in structural components of any repository (such as walls and floors) and are potential backfill materials, consequently an

understanding of their durability in an underground environment even without waste is important.

15.5. Hydraulic Cements

Portland cement is a hydraulic cement produced by pulverising clinkers consisting essentially of hydraulic calcium silicates with calcium sulphate (gypsum) as an inter-ground addition. Clinkers are produced by heating clay materials with lime at high temperatures ($>1500^{\circ}\text{C}$) to form nodules (5–25 mm diameter). The low cost and wide availability of limestone and naturally occurring silica sources make Portland cement one of the lowest cost materials used worldwide. The manufacture and composition of Portland cements, hydration processes, and cement chemical and physical properties have been extensively studied.

Portland cement comprises chiefly lime (60–65 wt.% CaO), silica (21–24 wt.% SiO_2), alumina (3–8 wt.% Al_2O_3), and ferric oxide (3–8 wt.% Fe_2O_3), but also contains small quantities of magnesia (0–2 wt.% MgO), sulphur trioxide (1–4 wt.% SO_3) and other oxides introduced as impurities from the raw materials used in its manufacture.

Major phases present in unhydrated Portland cement are alite (Ca_3SiO_5 – tricalcium silicate), belite (Ca_2SiO_4 – β -dicalcium silicate), aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$ – tricalcium aluminate), ferrite ($\text{Ca}_4(\text{Al,Fe})_2\text{O}_7$ – tetracalcium aluminoferrite).

Table 15.1 shows the compositions and abbreviations of these compounds.

Early hydration of cement is principally controlled by the amount and activity of C_3A , balanced by the amount and type of sulphate inter-ground with the cement. C_3A hydrates rapidly and influences the early bonding characteristics. Abnormal hydration of C_3A and poor control of its hydration by sulphate can lead to problems such as flash set, slump loss and cement–admixture incompatibility. Based on this information a number of cements were designed with different durabilities or high-early strengths. The five recognised Portland

Table 15.1: Principal compounds in Portland cement

Compound	Oxide composition	Abbreviation
Tricalcium silicate	$3\text{CaO} \cdot \text{SiO}_2$	C_3S
Dicalcium silicate	$2\text{CaO} \cdot \text{SiO}_2$	C_2S
Tricalcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	C_3A
Tetracalcium aluminoferrite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	C_4AF

cement types are listed in Table 15.2. Typical compositions of commercial Portland cements are given in Table 15.3.

Type I, termed normal Portland cement or ordinary Portland cement (OPC), is the most commonly used when the special properties of the other types are not required, for example when it is not subject to sulphate attack from waste, or where the heat generated by the hydration of the cement will not cause an unacceptable rise in temperature. Type I cements typically have compressive (crushing) strength after 7 days >19 MPa measured on 50-mm mortar cubes.

Type II, modified Portland cement with reduced levels of C_3S and C_3A , has a lower rate of hydration than type I and generates heat at a slower rate. It also has improved resistance to sulphate attack and is intended for use where added precautions against moderate sulphate attack are important.

Type III, high-early strength cement with high C_3S and lower C_2S levels, develops strength rapidly as a result of its high tricalcium aluminate and tricalcium silicate content. This rapid strength development is, however, accompanied by a high rate of heat production, which may preclude the use of type III cement for massive waste/cement monoliths.

Type IV, low-heat cement with low levels of C_3S and C_3A and hence high level of C_2S , can be used primarily for massive waste/cement monoliths. The

Table 15.2: Portland cement types and their uses

Cement type	Use
I	General purpose cement, when there are no extenuating conditions
II	Aids in providing moderate resistance to sulphate attack
III	When high-early strength is required
IV	When a low heat of hydration is desired (in massive structures)
V	When high sulphate resistance is required

Table 15.3: Compositions (wt.%) of commercial Portland cements

Cement type	C_3S	C_2S	C_3A	C_4AF	Others
I	50	24	11	8	7
II	42	33	5	13	7
III	60	13	9	8	10
IV	26	50	5	12	7
V	40	40	4	7	7

low rate of heat production in this cement type is attributable to its high dicalcium silicate content and corresponding low tricalcium silicate and tricalcium aluminate contents.

Type V is sulphate resistant cement due to its low tricalcium aluminate content. It is a special cement intended for use in monoliths exposed to severe sulphate action. It has a slower rate of strength gain than ordinary Portland cement.

Portland cement types I, II and III are normally used in the immobilisation of radioactive waste. While type II has enhanced resistance to sulphate attack, sodium sulphate solutions have been successfully solidified, with all three types having roughly the same loadings. Aqueous waste containing boric acid can be solidified if an alkaline material (e.g. slaked lime or NaOH) or sodium silicate is added to the cement as well as when the alkalinity of the solution is increased to pH 8–12. Types I, II and III have been shown to work with such additives. Type III is preferred for boric acid type liquid waste because of the rapid curing characteristics of this cement (Section 15.6), which in many cases counteracts the retarding effects in hydration induced by boric acid (Section 15.8).

15.6. Cement Hydration

When Portland cement powder is mixed with water, the hydratable phases undergo a series of chemical reactions that eventually lead to hardening. Hydration reactions are complex and not stoichiometrically rigorous because of variations both in the products formed and their compositions.

Basically, the two calcium silicates (C_3S and C_2S) that constitute about three quarters of Portland cement by weight react with water to produce two new compounds – calcium hydroxide and a calcium silicate hydrate called tobermorite gel. The tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) combine with considerably more water on a molar basis than do the calcium silicate compounds. A summary of the early stages of cement hydration is shown in Fig. 15.2.

Hydration reactions are conventionally divided into three periods – a dormant period that usually lasts for minutes, setting that occurs over hours and hardening that takes many days or longer to complete. Cement composition and fineness play a major role in controlling concrete properties. The average finenesses of cement range from 3000 to 5000 cm²/g. Greater fineness increases the surface available for hydration, causing greater early strength and more rapid heat generation. Coarse cement produces pastes with higher porosity than those produced by finer cement. The microstructure of the cement hydrates determines the mechanical behaviour and durability of the resulting concrete.

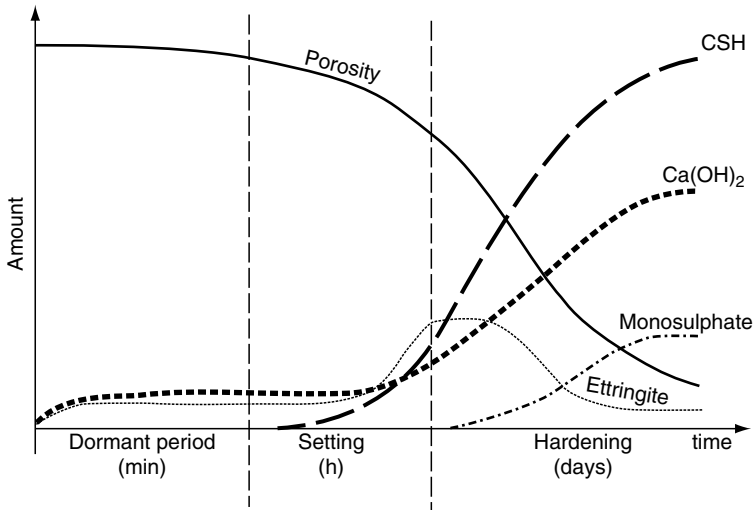


Figure 15.2: Schematic of cement hydration kinetics.

C_3S and C_2S have the most influence on long-term structure development. Aluminates may also contribute to formation of compounds such as ettringite (calcium-sulpho-aluminate hydrate $C_3A-3CaSO_4-32H_2O$), which can lead to fracture of the concrete. Cements high in C_3S hydrate more rapidly and develop higher early strength. However, the hydration products formed make it more difficult for late hydration to proceed resulting in a lower ultimate strength. Cements high in C_2S hydrate much more slowly, at $20^\circ C$ taking approximately 1 year to reach a good ultimate strength, leading to a denser ultimate structure and higher long-term strength.

15.7. Hydrated Cement Composition

Each of the phases formed during cement hydration influences its structure and properties. By far the most important is tobermorite gel, which is the main cementing component of concrete. Setting and hardening behaviour, strength and dimensional stability depend primarily on the tobermorite gel. Development of the microstructure of hydrated cement occurs after the concrete has set and continues for months (and even years) after placement. OPC is typically 95–98% hydrated after 12 months and comprises an aqueous phase, which is largely confined to filling pores less than $1\mu m$ in radius (pore water) and a heterogeneous paste matrix. Table 15.4 classifies the solid phases in hydrated cement.

Table 15.4: Phase composition of hydrated cement paste

Phase	Description	Notation
Crystalline		
Ettringite	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$	AFt
Monosulphate	$\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{SO}_4 \cdot 6\text{H}_2\text{O}$	AFm
Hydrogarnet	$\text{Ca}_3\text{Al}_2(\text{OH})_{12} - \text{Ca}_3\text{Al}_2\text{Si}(\text{OH})_8$	$\text{C}_3\text{AH}_6 - \text{C}_3\text{ASH}_4$
Portlandite	$\text{Ca}(\text{OH})_2$	CH
Amorphous		
Calcium silicate hydro-gel	Typical Ca/Si molar ratio 1.7 ± 0.1	C-S-H

The porosity φ of a porous material such as hydrated cement paste is defined as the ratio of the non-solid volume such as pores filled by water or gas $V_p(\text{m}^3)$ to the total volume of material $V_t(\text{m}^3)$:

$$\varphi = \frac{V_p}{V_t} \quad (15.9)$$

The porosity of a cement paste is a function of time (Fig. 15.2) with a typical ultimate porosity from 30 to 40%.

An important physical property of a porous medium is its permeability K (m/s), which determines the rate of flow of a fluid (water) through it. The rate of flow of water Q (m^3/s) through a bed of surface area S (m^2) made of a porous medium is described by Darcy's law:

$$Q = KS \frac{(H + h)}{H} \quad (15.10)$$

where H is the thickness of the bed (m) and h is the height of the water on the top of the bed (m). As the permeability of hydrated cement pastes depends on porosity the permeability is a function of time. Typical data on permeability of hydrated OPC as a function of curing time are given in Table 15.5.

Table 15.5: Permeability K of cement paste as a function of time

Age (days)	Fresh	5	6	8	13	24	Ultimate
K (m/s) ($\times 10^{-14}$)	2×10^7	4×10^3	1×10^3	4×10^2	50	10	6

The strength and chemical resistance of a cement paste is a strong function of the water/cement (w/c) ratio:

$$w/c = \frac{M_{H_2O}}{M_{\text{cement}}} \quad (15.11)$$

where M_{H_2O} is the mass of water used for hydration (kg) and M_{cement} is the mass of cement powder (kg) used to produce the cement paste. In making concrete, more water has to be used than required for hydration to make a workable and flowable mixture. High w/c ratios result in large void volumes, which affect the concrete's mechanical and chemical durability. For waste encapsulation cement paste permeability should be as low as possible. The relationship between permeability and the w/c ratio of mature (aged 28 days) Portland cement pastes is shown in Fig. 15.3 illustrating the drawback of higher w/c ratio.

High permeability (K) results in increased leachability (e.g. NR_i) and deterioration of the concrete when exposed to aggressive ground water.

15.8. Cementation of Radioactive Wastes

The practice of encapsulating radioactive waste in OPC began during the early years of the nuclear industry. This was primarily due to its low cost,

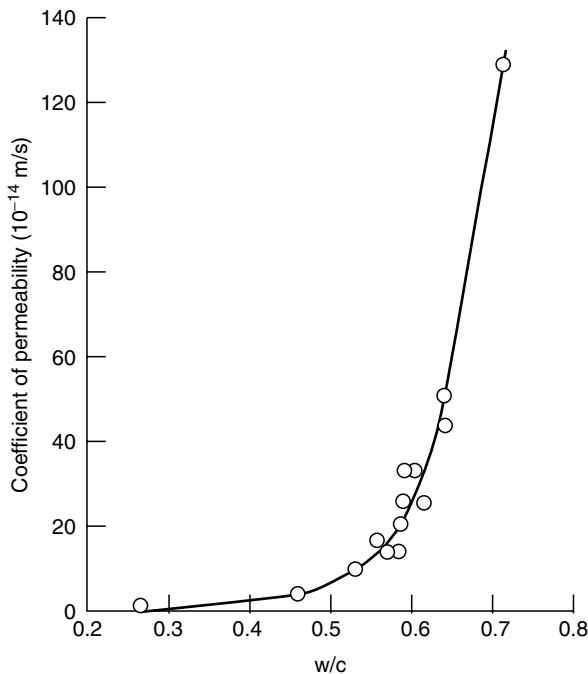


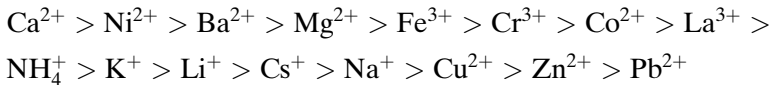
Figure 15.3: Permeability of hydrated cement paste as a function of w/c ratio.

availability and compatibility with aqueous waste. It was soon realised, however, that some wastes interact with the cement and retard the hydration reactions (Table 15.6).

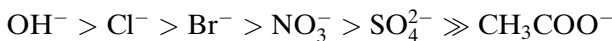
Table 15.6: Reactions occurring between cement and waste components

Waste component	Reaction
Soluble borates, Pb, Zn	Precipitated salts coat cement grains or amorphous precipitates inhibit hydration
Complexing agents: EDTA, sugar, citric acid	Interfere with Ca availability by complexation, retard hydration
Flocs	Uncertain action, retard hydration
Electropositive metals	Evolve H, reaction accelerated by OH ⁻ , solid reaction products, oxides/hydroxides are expansive
Organic ion exchangers	Take up water in high pH matrices and expand

Typically the impact of cations on cement hydration reactions follows the series:



whereas anions follow the series:



To overcome deleterious cement–waste interaction effects, one or more additives may be used and such mixtures are termed modified cements. Several of the more successful modified Portland cements have been commercialised.

15.9. Modified and Composite Cement Systems

OPC cements can be modified by using a range of additives. These may be defined as *additives* (at a level of ~5%) such as gypsum which acts to retard hydration, *replacements* (at high levels up to 90%) such as BFS or PFA in *blended* or *composite* cements or as *admixtures* (at levels of ~1%) such as super-plasticisers. The main cement modifiers (Tables 15.7 and 15.8) include slaked lime, sodium silicate, natural pozzolans and BFS.

Composite cements are used in the UK for ILW encapsulation. BNFL e.g. use a 9:1 ratio of BFS: OPC to reduce heats of hydration which for OPC cements would otherwise limit container volumes. Large containers (described in section 15.10) can therefore be safely used, without concern over heat from setting reactions causing water to boil off.

Table 15.7: Cement modifiers

Nature of modifier	Purpose
Polar, high molecular weight, water soluble organics (super-plasticisers)	Reduce grout* viscosity
Soluble organics	Accelerate or retard set, antifreeze, corrosion inhibitors
Slag, fly ash, silica fume, natural pozzolans	Reduce heat evolution, improve fluidity and decrease permeability, may increase strength after long times

*Grout is a paste mixture of cement powder and water that solidifies. Mortar is grout-containing sand. Concrete is mortar with added aggregate.

Modified or composite cements are used to immobilise waste containing specific components and contaminants. Table 15.8 gives data on modified Portland cements, additives and waste streams for which they are used.

Masonry cement is a mixture of Portland cement and slaked lime Ca(OH)_2 . When used for radioactive waste encapsulation, Portland cement and slaked lime are typically combined in equal proportions. In the presence of water, the extremely high alkalinity induced by the slaked lime induces a rapid set. Masonry cement is particularly useful for solidifying wastes such as boric acid and borate salts, bead resins and filter sludges, which tend to inhibit or retard hydration of other cements. Masonry cement also hydrates more quickly due to the alkalinity of the slaked lime. The bulk density of masonry cement is about 35% less than that of Portland cement so it can incorporate more waste per volume unit although the low density leads to low strength.

Sodium silicate cements use either sodium silicate ($2\text{Na}_2\text{O} \cdot \text{SiO}_2$, water glass) or sodium metasilicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2$) as an additive to Portland cement. Sodium

Table 15.8: Modified Portland cements and their use in waste immobilisation

Type	Additive	Waste stream	Additive function
Masonry cement	Lime	Boric acid	Adjusts pH
Portland sodium silicate cement	Sodium silicate	Organic liquids	Accelerates set, reduces porosity
Portland pozzolanic cement	Reactive silica	Sulphate	Reacts with Ca(OH)_2 , reduces porosity
Portland blast furnace slag cement	Slag	Sulphate	Reacts with Ca(OH)_2 , latently hydraulic

silicate is a liquid additive, while sodium metasilicate is a soluble granular solid. The action of both additives during solidification is similar. Multivalent cations in the waste as well as soluble multivalent cations in the cement react with the sodium silicate additive to form low-solubility silicate compounds that precipitate as a gel. Because this precipitation reaction is rapid, the sodium silicate additive is normally added after the cement and the waste have been mixed. Mixing after sodium silicate addition is limited so as to minimise disruption of the precipitated gel network that forms. This produces a waste–cement mixture that achieves an apparent set in a short time (in minutes) owing to the precipitate gel. The sodium silicate also accelerates the cement setting owing to its high alkalinity, although the formation of stable cement mineral hydrates (hardening) requires additional time, similar to that required for hardening in unmodified Portland cements. Sodium silicate cements are useful for encapsulating boric acid, borate salts and organic liquid wastes because of their rapid set.

A *pozzolana* is a material that is capable of reacting with lime in the presence of water at ordinary temperatures to produce cementitious compounds. Italian pozzolana, trass and Santorin earth are examples of naturally occurring pozzolans of volcanic origin. Artificial pozzolans are prepared by burning at suitable temperatures certain clays, shales and diatomaceous earths that contain clay. Diatomaceous silica and some natural amorphous silica deposits may also form pozzolans, either with or without heat treatment. Pulverised fuel ash (PFA or fly ash), a waste product from coal burning power stations is now used in many countries on a large scale as a pozzolana. Pozzolan cements are produced by grinding together Portland cement clinker and a pozzolan, or by mixing together a hydrated lime and a pozzolan. Pozzolan cements are particularly suitable for immobilisation since the permeability of the concrete is greatly reduced by the continuous filling of the pore volume during the hydration reaction. The absence of leachable free lime in the concrete also contributes to its low permeability and high resistance to sulphate attack from sulphate bearing waste streams or aggressive ground water.

Blast furnace slag is a by-product obtained in the manufacture of pig iron and is formed by combination of the earthy constituents of iron ore with limestone flux. Portland blast furnace cement or blended cement is a mixture of Portland cement and granulated slag containing anywhere from 20 to 95 wt.% slag, depending on standards established in different countries. Since some slags hydrate very slowly on contact with water, its hydration is activated by the addition of other compounds, such as calcium hydroxide, calcium sulphate, sodium carbonate and sodium sulphate. Lime for activation is most conveniently supplied by the hydration of the Portland cement in the mixture. The rate of the hydration reaction is mainly a function of slag concentration in the cement mixture. In addition to a reduced heat of hydration, the setting rate

of blast furnace slag cements is also reduced. This may be beneficial in processing systems where quick setting cement is not desirable such as involving large volume containers (Fig. 15.4).

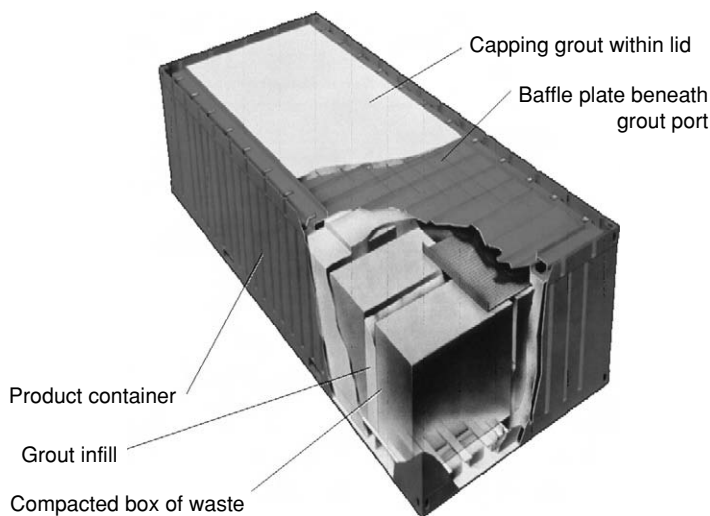


Figure 15.4: Container with cemented LLW at Drigg disposal site, UK.
Courtesy of BNFL.

Blast furnace slag cements have a lower permeability than Portland cements, which contributes to the lower diffusion rate of ions through the hardened cement and improved durability in the presence of salts such as chloride and sulphate. The microstructure of a composite cement system is shown in Fig. 15.5 revealing light grey angular BFS grains, and white unhydrated cement in a dark grey CSH matrix.

We have seen that composite cements have many advantages as encapsulating matrices for radwaste. Disadvantages already mentioned include the affect of certain waste chemicals and species on hydration reactions (Table 15.6) and the heat from exothermic setting reactions. Other problems with cementation include that the highly alkaline environment is not suitable for all wastes (Al metal, for instance, corrodes rapidly), that cements contain ‘free water’ which can give rise to porosity and increased permeability and provide a medium in which chemical reactions can take place and that the short-term testing of long-term durability (especially in the presence of differing wastes) is difficult. An additional benefit of cementation however is that radionuclides may be immobilised by phases in the cement microstructure providing chemical fixing as well as physical encapsulation.

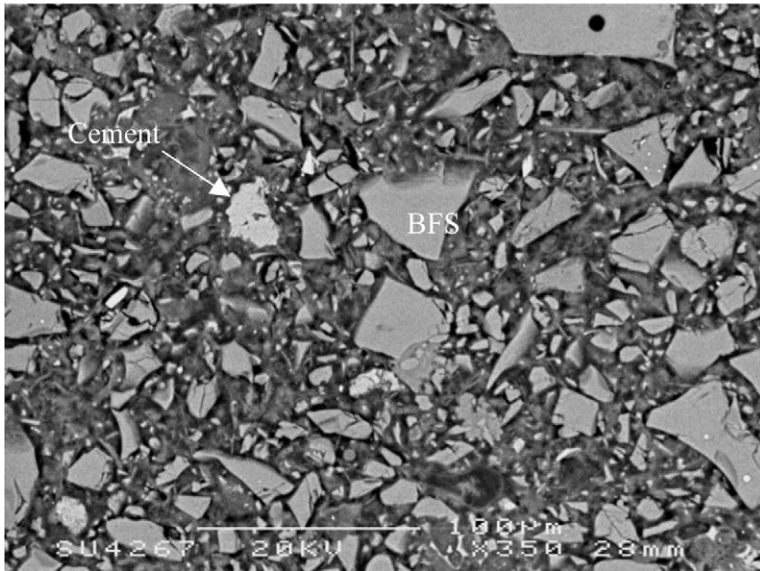


Figure 15.5: SEM image of 9:1 BFS:OPC cement, w:c 0.33 cured at 20 °C for 90 days. Picture courtesy of A. Setiadi, ISL University of Sheffield.

15.10. Cementation Technology

Waste–cement mixtures may be prepared either directly in the container (in-drum mixing) which is the final product container, or prior to pouring into the container (in-line mixing).

After in-drum mixing, the cement–waste mixture is allowed to set, the container is capped with a different composition cement to minimise void spaces and to avoid surface contamination, a lid is fitted. A simplified process flow diagram for a cement in-drum system is shown in Fig. 15.6.

A reusable mixer may be used which is removed before the container is capped and the mixture sets or a disposable mixer may be used which is left in the container. The latter is referred to as the lost paddle approach and involves the use of a paddle that is inexpensive to fabricate but capable of producing a homogeneous mix. A disadvantage of a reusable mixer is that the residue on the mixing paddle must be removed and the paddle washed to prevent area and container contamination.

Tumble mixing is a cementation process without mixing paddles. Figure 15.7 illustrates an in-drum mixing technique in which the drum and its contents are attached to a tumbling frame and rotated end over end to mix the contents thoroughly. In this process dry cement and a disposable mixing

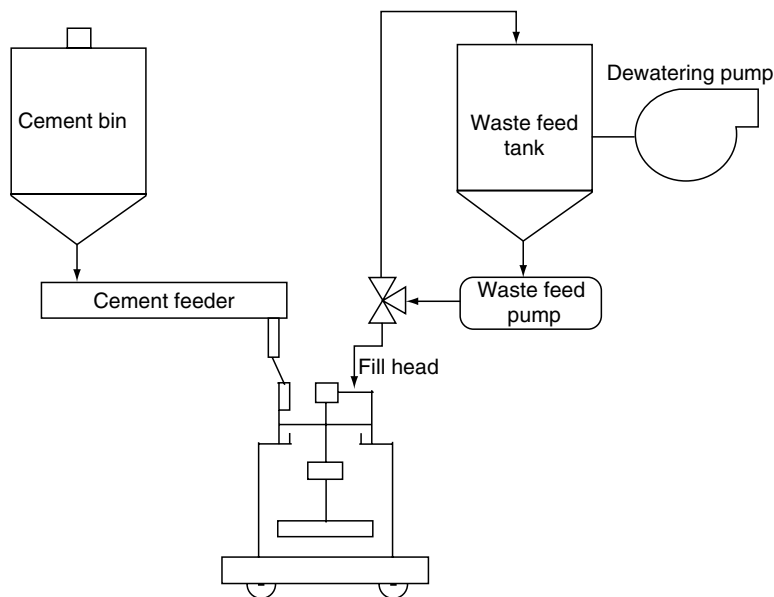


Figure 15.6: Schematic of in-drum mixing cementation.

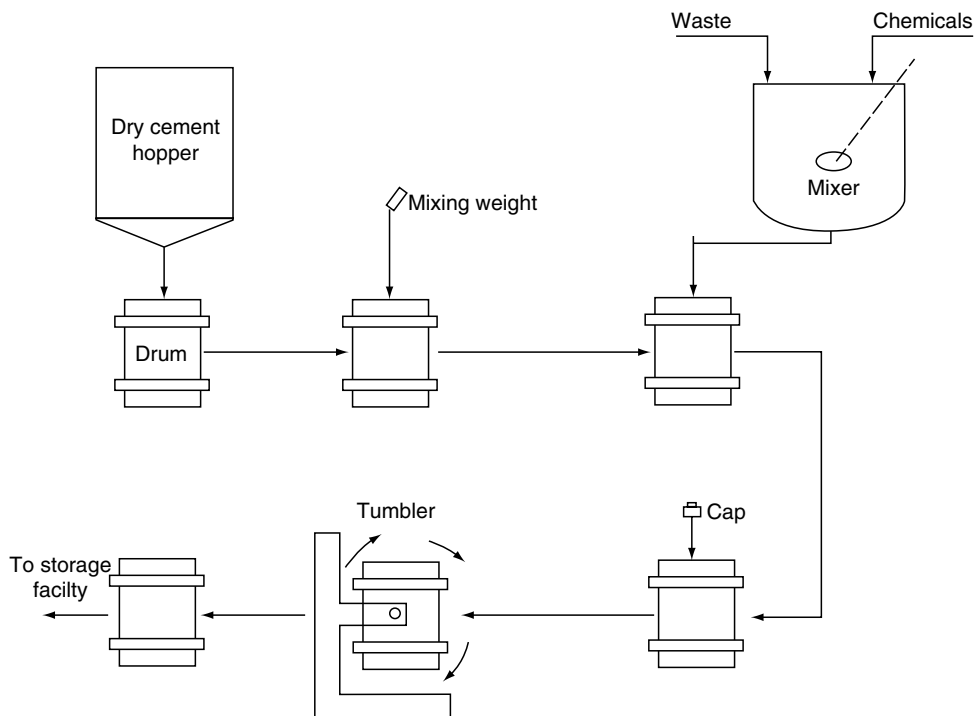


Figure 15.7: Schematic of tumble mixing.

weight are placed in a 220-L drum, followed by the waste and any additional chemicals. The drum is then capped prior to end over end tumbling. For this system, cap removal, filling, cap replacement and mixing are done automatically. Homogeneous mixing, however, cannot always be assured by tumble mixing.

In-line mixing processes combine the waste, any additives, water and cement before they are placed into a disposal container. A simplified schematic of in-line cementation is shown in Fig. 15.8. In this process the cement and the waste are separately metered into the mixer. The cement is fed by a screw feeder, while the waste is fed by a positive displacement pump. The cement–waste mix is released directly from the mixer into the container. The level of cement/waste in the container is monitored, possibly by ultrasonic or contact probes. The container is then sealed, decontaminated, monitored and sent for storage. The waste tank and mixer can be flushed through after each run. If desired, the rinsing water can be stored and used to prepare the feed slurry for the next run.

In-line type cementing facilities use different types of mixer such as mechanical, hydraulic and small volume vortex induction mixers. Figure 15.9 shows examples of LLW encapsulated via in-line cementation at the BNFL waste encapsulation plant at Sellafield, UK.

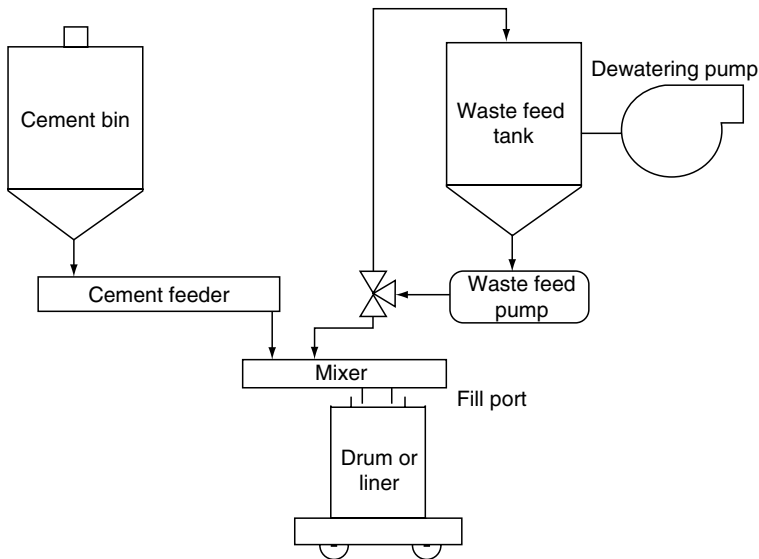


Figure 15.8: Schematic of in-line cementation.



Figure 15.9: Cement-encapsulated solid, liquid and slurry ILW in 500-L drums.
Courtesy of BNFL.

Operating cementation facilities are complex in design and operation, as they comprise a number of additional important technological operations to ensure reliable immobilisation and final product quality. A flow diagram of an industrial cementation facility is shown in Fig. 15.10. Additional vibration of drums enables void filling and development of a dense cement paste. Various additives are used to enhance workability and increase waste loading. For example, vermiculite, bentonite, clinoptilolite and shales enhance radionuclide retention enabling immobilisation of specific waste streams by cementation. For example, addition of 3 wt.% bentonite decreases cement leaching rate (NR_i) by an order of magnitude.

15.11. Acceptance Criteria

A key property of any waste-form is its leach resistance, which determines how well the radionuclides of concern are retained within the waste-form in a wet environment. There are two mechanisms that influence leaching behaviour. One is the creation of a physical (prophylactic) barrier between the radionuclide and the environment, which in part is how cement and bitumen systems work. The other mechanism involves chemical incorporation of radionuclides in the matrix structure (such as in glasses or ceramics, Sections 17.2 and 18.2 respectively) or reaction between the radionuclides and the matrix, which

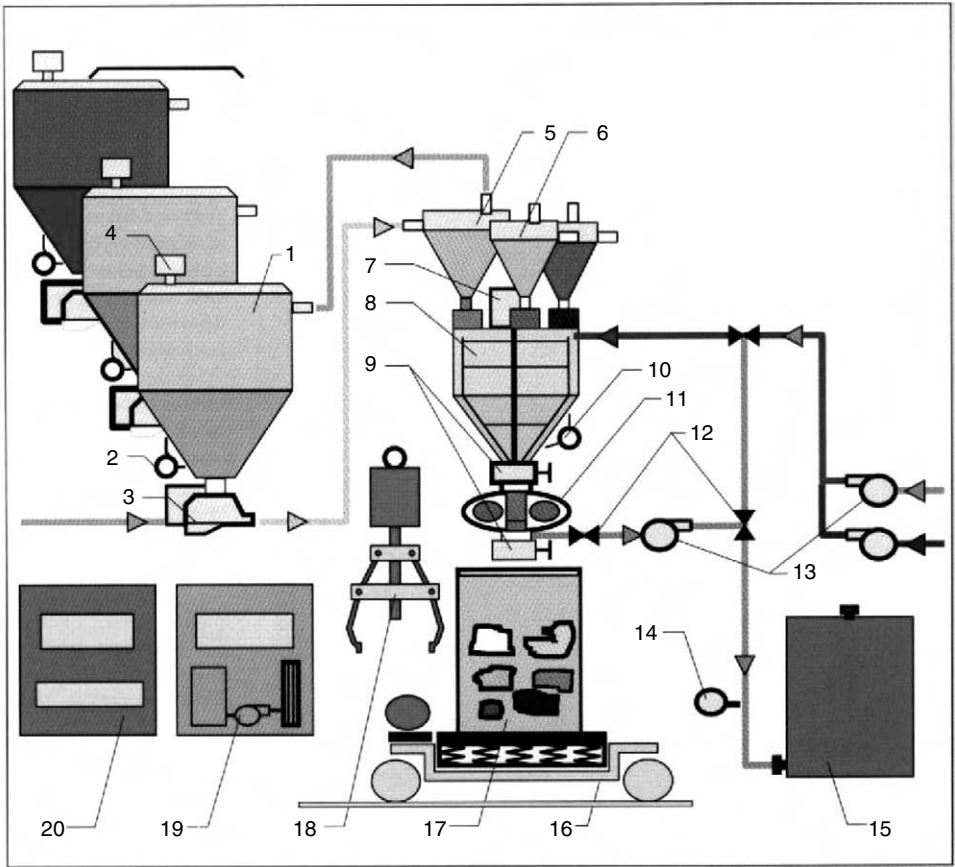


Figure 15.10: Schematic of a modular cementation plant. 1 – cement and additives bunkers; 2 – vibrator; 3 – jet pump; 4 – air valve; 5 – cement service bunker with batcher; 6 – additives service bunker with batcher; 7 – mixer drive; 8 – tank with mixer; 9 – hose bolts; 10 – vibrator; 11 – vortex type mixer; 12 – valves; 13 – pump-batchers; 14 – manometers; 15 – cartridge filter for impregnation; 16 – vibrating platform; 17 – drum with solid waste; 18 – crane; 19 – vortex mixer service desk; 20 – control desk.

may occur in cement-based systems. This behaviour is waste-form and radio-nuclide specific and can be altered by the waste chemistry, the formulation of the immobilisation matrix and the leaching water chemistry. Most transuranic elements are retained well by common cement phases owing to the high pH (basic) conditions and the chemical reactions that occur in the matrix.

The choice of cement type and cementation technology depends on a number of factors, although waste acceptance criteria are among the most important. Waste acceptance criteria (e.g. Table 15.9 from the Russian regulatory

Table 15.9: Acceptance criteria for cemented radioactive waste in Russian Federation

Criterion	Permitted limits
Specific radioactivity	
β-and γ-nuclides	$< 1 \times 10^{-3}$ Ci/kg
α-nuclides	$< 1 \times 10^{-6}$ Ci/kg
Leaching rate of ^{137}Cs and ^{90}Sr	$< 10^{-3}$ g/cm ² day
Mechanical durability (compressive strength)	Depending on transport requirements, interim storage and disposal, but not less than 5 MPa
Radiation durability	Mechanical durability not less than permitted (at least 5 MPa) at irradiation dose 10^8 rad
Thermal cycles durability	The same after 30 freeze thaw cycles ($-40, +40^\circ\text{C}$)
Durability to long-term water immersion	Mechanical durability not less than permitted (at least 5 MPa) after 90 days immersion in water

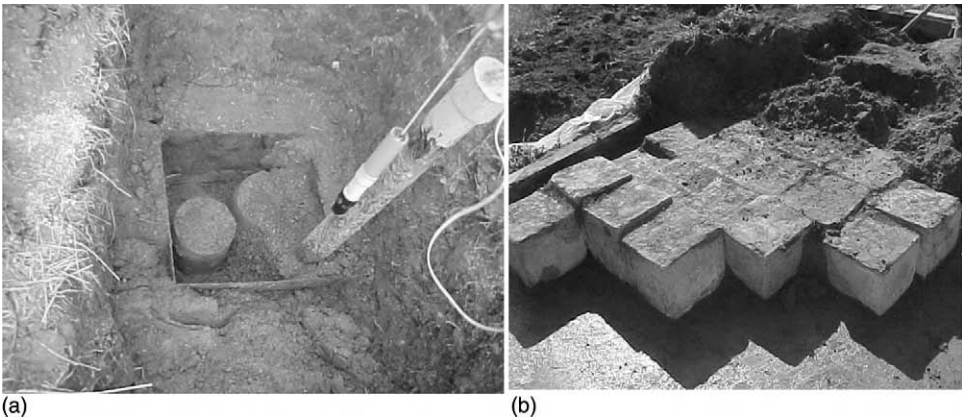


Figure 15.11: An experimental repository with cemented aqueous radioactive waste after 12 years (a) and view of cemented waste blocks after 40 years (b). Courtesy N. Ojovan, SIA RADON, Russia.

document RD 95 10497-93) specify the required characteristics of matrix materials and waste packages.

Cements are particularly suitable for immobilisation of low and intermediate level radioactive wastes. Figure 15.11 shows an opened experimental repository of cemented aqueous waste and of cement blocks extracted from a 40-year-old experimental burial.

The cementitious waste-forms have demonstrated limited degradation with time and a high retention of radionuclides under the disposal conditions. The normalised leaching rate for the main waste radionuclide ^{137}Cs is as low as $1.3 \times 10^{-6} \text{ g/cm}^2 \text{ day}$, which is at the level of some glasses and ceramics (see Fig. 15.1).

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Chapter 16

Immobilisation of Radioactive Wastes in Bitumen

16.1. Bituminisation

Embedding radioactive waste in bitumen has been used in immobilisation since the 1960s and the total volume of radioactive waste immobilised in bitumen currently exceeds $200\,000\text{ m}^3$. In the bituminisation process, radioactive wastes are embedded in molten bitumen and physically encapsulated when the bitumen cools. Bituminisation combines heated bitumen and a concentrate of the waste material in either a heated thin film evaporator or screw extruder which mix the bitumen and waste. The waste is usually in the form of a slurry, for example, salt aqueous concentrates or wet ion exchange resins. Water is evaporated from the mixture to about 0.5% moisture, intermixed with bitumen so that the final product is a homogeneous mixture of solids and bitumen, termed bitumen compound. Its retention properties usually exceed those of cements at higher waste loadings (Fig. 15.1). Bituminisation is particularly suitable for water-soluble radioactive wastes such as bottom residues from evaporation treatment and spent organic ion exchangers.

16.2. Composition and Properties of Bitumen

Bitumen is a generic term used to cover a wide range of high molecular weight hydrocarbons. Bituminous materials have been widely used in the building industry for many years. As early as 3800 BC they were used in construction because of their adhesive and waterproofing properties. Obtained from naturally occurring deposits, these bitumens were used by the rulers of the Assyrian, Sumerian and Chaldean empires to waterproof their palace walls. Core samples

from the natural Oklo reactor in Gabon contain inclusions incorporating bitumen, which probably acted as a reducing buffer and/or hydrophobic water shield suppressing oxidative dissolution of the uraninite cores.

Three main types of hydrocarbons occur in bituminous materials:

- asphaltenes,
- resins,
- oils (aliphatic hydrocarbons).

The bitumen properties depend on the ratio of these components: heavy-weight fractions such as asphaltenes impart visco-elastic properties to bitumen at ambient temperatures (10–40° C); light-weight fractions such as oils act as a carrier for the asphaltenes and resins. The viscous properties of bitumen are complex and affected by changes in its colloidal nature that occur with heating. However, when the temperature is high enough for the bitumen to be liquid it behaves as a Newtonian fluid and the rate of shear is directly proportional to the shearing stress.

The most important characteristics of bituminous materials are penetration, softening point and flash point. The penetration characterises their hardness and is measured from the depth of penetration that a weighted needle achieves after a known time at a known temperature. The most common penetration test is carried out with a weight of 100 g applied for 5 s at 25° C. Typical values obtained are approximately (mm) 10 for hard coating grade asphalts, 15–40 for roofing asphalts and up to 100 or more for certain waterproofing materials.

The softening point characterises the temperature at which a steel ball falls a known distance through the bitumen when the test assembly is heated at a known rate. The usual test is carried out with a 9.52-mm diameter steel ball sinking through a thick disc of bitumen held in a brass ring, with the whole assembly heated at 5° C/min. The softening point value is used to grade bituminous materials into groups. Typical values are up to 132° C for coating grade asphalts, from 60 to 105° C for roofing asphalts, down to approximately 45° C for waterproofing bituminous materials.

The flash point characterises the temperature at which a bituminous material ignites in an open-air crucible. Flash points and flammability temperatures of bitumen are higher than 200–350° C, depending on the type of bitumen. Harder bituminous materials have higher flash points. The normal solubility of water in bitumen is of the order of 0.001–0.01 wt.% and, in practice, is considered as negligible. The presence of water-soluble salts in the bitumen, result in a larger capacity for water absorption by osmosis.

16.3. Bituminous Materials for Waste Immobilisation

Several bitumen varieties are commercially available for immobilisation of radioactive waste including:

- direct distilled,
- oxidised,
- cracked,
- emulsions.

Direct-distilled bitumen is a residue from petroleum distillation while oxidised bitumen is created by blowing air through petroleum residues, which oxidises light fractions of the residues. Cracked bitumen is generated from thermal breakdown of heavy oil fractions in the oil refining industry and emulsions are produced by direct injection and emulsification of the bitumen in water. Bituminisation techniques used in radioactive waste immobilisation utilise different bituminous materials as shown in Table 16.1.

Advantages of bituminous materials as matrices for waste immobilisation are:

- water insolubility,
- low diffusion of water,
- chemical inertness,
- plasticity and good rheological properties,
- slow ageing rates,
- high incorporation capacity enabling high waste loadings,
- readily available and low cost.

However, bitumen is an organic material and therefore it has a number of inherent disadvantages such as:

- combustibility, although not easily flammable,
- lower stability against radiation than cement,
- ability to react with oxidising materials such as sodium nitrate.

Table 16.1: Applications of typical bitumen varieties for waste immobilisation

Bitumen type	Application
Direct distilled	Batch melter, thin film evaporator
Oxidised	Batch melter, extruder, thin film evaporator
Cracked	Extruder
Emulsion	Thin film evaporator

Table 16.2 shows typical parameters of several bituminous materials used to immobilise LILW in the Russian Federation. The radiation stability of bituminous materials depends on their type, although swelling occurs at relatively high absorbed doses >0.5–2 MGy. Bitumen compounds can be loaded with ~50 wt.% (~25% by volume) of nitrate-type aqueous radioactive wastes. This value is considered as a threshold level since above it, leaching of radionuclides increases stepwise (Fig. 16.1a) as a result of formation of percolating-type clusters made of contacting salt particles in the host bitumen matrix (Fig. 16.1b and c). Waste loading for ion exchangers is also up to 50%.

16.4. Bituminisation Technique

Immobilisation of radioactive wastes via bituminisation can be carried out as a batch or continuous process.

Batch processes usually involve drying the waste followed by mixing the dried material in molten bitumen. In this process waste is continuously introduced into a metered volume of molten bitumen at about 200° C. The mixing vessel is externally heated. Water evaporates and the solid residue particles are mixed with the bitumen. When the required composition of the waste-form is reached, no more waste is added. The mix is heated and stirred for some time to evaporate the residual water and is then discharged into drums or other

Table 16.2: Parameters of bitumen for radioactive waste immobilisation

Type of bitumen*	BN-II	BN-III	BN-IV	
Fractions (wt.%)	Oils (aliphatic hydrocarbons)	55.5	54.4	50.0
	Resins	17.5	15.0	11.0
	Asphaltenes	27.0	30.5	39.0
Penetration at (25° C) (mm)	81–120	41–80	21–40	
Softening temperature (°C)	40	45	70	
Flash point (open crucible) (°C)	200	200	230	

*Russian trade mark bitumens

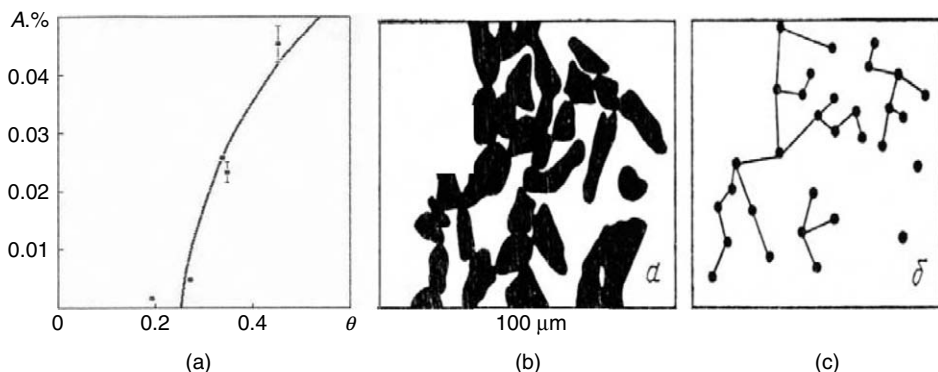


Figure 16.1: (a) Inventory of leached ^{137}Cs (A) from bituminised radioactive waste with waste loading volume fraction (θ) (points – experiment, curve – calculated by percolation theory). (b) A high-contrast micrograph of a percolating cluster made of (black) salt particles and (c) connectivity of the percolation cluster in (b). Courtesy N. Ojovan, SIA RADON, Russia.

containers to cool and solidify. Batch processes are not widely used and *continuously* operating bituminisation processes are more common, generally based on either extrusion or film evaporation systems. With *extrusion* systems the concentrates are fed into a multiple screw extruder together with bitumen at 130–200° C (Fig. 16.2). During passage through the heated extruder the waste and bitumen are intensively mixed with simultaneous evaporation of water. The temperature of the bitumen–waste matrix is kept reasonably low (130–140° C) although at lower temperatures the viscosity would be too high to maintain the extrusion process. The final product is uniform, with mineral residue particles from waste coated with a layer of bitumen. However, some waste constituents partially dissolve in the bitumen. The bituminised product is discharged

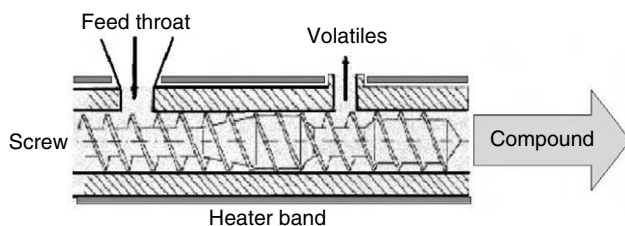


Figure 16.2: Schematic of an extrusion apparatus for bituminisation of radioactive waste.

into drums and allowed to cool and solidify. A typical extrusion bituminisation process is shown in Fig. 16.3.

In *film evaporator* systems liquid wastes are initially concentrated to about 60 wt.% dry matter. Preheated waste sludge and bitumen are fed separately to the top of the thin film rotary evaporator where the two streams mix and flow down the heated wall. The water in the mixture is progressively evaporated and the remnant mineral residue from the waste is mixed with bitumen. Rotary thin film evaporators use wiping blades to assist mixing of waste mineral residues and bitumen. The bituminised waste material is drained near the bottom into steel containers. The vapours generated are condensed, first in the built-in condenser in the evaporator and subsequently in an external condenser. Thin film evaporator bituminisation is used to immobilise both aqueous radioactive waste and spent organic ion exchangers (Fig. 16.4).

The first bituminisation plant in Russia was put into operation at Moscow SIA “Radon” in 1977. It uses an industrial steam heated rotary evaporator as the mixing unit operating at 135° C while the waste loading is up to 60 wt.%. The bitumen compound is poured into carbon steel containers. Parameters of the bituminous materials used at this plant are listed in Table 16.2 while Table 16.3 summarises the application of bituminisation processes worldwide.

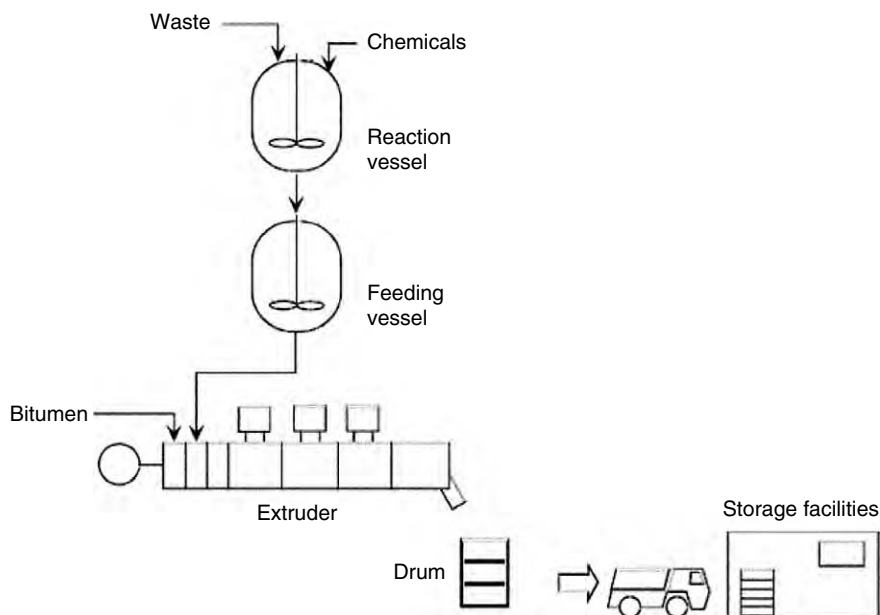
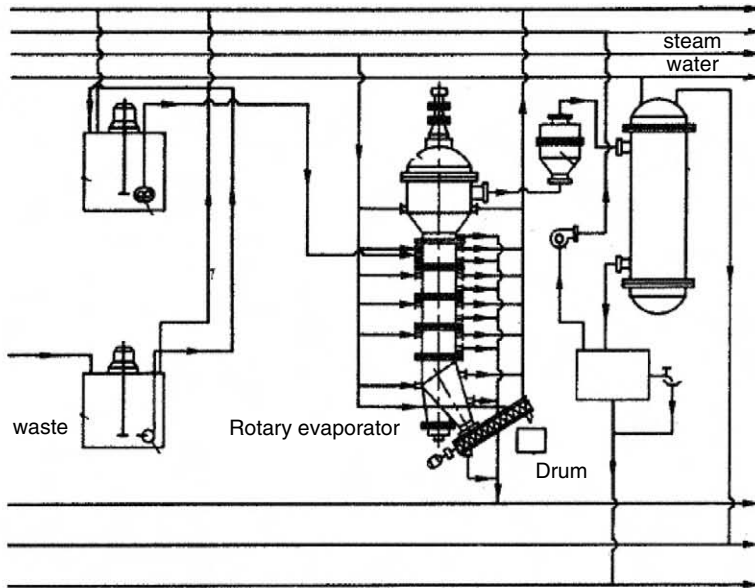
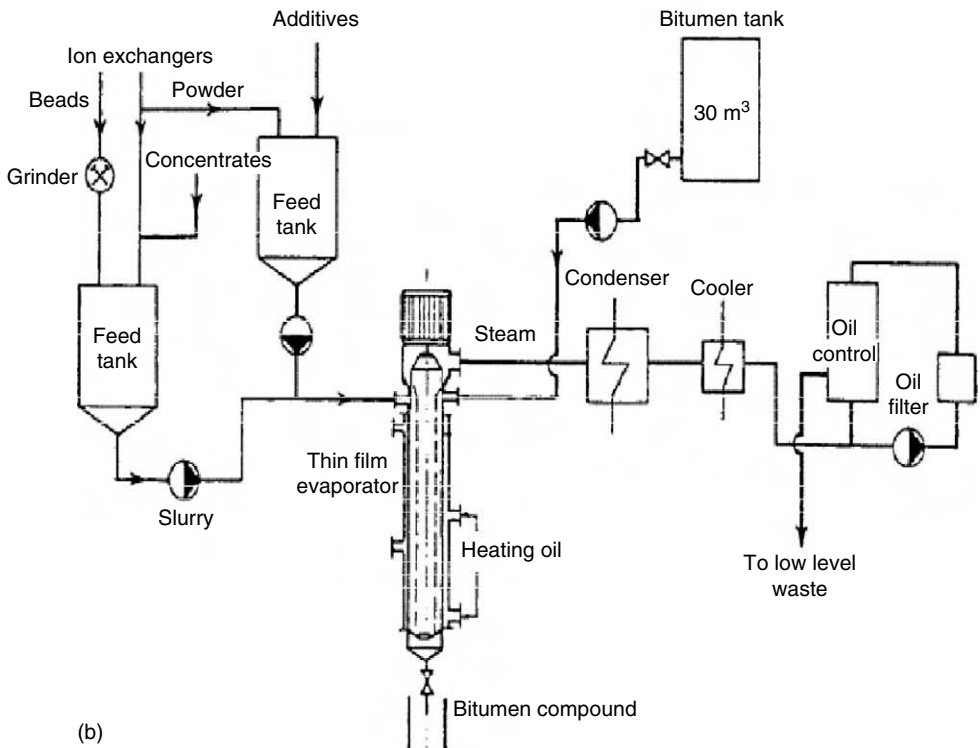


Figure 16.3: Schematic of extruder type bituminisation process at Tokai Works in Japan.



(a)



(b)

Figure 16.4: Schematics of thin film evaporator bituminisation processes: (a) liquid aqueous waste bituminisation process at Moscow SIA “Radon”, Russia; (b) spent ion exchange resin bituminisation plant at Barsebäck NPP, Sweden.

Table 16.3: Immobilisation of radioactive waste in bitumen

Bituminisation plant (country)	Reported operation period	Amount of immobilised waste
Marcoule, CEA (France)	1966–1998	60000 drums
STE 3, La Hague, COGEMA (France)	1989–1998	10000 drums (151000 m ³ of waste)
«Mummy», Belgoprocess (Belgium)	1988–1998	5000 m ³ of waste
Dukovany NPP (Czech Republic)	1978–1997	2800 m ³ of compound
Risø RNL (Denmark)	1970–1999	160 t of compound
JNC, Tokai Works (Japan)	1982–1997	30000 drums (7500 m ³ of waste)
PS-44, NPP Jaslovske Bohounice (Slovakia)	1995–1998	957 drums (508 m ³ of waste)
LUWA, NPP Trnava (Slovakia)	1995–1998	117 m ³ salt concentrate
NPP «Sarri» (USA)	1991–1992	623 m ³ salt concentrate
LUWA 210, Barseback (Sweden)	1975–1983	3500 drums (960 m ³ compound)
Forsmark NPP (Sweden)	to 1985	2000 drums (220 m ³ compound)
Asea-Atom, Olkiluoto (Finland)	1979–1984	2000 drums (390 m ³ compound)
RB-1000, Ignalina NPP (Lithuania)	1987–1998	9719 m ³ (15390 m ³ of liquid waste)
UBD-200, SIA “Radon” (Russia)	1977–1978	200 m ³ of waste
URB-8, SIA “Radon” (Russia)	1978–1988	500 m ³ /year
RB-800, Kalinin NPP (Russia)	1989–1998	1160 m ³ (467 t of salts)
TB-16, LSK “Radon” (Russia)	1978–1998	1500 m ³ (3000 m ³ of waste)
RB-1000-14, Leningrad NPP (Russia)	1984–1986	1650 m ³ of compound (3000 m ³ of waste)

16.5. Acceptance Criteria

Waste acceptance criteria for bitumen compounds used to immobilise radioactive waste are set into the state standard of the Russian Federation GOST 50927-96. The most important parameters are illustrated in Table 16.4. It is assumed that these requirements are met both for freshly prepared bitumen compounds and for compounds in storage and disposal.

Table 16.4: Minimal requirements to bitumen compounds

Parameter	Value	Testing method
Chemical durability (leaching rate Cs-137), g/cm ² day, less than	1×10^{-3}	GOST 29114
Stability to swelling (volume increase after 90-day immersion in water), %, less than	3	Change of volume
Content of free water		
For salt concentrates, %, less than	1	Loss of mass at heating up to 110° C
For ion exchange resins, %	3–5	
Thermal durability		
Flash point, °C, not below	200	GOST 12.1.044
Ignition temperature, °C, not below	250	
Self-ignition temperature, °C, not below	400	
Radiation durability, increase of volume after 10 ⁶ Gy, vol.%, not above	3	Change of volume
Biological stability	Absence of fungus	GOST 9.049

16.6. Bitumen versus Cement

Immobilisation in suitable matrices significantly reduces the potential for release of radionuclides into the environment. Average diminishing factors K_{wf} for the bituminised aqueous radioactive waste are of the order of several hundreds and those of cemented aqueous radioactive waste are similar. A comparison of cement and bitumen matrices for immobilisation of spent ion exchange resins is given in Table 16.5.

Bitumen has the advantage over cements of higher waste loading, but it also has some disadvantages, the most important being its potential fire hazard. The possibility of combustion in the case of an accidental fire has lead to certain restrictions on the use of bitumen as an immobilising matrix and it is not used in the UK or USA. Several fires have occurred in different countries during the

Table 16.5: Comparison of cement and bitumen as immobilising matrices for spent ion exchange resins

Property	Cement	Bitumen
Compressive strength	Excellent at correct formulations	Poor to moderate
Waste loading	10–25 wt.% ion exchangers	25–50 wt.% ion exchangers
Resistance to biodegradation	Stable	Moderate
Thermal stability	Good	Poor, can melt and ignite
Resistance to leaching	Poor to excellent	Excellent
Radiation durability	Excellent	Moderate
Gas generation	Low	Moderate
Chemical compatibility	Good with most materials, worse for boric acid, chelating agents	Good, worse for solvents and oils

filling of final storage drums at temperatures of about 120° C. Two significant fire incidents occurred in Belgium in 1981 and in Japan in 1997 in bitumen-containing nitrates from evaporator concentrates. Bituminisation facilities must therefore include fire suppression and extinguishing systems.

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Chapter 17

Immobilisation of Radioactive Wastes in Glass

17.1. Vitrification

Glass is one of the most ancient of all materials known and used by mankind. The natural glass, obsidian, was first used by man thousands of years ago to form knives, arrow tips and jewellery. Man-made glass objects from Mesopotamia have been dated as early as 4500 BC and from Egypt from 3000 BC. A new application of glass was discovered in the 20th century as a waste-immobilising material produced via vitrification technology. Vitrification is attractive because of the small volume of the resulting waste-form (Fig. 17.1), the large number of elements which can be incorporated in the open glass structure and glasses potentially high durability. The high chemical resistance of glass allows it to remain stable in corrosive environments for thousands and even millions of years. Several glasses are found in nature such as obsidians (volcanic glasses), fulgarites (formed by lightning strikes), tektites found on land in Australasia and associated microtektites from the bottom of the Indian Ocean, moldavites from central Europe, and Libyan Desert glass from western Egypt. Some of these glasses have been in the natural environment for about 300 million years with low alteration rates of only tenths of a millimetre per million years. Waste vitrification technology is a compromise between the desired durability of the final waste-form and its processing efficiency. The most durable materials would require very high processing temperatures ($>1500^{\circ}\text{C}$), which cannot be used because at high temperatures waste radionuclides occur in volatile species, generating large amounts of secondary wastes and diminishing the immobilisation efficiency. As a result the most common glasses used in vitrification of nuclear waste are borosilicates and phosphates which use lower processing temperatures ($\sim 1000^{\circ}\text{C}$) while still forming a durable product. Vitrification is also attractive because it can destroy hazardous organics in the waste while

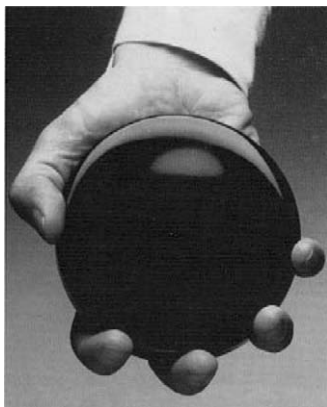


Figure 17.1: This volume of simulant borosilicate glass is sufficient to hold all the HLW arising from an 80-year lifetimes worth of nuclear-generated electricity for a single person (picture courtesy of BNFL).

chemically incorporating the waste inorganic constituents into a stable glass often with significant volume reduction which contributes towards reduced disposal costs. Vitrification has been used for nuclear waste immobilisation for more than 40 years in France, Germany, Belgium, Russia, UK, Japan and the USA. The total production of all vitrification plants by the end of 2000 was ~ 10000 t of radioactive glass in ~ 20000 canisters. Vitrification is also currently used for immobilisation of intermediate and low level radioactive wastes (LILW) from operation and decommissioning of nuclear power plants. Plans are in place to vitrify vast volumes of waste in the future; for example the vitrification of the low-level radioactive waste at Hanford, USA is expected to produce over 160000 m^3 of glass. At Hanford it is planned to use a bulk vitrification process in which liquid waste is mixed with controlled-composition soil in a disposable smelter. Electrodes will be inserted to vitrify the mixture and when cooled the smelter, its contents and the embedded electrodes will be buried as LLW. An *in situ* vitrification process was attempted in the clean up of heavily contaminated soil at a nuclear weapons test site at Maralinga in Australia in the late 1990s but this was abandoned after an explosion arising from lack of care in planning and implementation. The latter highlights the fact that mistakes are still being made by the world's nuclear industry.

17.2. Immobilisation Mechanisms

Vitrification involves melting of waste materials with glass-forming additives so that the final vitreous product incorporates the waste contaminants in its macro- and micro-structure. Hazardous waste constituents are immobilised either by

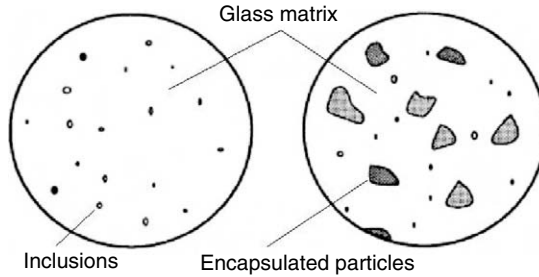


Figure 17.2: Schematic of waste retention in a glass matrix:
left – incorporation in a relatively homogeneous glass, with some bubbles and inclusions; right – encapsulation of waste particles in a glass matrix.

direct incorporation into the glass structure or by encapsulation. In the first case, waste constituents are dissolved in the glass melt, some being included into the glass network on cooling while others are confined as modifiers. Nuclear waste glasses are not completely homogeneous vitreous materials but contain significant proportions of bubbles, foreign inclusions such as refractory oxides and other immiscible components (Fig. 17.2).

Immobilisation by encapsulation is applied to elements and compounds with a reduced solubility which cannot fit into the glass network. The solubility limits of elements as oxides in silicate glasses are given in Table 17.1.

Immiscible nuclear waste constituents which do not mix easily into the molten glass are typically sulphates, chlorides and molybdates as well as noble metals such as Rh and Pd, refractory oxides with high liquidus temperatures such as PuO_2 , noble metal oxides and spinels. Low miscibility waste constituents are immobilised in the glass matrix by encapsulation and are dispersed in its microstructure (Fig. 17.2, right). Encapsulation is usually carried out by dispersion of insoluble compounds into the glass melt so that the waste-form produced is a glass composite material (GCM) not a truly homogeneous glass.

Table 17.1: Approximate solubility limits of elements in silicate glasses

Element	Solubility limit (wt.%)
Al, Si, P, Pb	>25
Li, B, Na, Mg, K, Ca, Fe, Zn, Rb, Sr, Cs, Ba, Fr, Ra, U	15–25
Ti, Cu, F, La, Ce, Pr, Nd, Gd, Th, Bi, Zr, Pu, Th	5–15
Mn, Cr, Co, Ni, Mo	3–5
C, S, Cl, As, Se, Tc, Sn, Sb, Te, Np	1–3
H, He, N, Ne, Ar, Br, Kr, Ru, Rh, Pd, Ag, I, Xe, Pt, Au, Hg, Rn	Less than 0.1

17.3. Retention of Radionuclides

The reliability of radionuclide immobilisation is characterised by the rate at which radionuclides can be released from the waste-form during long-term storage. As the most plausible path for re-introduction of radioactivity into the biosphere is via water, the most important parameters that characterise the ability of glass to hold on to the active species are the leach rates (Section 15.2). A set of standard tests to determine the water durability of vitrified waste and other waste-forms was developed at the Materials Characterization Centre (MCC) of Pacific Northwest National Laboratory, USA. These MCC tests are now the internationally approved standards used worldwide. The IAEA has recommended for durability tests the standard ISO 6961-1982 “Long-term leach testing of solidified radioactive waste-forms” (Geneva, 1982). This leaching test was developed by the International Standards Organization (ISO) and is similar to MCC-1 at normal room temperature. The most important tests are described in Table 17.2.

Vitrified radioactive waste is a chemically durable material which reliably retains active species. Typical normalised leaching rates NR of vitrified

Table 17.2: Standard tests on immobilisation reliability

Test	Conditions	Use
ISO 6961, MCC-1	Deionised water, static, monolithic specimen, sample surface to water volume (S/V) usually 10 m^{-1} , open to atmosphere	For comparison of waste-forms
MCC-2	Deionised water, temperature 90°C , closed	Same as MCC-1 but at higher temperature
PCT (MCC-3)	Performance consistency test, deionised water stirred with glass powder, closed	For durable waste-forms to accelerate leaching
SPFT (MCC-4)	Single pass flow through test, deionised water, open to atmosphere	The most informative test giving kinetic parameters of leaching for performance assessment
VHT	Vapour phase hydration, monolithic specimen, closed, high temperatures	Accelerates alteration product formation

waste-forms are below 10^{-5} to 10^{-6} g/cm² day (Section 15.2). Moreover, as glasses and GCMs are highly corrosion resistant, their high nuclide retention is expected to last for many millennia.

17.4. Nuclear Waste Glasses

Almost any melted substance, if cooled sufficiently fast, can be made as a glass. Glasses are amorphous materials with an internal structure made of a three-dimensional network of interconnected structural blocks, which in silicate glasses are SiO₄ tetrahedra. Upon heating, glasses continuously change most of their properties to those of a liquid-like state in contrast to crystals where such changes occur abruptly at a fixed temperature (the melting point). The solid-like behaviour of glass at low temperatures is separated from liquid-like behaviour at high temperatures by the glass transition temperature, T_g . The glass transition is a kinetically controlled, fairly sharp change in derivative properties such as thermal expansion coefficient or specific heat. T_g in fact depends on the rate of cooling, although empirically it can be assessed from the relation:

$$T_g \approx \frac{2}{3} T_L \quad (17.1)$$

where T_L is the liquidus temperature at which a phase diagram shows a crystal-free melt. Below T_g glasses have solid-like behaviour. A higher T_L provides a higher T_g , but high processing temperatures are not acceptable for an efficient waste immobilisation process. The most important parameters of nuclear waste glasses are: normalised radionuclide leaching rates NR_i (g/cm² day), mechanical strength (MPa), density ρ (g/cm³), thermal expansion coefficient κ (K⁻¹), specific heat C_p (J/kgK) and thermal conductivity λ (W/mK). Important glass processing parameters are melting temperature T_m , viscosity η (Pa s) and electrical conductivity σ (Ω^{-1} cm⁻¹) near the melting temperature. Vitrification can be performed efficiently at T_m values below 1200°C thereby avoiding excess radionuclide volatilisation and maintaining viscosities below 10 Pa s to ensure high throughput and controlled pouring into canisters. A more fluid glass is preferred to minimise blending problems.

17.5. Nuclear Waste Glass Compositions

The ability of cations to enter into the glass structure is characterised by their field strength, which is defined as

$$F = \frac{Z}{a^2} \quad (17.2)$$

where Z is the valence and a is the ionic distance (Å) in the oxide. Lower field strength ions (e.g. alkalis) are network modifiers, whereas ions with higher field strength (such as Si, P or B) are network formers. Table 17.3 lists cations according to their function in the glass structure.

Two main glass types have been accepted for nuclear waste immobilisation – borosilicates and phosphates. The exact compositions of nuclear waste glasses are tailored for easy preparation and melting, avoidance of phase separation and uncontrolled crystallisation, and acceptable leaching resistance. Table 17.4 gives typical nuclear waste glass compositions.

The internal structure of glasses made of interconnected structural blocks is characterised by the degree of polymerisation – the higher the degree of polymerisation the more developed its three-dimensional network. Nuclear waste glasses are highly polymerised structures. For example, nuclear waste borosilicate glasses are made up of four groups: (a) network forming SiO_2 , (b) charge balancing network formers MTO_2 ($T = \text{Al, B, Fe}^{+3}$, $M = \text{alkali}$), (c) network modifiers MO , excess alkali not tied to T , as well as alkaline earth oxides, and (d) lanthanide and actinide oxides. Nuclear waste glasses consist of approximately 77.5 mol% of fully polymerised SiO_2 and MTO_2 , and 22.5 mol% of partly depolymerised component.

17.6. Borosilicate Glasses

Borosilicate glasses are the first choice of material worldwide for immobilising both HLW and LILW. This selection is based on the flexibility of borosilicate glass with regards to waste loading and the ability to incorporate many different kinds of waste elements, coupled with good glass-forming ability, chemical durability, mechanical integrity, and excellent thermal and radiation stability. Borosilicate glasses generally have SiO_2 as the major component, relatively high B_2O_3 , CaO , MgO , Na_2O and Al_2O_3 content and minor amounts of many other oxides. SiO_2 , B_2O_3 and Al_2O_3 are generally network formers because they form strong covalent bonds involving SiO_4 , AlO_4 and BO_4 tetrahedra and BO_3 triangles.

Silicon is the main glass-forming element in a borosilicate waste glass and its basic elements are SiO_4 tetrahedra, which comprise bridging or cross-linking and non-bridging atoms of oxygen (NBO). In a silicate glass the SiO_4 -tetrahedra vertices connect these elements to each other through bridging oxygen atoms so that the network consists of chains of various lengths. The glass

Table 17.3: Function of cations in a glass structure

Element	Valence Z	Coordination number (CN)	Field strength <i>F</i>	Bond strength (kJ/mol)	Function in glass
Si	4	4	1.57	443	Network formers: $F \sim 1.5\text{--}2.0$
B	3	3	1.63	498	
	4	4	1.34	372	
P	5	4	2.1	368–464	Intermediates: $F \sim 0.5\text{--}1.0$
Ti	4	4	1.25	455	
	4	6	1.04	304	
Al	3	4	0.96	335–423	
	3	6	0.84	224–284	
Fe	3	4	0.85		
	3	6	0.76		
Be	2	4	0.86	263	
Zr	4	6	0.84	338	
	4	8	0.77	255	
Mg	2	4	0.53		
	2	6	0.45	155	
Fe	2	6	0.43		Network modifiers: $F \sim 0.1\text{--}0.4$
Pb	2	6	0.34	310	
	2	8	0.27	151	
Ca	2	8	0.33	134	
Sr	2	8	0.28	134	
Li	1	6	0.23	151	
Na	1	6	0.19	84	
K	1	8	0.13	54	
Cs	1	12	0.10	42	

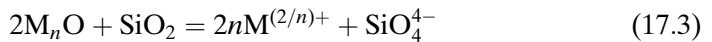
network is not regular as in the case of crystalline silica, for example the bond angle Si–O–Si can range from 120° to 180° while in quartz it is a constant $109^\circ 28'$, although the Si–O bond length remains constant (1.62 Å). Alkali, alkaline earth ions, transition metals, and ions of high charge and large size including actinides cannot readily substitute for Si, B or Al and so are network modifiers entering the gaps in the network structure. They generally have

Table 17.4: Compositions of nuclear waste glasses

Glass (country)	Oxide (wt.%)							
	SiO ₂	P ₂ O ₅	B ₂ O ₃	Al ₂ O ₃	CaO	MgO	Na ₂ O	Others
R7/T7 (France)	47.2	–	14.9	4.4	4.1	–	10.6	18.8
DWPF (USA)	49.8	–	8.0	4.0	1.0	1.4	8.7	27.1
Magnox Waste (UK)	47.2	–	16.9	4.8	–	5.3	8.4	17.4
PAMELA (Germany–Belgium)	52.7	–	13.2	2.7	4.6	2.2	5.9	18.7
Defence HLW (Russia)	–	52.0	–	19.0	–	–	21.2	7.8
K-26 Commercial LILW (Russia)	48.2	–	7.5	2.5	15.5	–	16.1	10.2
P0798 (Japan)	46.6	–	14.2	5.0	3.0	–	10.0	20.2
GC-12/9B (China)	46.2	–	13.4	4.2	2.5	1.5	9.1	23.1

coordination numbers of 6 and higher, form weaker bonds to oxygen than the network formers and act to charge-balance the negatively charged borosilicate or alumina–borosilicate network. This leads to break up of Si–O–Si bonds producing NBO SiO[–] ions localised to modifying ions. Figure 17.3 illustrates the structure of an alkali–silicate glass. The structure is typically described using the Q_n designation, where *n* represents the number of bridging oxygen per tetrahedral unit.

Energetically the most important depolymerisation process can be viewed as an acid–base reaction:



or in terms of elementary Q_n units:



where M is the modifying cation and *n* is its valence state. In practice adding a network modifier such as Na₂O progressively depolymerises the network; intermediate stages of polymerisation include Q₃ sheets, Q₂ chains and Q₁ dimers such as Si₂O₇ along with fully linked SiO₄-tetrahedra Q₄.

The degree of polymerisation of a glass *f_T* is given by the ratio of the number of network-forming cations to the number of oxygen atoms and can be expressed as

$$f_T = \frac{\sum \gamma_T}{\gamma_{M_2O} + \gamma_{MO} + 3\gamma_{M_2O_3} + 2\gamma_{MO_2} + 5\gamma_{M_2O_5} + 3\gamma_{MO_3}} \quad (17.5)$$

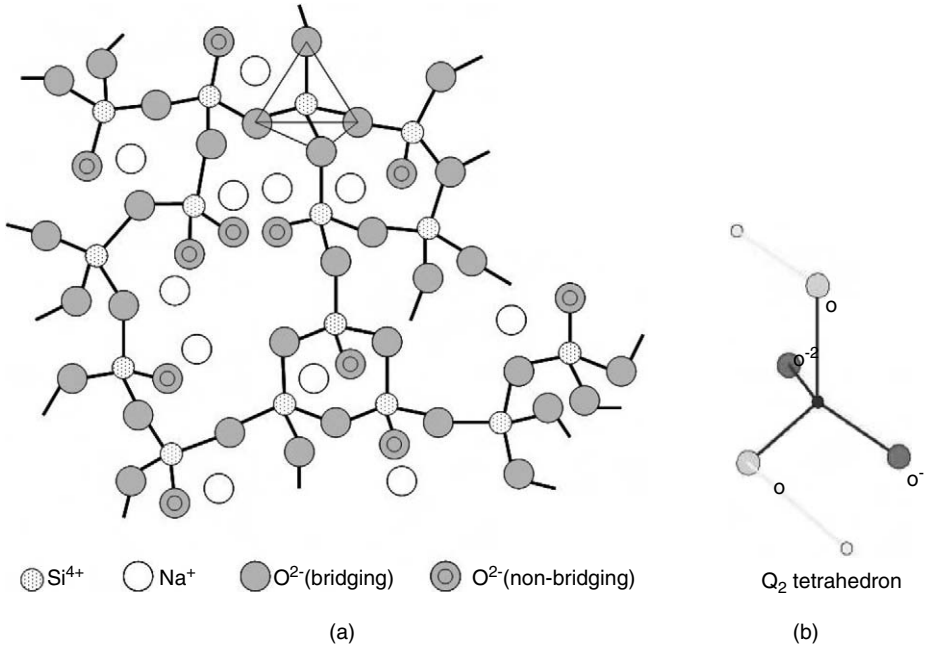


Figure 17.3: (a) Structure of alkali-silicate glasses; (b) a Q_n structural unit: Q₂ comprises two bridging oxygen atoms and two NBO.

where γ_x is the molar fraction of a given oxide (x) in the glass and γ_T is the molar fraction of network-forming oxides. Often the polymerisation of silicate glasses is expressed on the basis of the ratio $f_{Si} = [Si]/[O]$, where [Si] and [O] are the numbers of silicon and oxygen atoms in the glass. Table 17.5 gives typical values of the degree of polymerisation of silicate glasses.

The degree of polymerisation reaches a maximum at ratio $f_{Si} = 0.50$ for vitreous silica dropping to 0.25 for modified glasses. The most durable waste-immobilising glass should be a silica glass containing a minimum amount of waste oxides. However, such a waste-form is not used both because of the high processing temperature required and very low content of waste it can accommodate. In waste vitrification melting should be done in the range $\leq 1100\text{--}1250^\circ\text{C}$ since at higher temperatures excessive volatilisation of both radioactive and non-radioactive constituents occurs. Glass formers other than silica such as boron oxide have to be added to lower the processing temperature. Generally, no more than two parts by weight of glass-making additives are required to convert one part of radioactive waste, as oxide, to a satisfactory glass. Empirical studies have provided guidelines for formulation of acceptable nuclear waste glasses (Table 17.6).

Table 17.5: Structure of silicate glasses at different polymerisation degrees

Glass	Structure	Ratio $f_{\text{Si}} = [\text{Si}]/[\text{O}]$
SiO_2	3-dimensional network (silica)	0.500
$\text{Me}_2\text{O} \cdot 2\text{SiO}_2$	2-dimensional network (micas)	0.400
$\text{MeO} \cdot 2\text{SiO}_2$		
$\text{Me}_2\text{O} \cdot \text{SiO}_2$	1-dimensional network (metasilicates): chains, trinomial or 6-member coils	0.333
$\text{MeO} \cdot \text{SiO}_2$		
$[\text{Si}_2\text{O}_7]_2$	Discrete double tetrahedra (pyrosilicates)	0.286
$2\text{Me}_2\text{O} \cdot \text{SiO}_2$	Discrete tetrahedra (orthosilicates)	0.250
$2\text{MeO} \cdot \text{SiO}_2$		

Table 17.6: Important ratios for borosilicate glass formulations

Designation	Molar ratio	Empirical optimum
A	Si/Al, B	Higher or about 1.5
B	Oxygen/network formers	2.2–2.4
C	Network formers/network modifiers	About 2

When ratio $A > 1.5$, radionuclide leachability is low although the melting temperature of the glass increases as A increases. Glass formation is best and leachability low when $2.2 \leq B \leq 2.4$. Excess oxygen is needed to balance the electrical charge of the network modifiers. Density increases as A decreases and B increases. Ratio C should be ~ 2 for good glass formation. As C decreases, the glass network is disrupted and glass-forming ability decreases.

Table 17.7 gives properties of a HLW borosilicate glass studied in Russia.

17.7. Role of Boron Oxide

Boron oxide is commonly substituted for silica in nuclear waste glasses. Introduction of B breaks up Q_3 units and creates Q_2 , Q_4 and also small amounts of Q_1 . The presence of B has several positive effects. B at less than 15 wt.% reduces the thermal expansion coefficient, improves chemical durability and resistance to mechanical abrasion. At relatively low temperatures ($< 500\text{--}600^\circ\text{C}$) boron stabilises the glass structure forming BO_4 groups. At high temperatures B follows the general trend towards lower coordination number for cations, which may

Table 17.7: Parameters of Russian borosilicate nuclear waste glass

Density (g/cm ³)	Compressive strength (MPa)	NR (IAEA, 28th day), ($\times 10^{-6}$) (g/(cm ² day))	Thermal stability (° C)	Damaging dose (Gy)	Specific heat (kJ/kg K)	Thermal conductivity (W/m K)	Expansion coefficient (K ⁻¹)
2.7	22–54	0.9 (Na); 0.3 (Cs); 0.2 (Sr)	550	$> 10^5$	0.71	1.17	80^{-6}

occur in more than one-coordination geometry. B then assumes trigonal plane coordination with three oxygens and becomes a network modifier. B reduces the viscosity of glasses at high temperature and raises it at low temperature and as a result the glass becomes “shorter”, which is beneficial for vitrification. A short glass is one with a sharp dependence of viscosity on temperature. A long glass has a smoother dependence of viscosity on temperature.

Borate glasses are dominated by superstructure units, which comprise well-defined arrangements of the basic BO_3 triangular and BO_4 tetrahedral structural units with no internal degrees of freedom in the form of variable bond or torsion angles, for example boroxol (B_3O_6) and triborate (B_3O_7) units. On adding a network modifier (such as an alkali oxide) to boron oxide, the glass properties do not change as a monotonic function of composition but exhibit a maximum or minimum value at a specific composition – the so-called *boron oxide anomaly*. The addition of a network modifier to vitreous B_2O_3 initially leads to an increase in the coordination number of the boron atoms from 3 to 4, rather than to the formation of NBO atoms, (i.e. the conversion of BO_3 triangles into BO_4 tetrahedra) and an important structural parameter is the fraction of the boron atoms which are 4-coordinated.

Boron in a 3-coordinated position in a borosilicate glass is a relatively unstable component. Acids easily leach this boron along with sodium bonded to it. Boron remains in a 3-coordinated position in a sodium–borosilicate glass until the concentration of alkali metal is low according to

$$\Psi_{\text{B}} = \frac{\gamma_{\text{Na}_2\text{O}}}{\gamma_{\text{B}_2\text{O}_3}} < \frac{1}{3} \quad (17.6)$$

where $\gamma_{\text{Na}_2\text{O}}$ and $\gamma_{\text{B}_2\text{O}_3}$ are the molar fractions of sodium and boron oxides in the glass. Two structural networks coexist when $\Psi_{\text{B}} < 1/3$ and metastable phase separation (liquation) occurs in such a glass on heating, with formation of microscopic volumes of different composition of high silica and sodium borate content. By acid etching the sodium borate phase from this glass, porous glass can be produced. BO_4 tetrahedra occur for higher concentrations of Na_2O when $\Psi_{\text{B}} > 1/3$. Ions of Na^+ localise near these tetrahedra by forming $[(\text{BO}_{4/2})\text{Na}^+]^-$ complexes.

17.8. Role of Intermediates and Modifiers

Cations with intermediate ionic strength such as Ti, Al, Be, Zr are intermediate elements. Al creates Q_3 at the expense of Q_4 and Q_2 units in silicate glasses. Al “lengthens” the glass, i.e. increases its working range, improves mechanical and chemical resistance and reduces the tendency for de-mixing. Al is a network former at low concentrations and occurs as AlO_4 tetrahedra in the glass

structure. This structural unit improves the glass stability and hence the chemical durability. Alkalis (e.g. Na) are located near AlO_4 tetrahedra and balance their negative charge so that alkalis (Na) are no longer modifiers in the silicate network. Being strongly bonded to AlO_4 tetrahedra these alkali cations are not readily leached compared to alkalis more weakly bonded to NBO. This is true if the content of Al is relatively small, when the ratio $\gamma_{\text{Na}_2\text{O}}/\gamma_{\text{Al}_2\text{O}_3} > 1$. Al_2O_3 in glasses significantly reduces the diffusion coefficient of water, which also improves glass durability. Increasing the Al_2O_3 content has the same effect as decreasing the total alkali oxide content. However, adding too much Al_2O_3 may be deleterious for the processing efficiency as higher processing temperatures are required. In practice partial replacement of SiO_2 by Al_2O_3 from 3 to 10% is considered to significantly improve the water stability of the glasses. The states of B and Al in borosilicate glasses as a function of Ψ_B are given in Table 17.8.

Table 17.8: Structural states of Al and B in borosilicate glasses

Ratio Ψ_B	Structural states of B and Al		
$\Psi_B > 1$	$[\text{AlO}_4]$	$[\text{BO}_4]$	–
$1/3 < \Psi_B < 1$	$[\text{AlO}_4]$	$[\text{BO}_4]$	$[\text{BO}_3]$
$0 < \Psi_B < 1/3$	$[\text{AlO}_4]$	–	$[\text{BO}_3]$

Ti is a network former in silicate glasses as the TiO_4 tetrahedra form glass-structural units and like Al, Ti increases the viscosity and stabilises the glass. Ti is unique among cations as it readily takes up fourfold, fivefold or sixfold coordination in glasses and crystals. Five-coordinated Ti is the dominant species in glasses rich in TiO_2 at concentrations exceeding 16 wt.%. It behaves simultaneously as a network former and network modifier although dominant in the former role. Five-coordinated Ti is likely to bond to both NBO and bridging oxygens, acting as a new Q_4 species with one additional NBO.

Li is usually added to improve glass properties. Other modifiers, particularly Na, can be present in the waste. Na is a network modifier that tends to increase the number of NBO and apparently increases glass alterability by destabilising its structure. A similar adverse effect on the initial alteration rate is observed for all the alkali metals but over quite different composition ranges.

The mixed alkali effect is made use of in design of waste-immobilising glasses and is manifested in silicate glasses as a non-linear variation in properties related to ionic transport such as ion exchange (see Section 20.6) when a fraction of the mobile ions such as Na^+ is substituted by another type of mobile ion such as Li^+ . At approximately equal contents of both alkalis the durability

of the glass reaches a maximum value compared to glasses with a single alkali ion.

CaO, MgO and ZnO increase the viscosity of alkali silicate glasses at low temperatures (400–600°C) but decrease it at high temperatures (1000–1300°C). The overall effect on viscosity is that a shorter glass results. Ca, Mg and Zn improve glass durability by stabilising the glass structure. Oxygen atoms bound to silicon form the coordination polyhedral cells around Ca, Mg and Zn. However, volatility is increased with addition of CaO as well as Na₂O and B₂O₃, so that a technological compromise must be found, which depends on waste composition.

17.9. Difficult Elements

S, Cl and Mo are less glass-compatible elements. Sulphur can be incorporated in the borosilicate glass structure as up to 1 wt.% of SO₃ equivalent. Greater than 1% SO₃ causes formation of a separate water-soluble (yellow) phase. The solubility of 6-valent Mo is also very limited. During vitrification both Mo and S separate from the melt forming on its surface, a so-called yellow phase (Fig. 17.4). This phase contains alkali sulphates, alkali chromates, alkali molybdates, CaMoO₄ and Ba(Sr)CrO₄.

F can be retained in silicate which melts by the addition of Ca to form CaF₂ giving an opacified glass. RuO₂, if present, is not soluble in the glass melt and is

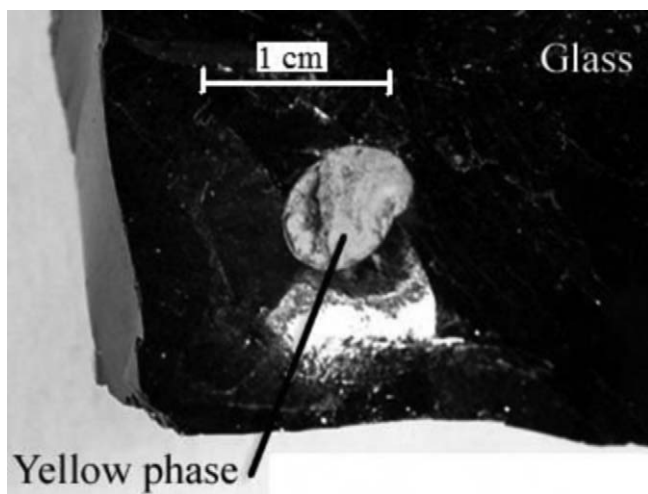


Figure 17.4: Yellow phase “peanut” in a British Magnox waste simulant glass.
Courtesy R. Short, ISL, University of Sheffield.

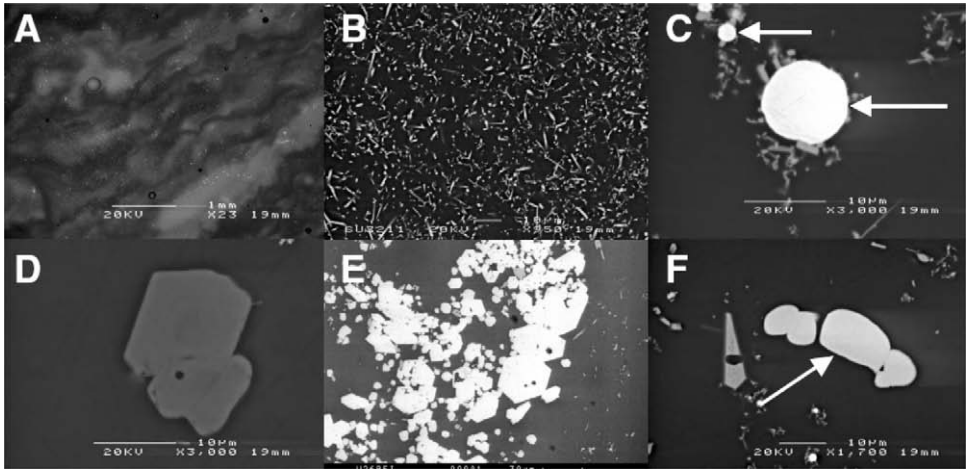


Figure 17.5: Gas bubbles (a) and crystalline phases (b–f) in an as-cast British Magnox waste simulants glass. (b) RuO_2 , (c) Pd (arrowed), (d) Cr, Fe, Ni-spinels, (e) lanthanide-rich phase and (f) Zr-rich phase (arrowed). Courtesy P.B. Rose, ISL, University of Sheffield.

readily encapsulated in the form of separate particles (Fig. 17.5). Lanthanides and actinides in borosilicate glasses are microscopically immiscible, being inclined to nano-scale phase separation although the glasses remain macroscopically homogeneous. Table 17.9 gives a simplified summary of the qualitative influence of various oxides on properties of nuclear waste glasses.

17.10. Phosphate Glasses

Phosphate glasses have been intensively studied in Russia, at the Eurochemic Corporation at Mol, Belgium, at Oak Ridge National Laboratory and the University of Missouri-Rolla in the USA. Russia has immobilised HLW from nuclear fuel reprocessing plant RT-1 in the Ural region in alumina–phosphate glass since 1987. Molten phosphate glasses are highly corrosive to refractory linings, behaviour which has limited their application. Novel Fe–Pb–phosphate glasses are particularly attractive due to their ability to accommodate enhanced amounts of refractory oxides and their high chemical durability. A number of Na–Al–phosphate, Fe–Al–phosphate and zinc phosphate compositions exhibit improved chemical durability. Fe–Pb–phosphate glasses which melt from 800 to 1000° C are not as corrosive as earlier phosphate compositions.

Phosphate glass structure is built around PO_4 tetrahedral units described using the Q_n designation (Fig. 17.6).

Table 17.9: Qualitative influence of oxides on glass properties: plus (+) indicates an increase and minus (–) a decrease of corresponding parameter

Oxide	Property					
	Melting temperature	Viscosity	Density	Durability	Chemical stability	Tendency to crystallisation
SiO ₂	+	+	+	+	+	+
Li ₂ O	–	–	+	–	–	+
K ₂ O	–	–	+	–	–	–
Na ₂ O	–	–	+	–	–	–
CaO	–	–	+	+	+	+
MgO	+(< 6 mol%)	+	+	–	–	–
MgO	–(< 6 mol%)	+	+	–	+(CaO + MgO)	–
BaO	–	–	+	–	–	–
ZnO	–	–	+	+	+	+
PbO	–	–	+	–	–	–
Al ₂ O ₃	+	+	+	+	+	–
Fe ₂ O ₃	–	–	+	+	+	+
ZrO ₄	+	+	+	+	+	+
B ₂ O ₃	–	–	–	+	+	–
TiO ₂	–	–	+		+	–

In a pure P₂O₅ system, the glass is a 3-dimensional network of branching Q₃ units with three bridging oxygen atoms and one doubly bonded oxygen per tetrahedral unit. Addition of modifying alkali or alkaline earth cations replaces Q₃ units with Q₂ units with the cations creating ionic cross-links between the phosphate units. At a P₂O₅ concentration of approximately 50 mol%, the Q₃ units disappear and the structure consists of only Q₂ units in the form of linear phosphate chains. Further addition of modifying cations at concentrations greater than 50 mol% begins to convert Q₂ units to Q₁ units and finally Q₀ units.

Phosphate glass is particularly attractive for immobilisation of high Al and Na wastes. Figure 17.7 shows the glass-forming regions of the Na₂O–Al₂O₃–P₂O₅ system. For low-to-moderate melting temperatures, the optimum range of the Na to P ratio is from 1.0 to 1.3. This ratio can be increased at higher temperatures, and at 1400–1500°C phosphate glasses can be made with up to 40% Al₂O₃. In contrast to borosilicate glasses phosphate glasses incorporate significantly larger amounts of corrosion products as well as actinide oxides, molybdates and sulphates. Lanthanides and actinides in phosphate glasses tend

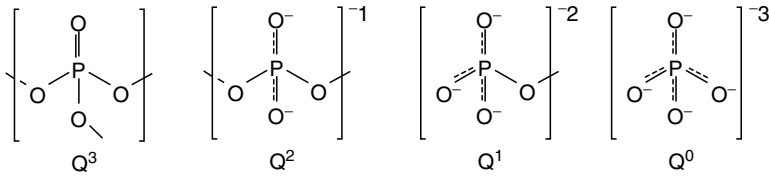


Figure 17.6: Structural units of phosphate glasses.

to complex strongly with phosphate ions. Table 17.10 gives data on solubility of some HLW components in melted Russian phosphate glass at 1000°C while some properties of alumina–phosphate glass composition (wt.%) 21.2Na₂O–3Cs₂O–19Al₂O₃–1.5Fe₂O₃–0.1Cr₂O₃–52P₂O₅–3SrO used to immobilise HLW in Russia are given in Table 17.11. The thermal stability of a glass is characterised by the temperature at which the leaching rates for Na, Cs and Sr are increased by more than 100 times.

17.11. Glass Composites

Glass composite materials (GCMs) are used to immobilise glass-immiscible waste components such as sulphates, chlorides, molybdates and refractory

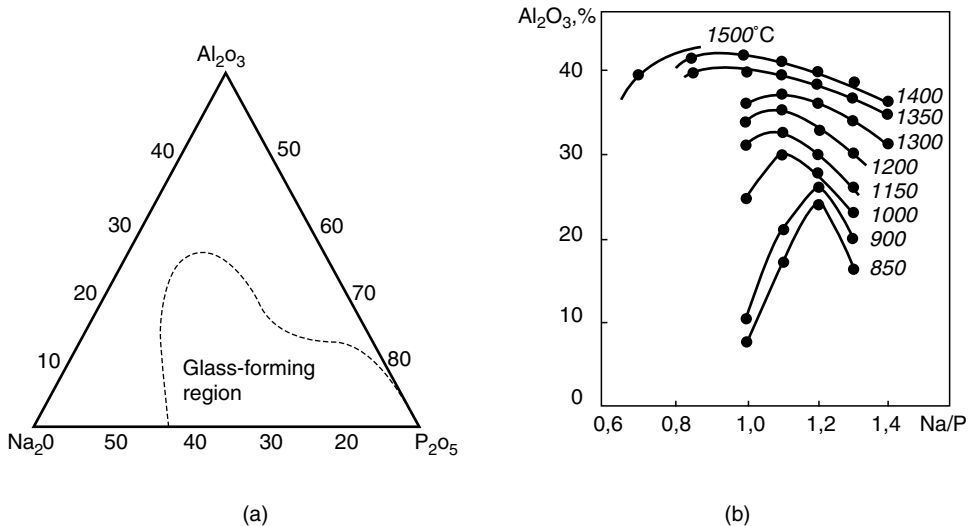


Figure 17.7: (a) Glass formation areas in the system Na₂O–Al₂O₃–P₂O₅ at 1000°C, compositions in wt.%. (b) The content of Al₂O₃ as a function of (Na/P) ratio at different temperatures.

Table 17.10: Solubility of elements in phosphate glass

Element	Ru	Rh	Pa	Ag	Te	Zr	Mo	La	Ce	Nd	Sm	Fe	Cr	Ni
Solubility (ppm)	20–60	20–60	300–600	$\geq 2.6 \cdot 10^3$	$\geq 10^3$	$\geq 7 \cdot 10^3$	$\geq 7 \cdot 10^3$	(1.1–1.4) 10^4	(1.2–1.6) 10^4	(2–2.4) 10^4	(2.8–3.2) 10^4	$5 \cdot 10^3$	500–2 10^3	500–2 10^3

Table 17.11: Phosphate nuclear waste glass properties

Density (g/cm³)	Compressive strength (MPa)	NR (IAEA, 28th day) ($\times 10^{-6}$) g/(cm² day)	Thermal stability (° C)	Damaging dose (Gy)	Specific heat (kJ/kgK)	Thermal conductivity (W/mK)	Expansion coefficient (K⁻¹)
2.6	9–14	0.8 (Na); 1.1 (Cs); 0.4 (Sr).	> 450	> 10 ⁷	0.96	0.74	1.50 ⁻⁶

materials requiring unacceptably high melting temperatures. GCMs comprise both vitreous and crystalline components. Depending on the intended application, the major component may be a crystalline phase with a vitreous phase acting as a bonding agent, or, alternatively, the vitreous phase may be the major component, with particles of a crystalline phase dispersed in the glass matrix. GCMs may be produced by dispersing both melted materials and fine crystalline particles in a glass melt and may be used to immobilise long-lived radionuclides (such as actinide species) by incorporating them into the more durable crystalline phases, whereas the short-lived radionuclides may be accommodated in the less durable vitreous phase. Synroc-glass is an example of GCM with Synroc crystalline phases in a vitreous matrix (Fig. 17.8a). Synroc-glass has been developed for sodium-rich wastes such as those at the Hanford site in the USA. Crystalline phases such as zirconolite and perovskite are the hosts for actinides and waste loadings of 50–70% by weight have been demonstrated in such composites with a high durability. The French have developed a U–Mo GCM to immobilise Mo-rich HLW. Another example is the GCM developed to immobilise sulphur-enriched waste streams in Russia (Fig. 17.8b) containing conventional borosilicate glass vitreous phase with uniformly distributed particles comprising up to 15% by volume of yellow phase. The durability of this GCM is similar to that of conventional waste-form glasses (Table 17.12). GCMs are potential host materials for highly volatile radionuclides such as ^{129}I (Fig. 17.8c). Such GCMs can be produced by sintering an intimate mixture of glass powders and iodine-containing sorbents, possibly under applied pressure.

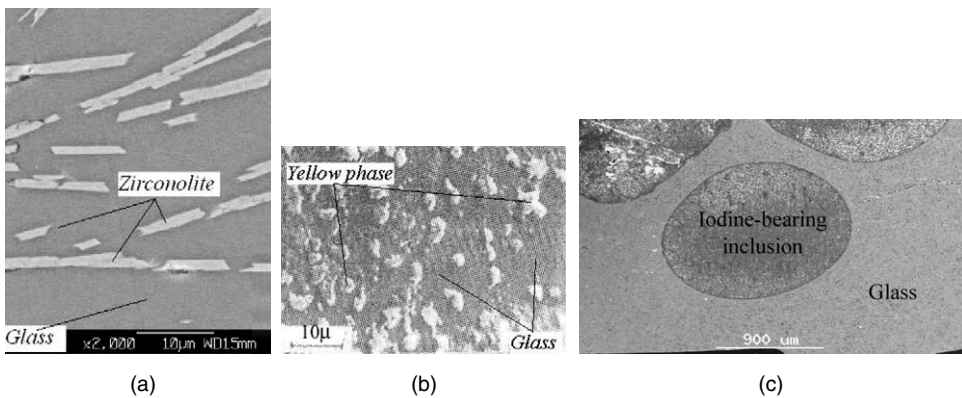


Figure 17.8: Waste encapsulation in GCMs: microstructure of (a) Synroc-glass with zirconolite crystalline phase; (b) GCM for immobilising yellow phase; (c) GCM for immobilising iodine. Courtesy D. Perera, ANSTO.

Table 17.12: Basic properties of borosilicate glasses and glass composite materials

Properties	Borosilicate glasses, containing high sodium LILW	GCM
Waste oxide content (wt.%)	30–35	30–35 with up to 15 vol.% yellow phase
Viscosity (Pa s) at 1200° C	3.5–5.0	3.0–6.0
Resistivity (Ω m) at 1200° C	0.03–0.05	0.03–0.05
Density (g/cm ³)	2.5–2.7	2.4–2.7
Compressive strength (MPa)	80–100	50–80
Leach rate (g/cm ² day) (28-day IAEA test)		
¹³⁷ Cs	10 ⁻⁵ to 10 ⁻⁶	~10 ⁻⁵
⁹⁰ Sr	10 ⁻⁶ to 10 ⁻⁷	10 ⁻⁶ to 10 ⁻⁷
Cr, Mn, Fe, Co, Ni	~10 ⁻⁷ to 10 ⁻⁸	10 ⁻⁷ to 10 ⁻⁸
REE, An	~10 ⁻⁸	~10 ⁻⁸
Na	10 ⁻⁵ to 10 ⁻⁶	10 ⁻⁴ to 10 ⁻⁵
B	<10 ⁻⁸	≤10 ⁻⁸
SO ₄ ²⁻	~10 ⁻⁵ to 10 ⁻⁶	~10 ⁻⁴ to 10 ⁻⁵ with up to 15 vol.% yellow phase

17.12. Vitrification Processes

Immobilisation of HLW by vitrification has been studied extensively over the last 40 years in Denmark, Canada, China, Germany, Belgium, Italy, India, Japan, Korea, Russia (former USSR), the UK and the USA. The potential use of glass to immobilise nuclear waste was initially investigated in the early 1950s in Canada using natural nepheline syenite as the starting material. This was mixed with an acidic solution of the waste material together with lime, and the mixture melted at 1250–1350° C in a fireclay crucible. An active pilot plant was subsequently constructed at Chalk River to demonstrate the feasibility of the vitrification process on a larger scale. Radioactive blocks of glass were produced between 1958 and 1960 although the vitrification programme was terminated in 1960 because no fuel reprocessing was foreseen in Canada at that time.

Battelle Pacific Northwest National Laboratory (PNNL) in the USA developed an “In-Can-Melter” technique (Fig. 17.9) utilising a spray calciner directly attached to the disposal canister, which also acts as the glass-manufacturing vessel. Glass frit is added to the calcine as it drops into the container, which is surrounded by a zoned furnace. The calcine-frit mixture is heated to 1000–1100° C forming a molten glass. As the canister is filled, the heating band of the furnace is raised to match the reaction zone. The containers are generally filled to the 90% level, at which time the calcine-frit feed is moved to a second

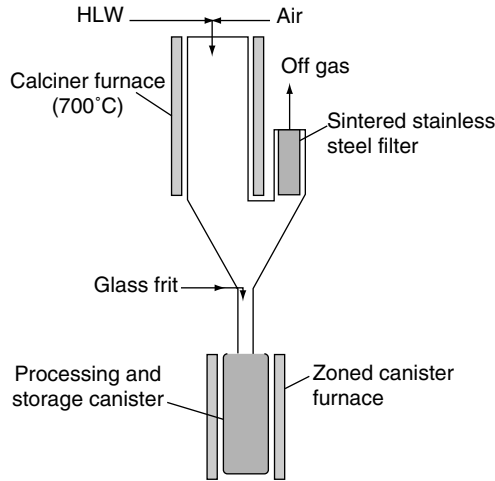


Figure 17.9: In-Can-Melter vitrification process.

canister already in place. The filled “can” is then removed and replaced by an empty one ready for the next switching operation.

A fluidised bed calciner in conjunction with the in-can production technique is less developed although PNNL later developed another process based on application of Joule-heated ceramic melters (JHCM).

In the UK also, work started in the 1950s, initially using natural soils as the base material for glass formation. These glasses had to be melted at high temperatures (about 1500°C) to produce homogeneous, bubble-free product. Subsequently, alkali borosilicate glass compositions were developed that could dissolve up to 30% waste oxides and that could be melted at lower temperatures. Between 1958 and 1962 a vitrification pot process was developed at the UK Atomic Energy Authority’s Harwell laboratory called the fixation in glass of active liquors (FINGAL) process. HLW plus glass-forming additives were fed into the final storage container, which was surrounded by a zoned furnace (Fig. 17.10). Heating begins at the lowest portion of the furnace, and three layers form – molten glass at the bottom, covered by calcine, and with a layer of boiling liquid on top. As the glass level is raised, the higher heating elements of the furnace were activated. After the glass and waste had been calcined, melted and homogenised, the pot was removed and replaced with another pot containing waste and frit ready to be calcined and melted. The FINGAL process was later modified and scaled up, to be known as the highly active residue vitrification experimental studies (HARVEST) process. The HARVEST process included the use of an annular container, with an additional heater in the annulus, and utilisation of internal fins in the container for heat removal.

Simple pot vitrification processes that do not employ a separate calcination stage have been used in France (Pilote Verre – PIVER), Italy and China. Such a

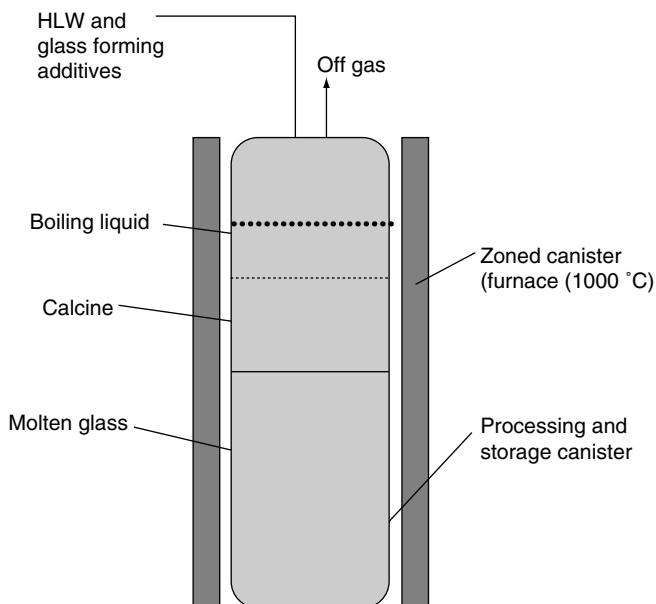


Figure 17.10: British rising glass vitrification process FINGAL.

process is currently used commercially in India (WIP, Tarapur) for the immobilisation of HLW generated during the reprocessing of spent fuel.

France has pioneered development of vitrification processes. Several types of matrices were investigated, including crystalline materials, phosphate and borosilicate glasses. The first laboratory scale unit was named “Vulcain”. It was commissioned in 1957 and was followed by a first vitrification pilot unit, Gulliver, commissioned in 1964. This early work culminated in the pilot-scale facility PIVER, featuring a single induction-heated pot in which the three operations of evaporation of the HLW solutions, calcination of the residue and glass formulation were performed. PIVER operated successfully from 1969 to 1973 to produce 12 t of glass containing 50^6 Ci of activity. PIVER resumed operation in 1979 to vitrify HLW from the reprocessing of fast-breeder fuels. It was decommissioned between 1988 and 1990. Although these and other related vitrification processes were successful in pilot plant trials, batch processing considerations led France to choose a continuous melting process for full scale development. The French process includes a separate calcining stage. Waste is first calcined employing a rotary kiln before being fed under gravity into a metallic pot heated inductively (Fig. 17.11). This is a continuous process with new glass frit and waste material being supplied to the furnace and molten glass being fed from the furnace via a freeze-thaw valve directly into a separate

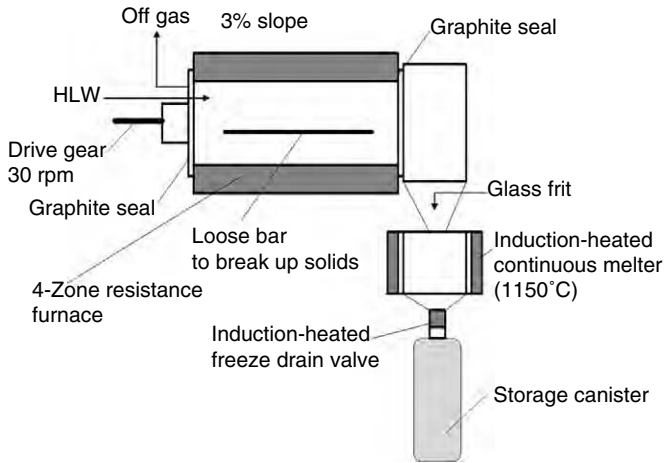


Figure 17.11: Two-stage AVM vitrification process.

storage canister. The major advantage of this process is that much higher throughputs can be achieved.

The AVM (Atelier de Vitrification de Marcoule) was the first in-line vitrification facility that proved the technology of the French two-step vitrification process, which converted HLW solutions to a solid form in a rotary calciner and then vitrified them in an induction-heated metallic melter. The first industrial HLW vitrification plant using AVM technology started operation in 1978 at Marcoule. Similar plants (R7 and T7) have been built at La Hague (Fig. 17.12). HLW vitrification plants R7 and T7 are designed to produce 600 canisters of glass per year. R7 entered active service in June 1989 whereas the T7 facility entered active service in July 1992. By 2000 the R7 and T7 HLW vitrification plants had produced more than 10 000 glass canisters (4000 t) with overall radioactivity of about 3.50^6 Ci.

An alternative continuous process involves melting the glass in a tank constructed from refractory ceramic blocks by passing an electric current through the molten glass using submerged electrodes. Such melters are examples of JHCM. Calcined HLW is mixed with glass frit or glass-forming additives and fed into the JHCM (Fig. 17.13). Cold material covering the surface of the molten glass (the so-called cold cap) reduces evaporation losses. A pilot vitrification plant based on JHCM was commissioned at PNNL, USA in 1984.

In 1985 the joint German–Belgian vitrification plant PAMELA at Mol (Belgium) was commissioned. This plant uses a continuous vitrification process in which HLW slurry together with glass frit is fed into a JHCM equipped with

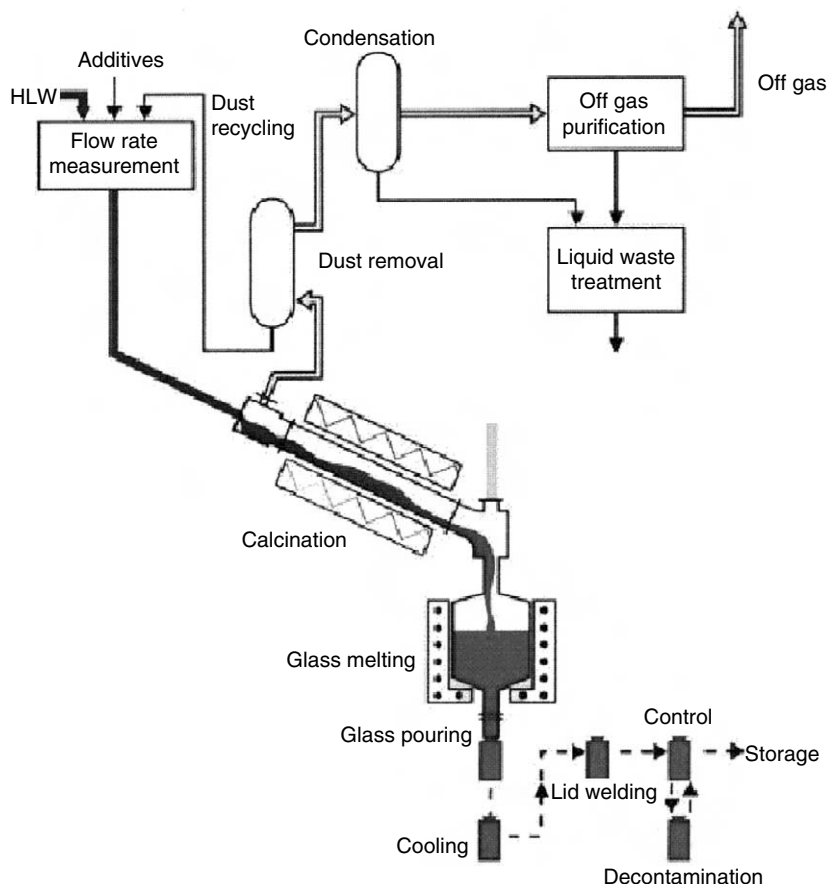


Figure 17.12: Schematic of HLW vitrification plants R7/T7, La Hague, France.

two drainage systems. One drain is employed to produce glass blocks, while the second drain is used to feed a glass bead production unit. This produces glass beads with a diameter of 50 mm. The beads are subsequently dispersed in a lead alloy matrix to produce a product called “vitromet”. The PAMELA melter has four Inconel 690 electrodes and can operate at power levels up to 100 kW with MoSi_2 elements enabling start up. PAMELA produced 64 t of waste glass in 411 canisters in 1985–1986. PAMELA revealed that noble metals (e.g. Pd, Rh and Ru) gradually accumulate at the bottom of the furnace and lead to increased power consumption due to the higher electrical conductivity of this layer. It is now recognised that a sloped furnace bottom is desirable, thus enabling the viscous noble metal rich layer to be purged more easily from the furnace.

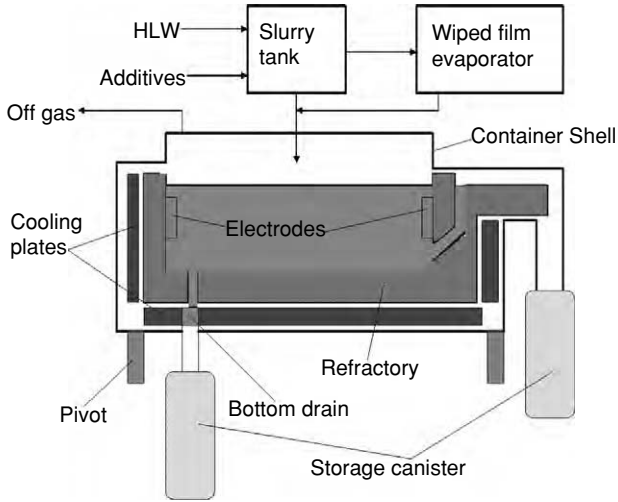


Figure 17.13: Schematic of one-stage vitrification processes in a JHCM used in USA, Russia, Germany–Belgium and Japan.

In 1987 Russia commissioned its first JHCM-based HLW vitrification plant EP-500 in the Ural Region. This plant had a capacity of 500 L/h in terms of initial HLW. About 1000 m³ of HLW was vitrified during the next 18 months producing 160 t of waste glass with overall radioactivity about 40⁶ Ci. EP-500 was heated by a number of water-cooled molybdenum electrodes located at the melter bottom. Electrical current to the electrodes was supplied through water-cooled stainless steel tubes and the maximum power requirement of the melter was around 1.5 MW. In 1988 EP-500 was shut down due to a current supply failure and in 1991 a second EP-500 type JHCM type was put into operation. Over the next three years 6300 m³ of HLW were vitrified producing 460 m³ (1200 t) of radioactive glass. Total activity of radionuclides incorporated into this glass was 1510⁶ Ci.

In 1991 the UK started its HLW vitrification at Windscale, now Sellafield. The advantages offered by the AVM process, coupled with its successful full-scale operation in France, led the UK to choose this process, in preference to the HARVEST method, for its commercial waste vitrification programme. The process at Sellafield is the AVH (Atelier de Vitrification de la Hague) process, which differs from AVM in that an elliptical rather than cylindrical-shaped melter is used. Currently, the HLW vitrification plant at Sellafield has three production lines producing 475–600 containers of vitrified waste per annum and up to 2005 the Sellafield waste vitrification plant has produced 3179 containers of vitrified waste.

In 1995 Japan inaugurated its industrial HLW vitrification plant in Tokai. It employs a JHCM with a steeply sloped floor. Use of a three-electrode assembly allows effective heating and stirring of the melt, presumably resulting in a more homogeneous product. The total waste glass produced by the Japan HLW vitrification plant to date is less than 100 t.

In the mid 1990s two large-scale HLW vitrification plants based on JHCM became operational in the USA. In March 1996 the Savannah River Defence Waste Processing Facility (DWPF) became the first plant in the USA to vitrify HLW. The facility produced 200–250 canisters of vitrified waste per year. DWPF produced 738 canisters of radioactive glass (about 1500 t) upto 1999 and is still in operation. The West Valley vitrification plant WVDP (West Valley Demonstration Project) has also nearly completed its campaign. Since June 1996, the West Valley WVDP produced more than 240 canisters of glass, immobilising more than 220 t of HLW. The more recent HLW vitrification plant at Hanford has moved into the construction stage.

In Germany (Karlsruhe) a vitrification plant is currently under construction with a compact-size JHCM with a sloped bottom avoiding sedimentation of noble metals upon melting. Vitrification is planned of about 70 m³ of HLW with a gross activity of 240⁶ Ci within the decommissioning programme of the former German pilot reprocessing plant that operated for 20 years terminating in 1990.

17.13. Cold Crucible Melters

Recent developments include application of cold crucible induction heated melters (CCMs) to immobilisation of wastes, which are difficult to melt as well as production of GCM and mineral-like immobilising materials. In a CCM the glass melt is heated by induction currents. The melt is preserved inside a cooled volume of glass-batch material (termed the skull, CCM is also known as skull melting) that isolates the high-temperature melt from the water-cooled stainless steel or copper tubes which make up the cold crucible walls (Fig. 17.14). CCMs are used either to melt waste with glass-forming additives (Russia) or calcined waste with glass frit (France). A colder surface layer or cold cap of dried batch is formed in the one-stage vitrification CCM as forms in a JHCM, diminishing losses of aerosols and volatilised radionuclides from the glass.

The construction elements of a CCM are transparent to the electromagnetic field produced by the induction coils allowing induction currents to be generated inside the material contained in the crucible. The cooling water in the tubes is at a temperature less than 100° C so that molten glass in contact with them can be kept at ~200° C. Even during melting the tubes remain cold and a

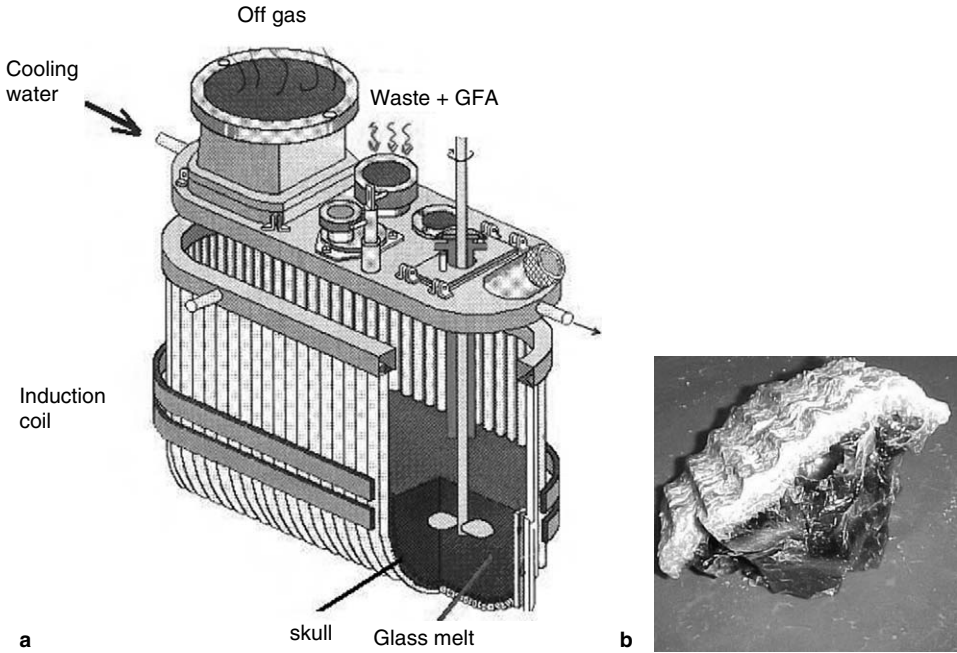


Figure 17.14: (a) Schematic of Russian stainless steel cold crucible melters (CCMs). The stirrer in this CCM enables production of GCM, GFA are glass forming additives. (b) A sample of glass from the CCM: the white layer is a part of the glass-forming batch (skull) that remains unmelted (authors' photo).

protective layer made of glass batch material forms between the melt glass and tubes insulating them from the melt. This protective skull (Fig. 17.14b) means that refractory liners required in other melters are not needed. Since active refractory materials are difficult to immobilise (they cannot, e.g. be melted easily) this is a distinct advantage.

CCMs are well suited to obtaining high throughput in a small volume. CCMs supplied with stirrers (Fig. 17.14a) have enhanced throughputs as well as enabling production of GCM to immobilise wastes which are difficult to melt. Low crucible weight facilitates easy dismantling and small amounts of secondary waste compared to conventional melters. Neither glass nor metal adheres to the cooled wall, which is therefore never subject to strong contamination. CCMs have the advantages of extended operational lifetime, flexibility to glass formulations, larger operation temperature range and high glass output at significantly smaller sizes. Since CCMs are protected from the glass melt by a cold glass batch layer, glass can be produced at higher temperatures, which increases the glass formulation range. In addition, because the melt comes in contact only

with solid material of the same composition as the glass batch the final product has a high degree of purity, which is particularly important for meeting product specification. Waste vitrification using CCM may be either one- or two-stage, i.e. with preliminary calcination or with calcination occurring in the melter. One disadvantage of CCMs is their high specific energy consumption. Table 17.13 illustrates the main process parameters of a CCM compared to a JHCM.

The first LILW vitrification plant based on CCM was put into operation in 1998/1999 in Russia (SIA “Radon”). This plant with a melt capacity of 75 kg/h is currently operated as a prototype plant for the vitrification of operational radioactive waste from nuclear power plants (NPP). A pilot HLW vitrification plant with CCM is currently under test at SNF reprocessing plant RT-1 in the Ural Region, Russia. It started test operations in 1994 aiming to immobilise partitioned radionuclides in glasses, GCM, Synroc-type and other mineral-like materials.

France is intensively developing CCM for both HLW and LILW including joint projects with Russia and the Czech Republic. Several CCM test platforms have been built at the Marcoule pilot facilities. These programmes were initially focused on the treatment of HLW solutions from light water reactor fuel, producing simulated R7/T7 glass. The feeding systems allow simultaneous controlled feeding of solids (frit, powders) and liquids (surrogate solutions, sludges). Figure 17.15 shows the microstructure of a GCM for immobilisation of molybdenum-enriched HLW made via CCM.

South Korea also plans to operate a waste vitrification plant based on CCM to vitrify LILW from its nuclear power plants. Pilot plant tests have been

Table 17.13: Process parameters of JHCM and CCM

Parameter	Melter type	
	Joule heated	Cold crucible induction
Melt capacity (kg/h)	25	25
Specific melt capacity (kg/m ² h)	40–120	170
Melting ratio (kWh/kg)	2.5–3.2	4.4–6.4
Operating temperature (°C)	<1300	<3000
Corroding in melt	Refractory and electrodes	nothing
Gross weight of loaded melter (kg)	>1000	<200
Operating mode	Continuous	Continuous or batch

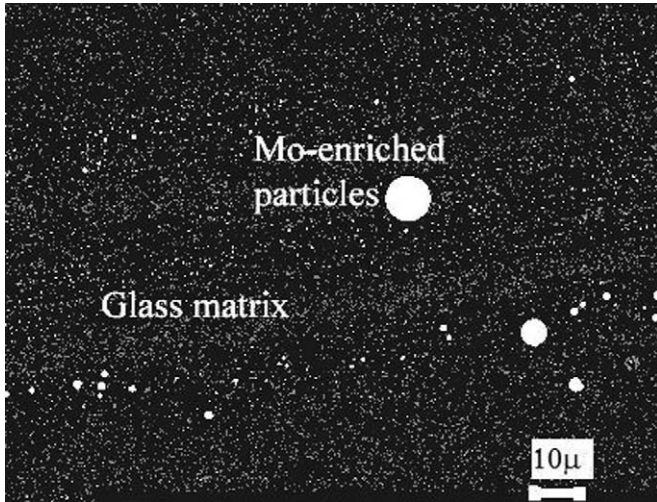


Figure 17.15: GCM made of a silicate host glass encapsulating Mo-enriched phases to immobilise U–Mo HLW. Courtesy E. Vernaz, CEA, France.

successfully completed for various waste types. CCM melting has also been intensively studied for Hanford site wastes in the USA.

17.14. Vitrification Technology

The vitrification technology comprises several stages, starting with evaporation of excess water from liquid radioactive waste, followed by batch preparation, calcination, glass melting, and ending with vitrified waste blocks and potentially small amounts of secondary waste. Thin film evaporators (Section 14.2.1) are used and the remaining salt concentrate is mixed with the necessary additives and depending on the type of vitrification process is directed to one or another process apparatus. In the one-stage vitrification process glass-forming additives are mixed with concentrated liquid wastes and so a glass-forming batch is formed (often in the form of a paste). This batch is then fed into the melter (JHCM or CCM) where further water evaporation occurs, followed by calcination and glass melting. Figure 17.16 illustrates single-stage vitrification technology with an indication of materials used for immobilising nitrate-type radioactive wastes.

In the two-stage vitrification process (with separate calcination, Section 17.15) the waste concentrate is fed into the calciner. After calcination the

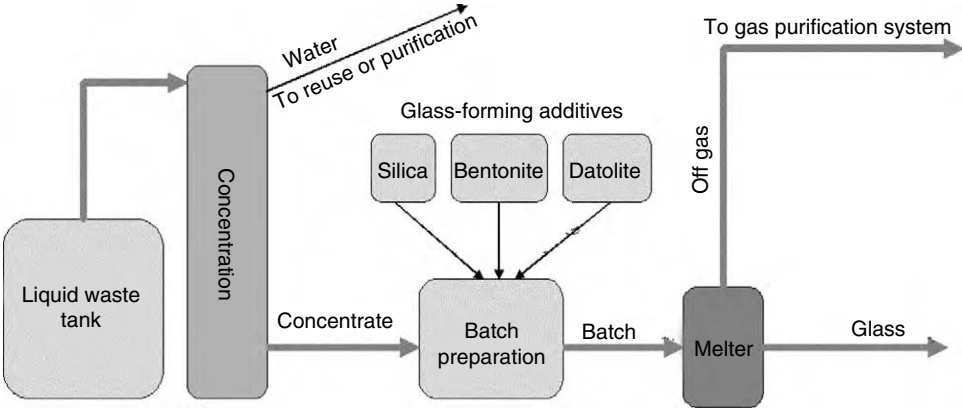


Figure 17.16: Schematic of one-stage waste vitrification technology. Datolite is a natural B-containing mineral

required glass-forming additives (usually as a glass frit) together with the calcine are fed into the melter. Two streams come from the melter – first is the glass melt containing most of the radioactivity and second is the off-gas flow, which contains off gases and aerosols. The melt waste glass is poured into containers, which may be slowly cooled in an annealing furnace to avoid accumulation of mechanical stresses in the glass. When annealing is not applied, cracking occurs resulting in a large surface area potentially available for attack by water in a repository environment. Table 17.14 estimates the final surface area S_f of unannealed nuclear waste glass in cylindrical containers compared to the surface area of annealed samples, when the minimum final surface area is S_a . Despite the higher final surface areas of unannealed glasses these are sufficiently durable to ensure a suitable degree of radionuclide retention. Hence in many cases annealing is not applied in vitrification facilities.

Containers of vitrified waste are the final product containing the vast majority of the waste contaminants. Comparing the volume of the glass blocks produced to the initial waste volume gives the volume reduction factor (VRF), which is one of the most important factors characterising the efficiency

Table 17.14: Increase of surface area of nuclear waste glasses due to cooling regime

Cooling regime	S_f/S_a
Annealed	1
Slow cooled	4
Free air cooled	12
Water quenched	22

of the processing technology (see section 14.1). VRF is crucially dependent on the waste composition and for a typical vitrification process is of the order of 5.

The second stream from the melter goes to the gas purification system (Fig. 17.16), which is usually a complex system that removes from the off gas not only radionuclide but also chemical contaminants. Operation of this purification system leads to generation of a small amount of secondary waste.

17.15. Calcination

Two-stage vitrification processes utilise preliminary calcination of the waste. The term calcination is used to describe the decomposition of oxysalts such as hydroxides and nitrates to oxides with the release of vapour species. In the vitrification process the resulting oxides can be incorporated into the waste form product by reaction with a suitable melted base glass. The oldest of the calcination techniques is pot calcination in which the entire procedure takes place in a “pot”. The liquid waste is added in batches to the container, which is enclosed in a zoned furnace. As the water boils off and oxides form, a crust of calcine forms on the sides and bottom. The process is continued until the container is about 90% filled. The batch nature of this process limits its use for any large-scale application, and quality control is more difficult than in other methods.

In spray calcination (Fig. 17.17a) the waste is introduced into the top of an externally heated reaction chamber through a spray orifice along with a jet of atomising air. Water is driven off of the falling droplets and the waste is largely converted to oxides and is collected in the form of fine (≤ 1 mm) spheroidal powder granules. The reaction furnace is operated to produce a 100° C wall temperature, although the calcine temperature itself is typically in the 350–550° C range. The technique is able to handle waste of almost any concentration.

Fluidised bed calcination (Fig. 17.17b) also accepts wastes at almost all concentrations. In this process the wastes are kept in suspension by air jets from below and heated internally to 500–600° C. Evaporation occurs from the surfaces of the original bed particles and results in a product consisting of granular bed material and powdered calcine, both of which are continuously removed from the reactor. Heating of the bed was originally done by means of an exterior furnace, but this resulted in high losses of Ru and Cs. Heating accomplished by kerosene combustion in the bed resolves this problem.

The stirred bed reactor is a variation of the fluidised bed approach (Fig. 17.17c), the materials being stirred as well as fluidised by air jets. The stirring approach allows better control of particle size in the finished product. This is particularly important for high-alumina wastes. Addition of phosphate to the waste feed produces metal phosphates and a substantial amount of aluminium phosphate that acts as a secondary

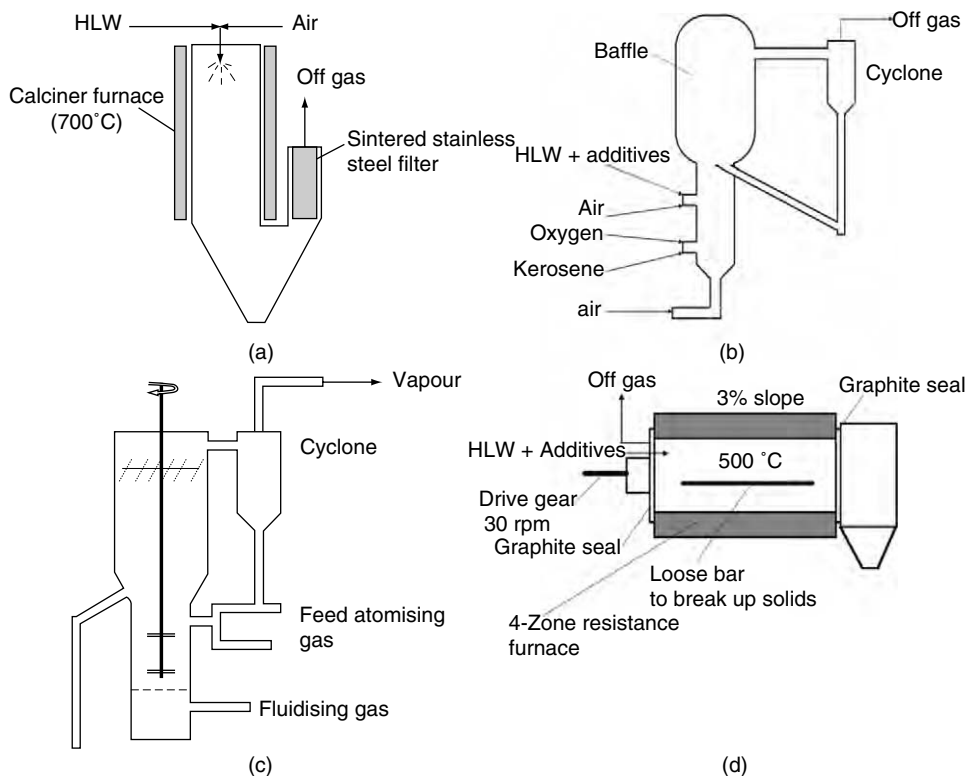


Figure 17.17: Schematic of four main types of calciners: (a) spray, (b) fluidised bed, (c) stirred bed and (d) rotary kiln.

containment. Leachability characteristics are considerably improved, and the product is termed super-calcine.

The rotary kiln calciner (Fig. 17.17d) has been largely developed by the French. The equipment consists of an externally heated (500–600°C) rotating cylinder tilted at a slight angle from the horizontal so that the waste introduced at the upper end is dried and almost completely denitrated before it exits at the lower end. A loose bar in the barrel keeps the calcine free-flowing and prevents wall deposits building up.

Calcines are typically fine powders and thus relatively dispersible, this being a serious consideration in the event of a transportation accident. The untreated materials are also easily soluble in water. These two characteristics have largely eliminated calcines from consideration as a final disposal form. They can be highly reactive chemically and excellent raw materials for further processing. A high sodium nitrate content, typical of many wastes, creates problems in all of

the calcination processes. This salt has a melting temperature of 307°C and, upon melting, forms a viscous, sticky mass that resists further decomposition. The addition of finely divided metallic iron to the wastes helps with this problem. Powdered silica has been added to the feed stream to enrich calcines in silicates, which are more readily knocked loose by vibrating hammers acting on the outside of the walls. Processes have also been developed where much of the nitrate in the wastes is destroyed by pre-treatment with formaldehyde or formic acid. Most calcines as originally produced will still contain traces to substantial amounts of un-decomposed nitrate salts as well as small amounts of residual water. Calcines produced by the fluidised bed process typically have high levels of either alumina or zirconia. Table 17.15 presents some data on calcination products. These properties are obviously highly dependent on the compositions of the original wastes, which can vary considerably. Most current waste vitrification plants use rotary kiln calcination.

Table 17.15: Properties of calcines

Property	Calcine type			
	Pot	Fluidised bed	Spray	Rotary kiln
Bulk density (g/cm ³)	1.1–1.4	2.0–2.4	1.0–2.4	1.0–1.3
Highest operating temperature (°C)	420	500–600	700	500
Thermal conductivity (W/mK)	0.35–1.0	0.2–0.3	0.2	0.2
Specific area (m ² /g)	0.1–5.0	0.1–5.0	10–20	0.1–5.0
Porosity (%)	40–85	45–80	30–75	70–80

17.16. Radionuclide Volatility

Many waste radionuclides as well as inactive elements may be lost to varying degrees during the melting process. Figure 17.18 shows typical volatilisation behaviour of radionuclides as a function of temperature.

The elements of most concern are ruthenium and caesium because of the ¹⁰³, ¹⁰⁶Ru and ¹³⁴, ¹³⁷Cs radionuclides in the waste. Caesium is not volatilised up to about 400°C. Caesium nitrate is decomposed at 414°C with formation of caesium oxide, caesium peroxide and metallic caesium, which are highly volatile. To suppress caesium volatility acidic oxides are added that form stable silicates or phosphates. Caesium volatility in glass melts is effectively suppressed by boron and titanium oxides.

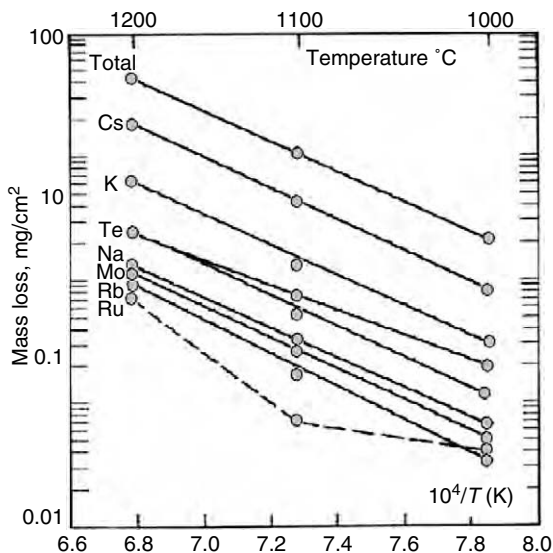


Figure 17.18: Volatilisation of nuclides with temperature.

Both radioactive and inactive ruthenium form during fission of nuclear fuel. Waste Ru, if volatilised, may subsequently condense and generate plugging problems. As much as 50% of the Ru in spent oxide fuel elements may remain in insoluble form in the reprocessing plant dissolver. This refractory material is in the form of colloidal RuO_2 particles. The fraction that does go into solution is in the form of nitrosyl complexes. These nitrosyl complexes are thought to be converted in the high-temperature processes to higher Ru oxides such as RuO_4 , generally assumed to be responsible for the Ru losses, although it has been demonstrated that RuO_2 also volatilises at 1100°C and above. Sugar is often added in calcination or melting to suppress Ru volatilisation.

Technetium is also easily volatilised. Tc can be in the waste in two oxidation states – IV and VII. Tc is volatilised even during the evaporation stage when removing excess water from HLW that contains acidic solutions of Tc(VII) as pertechnetate (TcO_4^-). Tc(IV) (TcO_2), while not so volatile as Tc(VII) , also has a high vapour pressure at glass-melting temperatures.

Other waste radionuclides are not so volatile. However, losses of radionuclides are caused also by mechanical and aerosol carryover from the melter. Batch composition largely governs the total carryover. For example, the presence of chlorides enhances losses of corrosion products whereas reducing agents such as sugar diminish radionuclide volatilisation. Liquation (phase separation) also influences total carryover of radionuclides. Some refractory particles from the HLW solutions remain during the melting process in

non-dissolved form being incorporated in the glass matrix as inclusions. This has a beneficial effect on suppression of radionuclide volatilisation. Typical and acceptable losses of the volatile radionuclides from melters are 1–4%.

17.18. Acceptance Criteria

Vitrification of nuclear wastes ensures maximum reduction of the potential for radionuclide release into the environment. Average diminishing factors K_{wf} for the vitrified aqueous radioactive waste are of the order of 10^4 – 10^5 sufficient to provide safe long-term storage of HLW in above-ground facilities as well as safe transportation and final disposal. For LILW vitrification enables simplified near-surface disposal facilities with better radionuclide retention than cements and bitumen. Although vitrification is a complex technique it is competitive due to the high VRF values and excellent retention capabilities of the waste-form. Acceptance criteria for vitrified wastes specify the minimum requirements to be met by the waste-form. Compliance with these criteria ensures safe operation of storage and disposal facilities. Table 17.16 illustrates the acceptance criteria for vitrified HLW in Russia according to the state standard GOST P 50926-96.

Table 17.16: Minimal requirements to vitrified HLW

Parameter	Limits
Chemical durability (NR, g/cm ² day): ¹³⁷ Cs, ⁹⁰ Sr, Pu	$<10^{-5}$; $<10^{-6}$; $<10^{-7}$
Homogeneity of the glass bulk: structure; chemical composition (wt.%)	Homogeneous ± 10
Thermal durability (absence of changes in structure and chemical composition) (°C)	> 550
Radiation stability	
To β and γ radiation (Gy)	$> 10^8$
To α radiation (decays/g)	$> 10^{18}$ – 10^{19}
Compressive strength MPa	> 9
Flexural strength MPa	> 41
Elastic modulus GPa	> 54
Thermal expansion coefficient (K ⁻¹)	$< 90 \cdot 10^{-6}$
Thermal conductivity from 20 to 500°C (W/mK)	1–2
Content of fissile materials (wt.%)	< 2

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Chapter 18

New Immobilising Hosts and Technologies

18.1. New Approaches

The main immobilisation technologies that are available commercially and have been demonstrated to be viable are cementation, bituminisation and vitrification. The highest degree of volume reduction and safety is achieved through vitrification although this is the most complex and expensive method requiring a relatively high initial capital investment. Current immobilising technologies ensure a satisfactory level of safety although they have limitations as discussed in Chapters 15–17. Furthermore, difficult legacy waste streams are known for which current technology is inadequate, so that new approaches must be developed. These comprise development of new waste-forms such as crystalline (mineral-like) and composite radionuclide hosts as well as of new immobilising technologies such as thermochemical and *in situ* methods. New approaches aim also to create geochemically stable materials in equilibrium with the disposal environment to ensure a safer nuclear waste disposal scenario.

Wastes may be difficult for a number of reasons. They may be highly radioactive emitting high-energy radiation, have very long half-lives, be highly mobile, easily assimilated and have a long biological half-life. Furthermore, many legacy wastes are ill-characterised. Elements which are inherently difficult to immobilise include Tc, halogens (^{36}Cl , ^{129}I) and ^{14}C . In the UK ^{99}Tc has, for many years, been discharged into the sea but a new process using tetraphenylphosphonium bromide separates the ^{99}Tc from liquid wastes as pertechnetate, TcO_4^- . No waste-form is currently available for the TcO_4^- . Halogens are ubiquitous in nuclear wastes; e.g. chlorides arise from HCl dissolution of defence wastes, from use of HCl in decontamination operations during decommissioning and in molten salts used in electro-refining, a future alternative to the

current Purex technology and in the Generation IV Molten Salt Reactor. ^{129}I is a fission product in fuel with a 15.7 million year half-life. Both chlorine and iodine are not amenable to conventional vitrification and cementation routes as they have low solubility in vitreous waste-forms and are volatile at the processing temperatures (see Chapter 17) and halide anions are highly soluble in cement pore water. Furthermore, halide species are biologically active, with I being selectively absorbed by the thyroid gland, and they are highly soluble and mobile in ground water. Massive volumes of irradiated graphite have been accumulated worldwide (Section 11.2). Significant issues related to this waste are stored Wigner energy and potential flammability and instability. Irradiated waste graphite contains various radioactive isotopes, the most problematic being ^{14}C , ^{36}Cl and ^3H . There is presently no internationally accepted method for dealing with irradiated graphite waste although the two main options (packaging and direct disposal or incineration and ash immobilisation) were mentioned in Section 11.2. Finally, wastes may have a difficult morphology, e.g. as ill-defined corrosion product sludges [such as $\text{Mg}(\text{OH})_2$] or as highly active flocs (such as iron hydroxide) used to scavenge for actinides. They may have elements of both of these problems as with ^{14}C in large volume blocks of graphite or crushed powders. Many of the legacy, and potential future, wastes from proposed Generation IV reactors have no satisfactory current immobilisation scheme. In some cases schemes have been proposed for separating and concentrating the difficult species but suitable hosts for them once separated are still needed.

18.2. Crystalline Waste-Forms

Thermodynamically stable crystalline materials sometimes have high natural radionuclide contents, which are retained for millions of years. Many durable crystals have a high isomorphic capacity for incorporation of elements including radionuclides from nuclear waste. The basic idea is to use as immobilising waste-forms those durable minerals that have been preserved in natural conditions for geological times, so-called natural analogues. Some potential host minerals are given in Table 18.1 with data on radionuclides that can most efficiently be immobilised, radiation durability and characteristic normalised leaching rates (NR). The radiation durability is given in dpa – number of displacements per atom caused by the irradiation.

The mechanisms by which radionuclides are accommodated vary with species and crystal type but include direct substitution of isovalent species on particular lattice sites, alter-valent substitution facilitated by charge compensation on a nearby site, insertion into open channels within the crystal structure and

Table 18.1: Some potential nuclear waste host minerals, where Ln = lanthanides and An = actinides

Mineral/Ceramic	Elements from waste	Radiation durability (dpa)	Typical NR (g/cm ² day)	Structure
Monazite: (Ce, La, Nd, Th)PO ₄	Ln, An	>10	10 ⁻⁷	Monoclinic, <i>P21/n</i>
Zircon: ZrSiO ₄	Ln, An, Nb, Ta, Hf	0.3–0.4	4 × 10 ⁻⁷	Tetragonal <i>I4/amd</i>
Zirconolite: CaZrTi ₂ O ₇	Ln, An, Nb, Sc, Y, Hf	0.2–0.3	4.5 × 10 ⁻⁶	Monoclinic
Pyrochlore: AB ₂ X ₇ Y (A = Ca, Na, REE, An, Zr, Ti; B = Ti, Zr, Th, U, Nb, Ta, Sn, Al, Fe; X = O, F; Y = O, OH, F)	Na, Y, Ln, An, Ti, Nb, Ta, W, Cl, I	0.3–0.4	1.5 × 10 ⁻⁶	Cubic, <i>Fd3m</i>
Zirconia: ZrO ₂	Zr, Ln, An	>10		Several polymorphs; the mineral form is baddeleyite, monoclinic <i>P2/c</i>
Garnet: A ^{VIII} ₃ B ^{VI} ₂ [SiO ₄] ₃	Cr, Mn, Fe, Co, Ni	0.2		Cubic, <i>Ia3d</i>
Hollandite: AB ₈ O ₁₆ (A = Na, K, Rb, Cs, Sr, Ba, Pb; B = Co, Ni, Fe, Cr, Si, Ti, Mn)	Na, K, Rb, Cs, Sr, Ba, Ra, Ti, Cr, Mn, Fe, Co, Ni, Mo, Pb, Bi, Ag		10 ⁻⁶	Monoclinic, <i>I4/m</i>
Perovskite: ABO ₃ CaTiO ₃	Nb, Fe, Ta, Ln, An, Na, Sr, Y	0.4–1	2.5 × 10 ⁻⁸	Cubic, <i>Im3</i>
Apatite: Me ₁₀ (XO ₄) ₆ Y ₂	Na, Sr, Ln, An, S, I, Y, Mn	0.24	2 × 10 ⁻⁷	
Britholite: Ca ₂ Ln ₈ (SiO ₄) ₆ O ₂		0.3–0.4	2.5 × 10 ⁻⁶	
Murataite: (Y, Na) ₆ (Zn, Fe) ₅ Ti ₁₂ O ₂₉ (O, F) ₁₀ F ₄	Na, Ca, Al, Ti, Mn, Fe, Ni, Ln, Ce, Nd, An	0.2	10 ⁻⁹	Cubic, <i>F4̄3m</i>
NZP: NaZr ₂ (PO ₄) ₃	Na, K, Rb, Cs, Sr, Ln, An, Fe			
TiC-Al ₂ O ₃ composite	¹⁴ C		10 ⁻⁶	Cubic, <i>Fm3m</i> Rhombohedral, <i>R3̄c</i>

incorporation by generation of planar defects such as twins and crystallographic shear planes.

Monazite is a phosphate mineral $[(\text{Ce}, \text{La}, \text{Nd}, \text{Th})\text{PO}_4]$, the major commercial source of Ce. Occurring as small heavy crystals in granitic and gneissic rocks and their detritus (called monazite sands), monazite contains up to 27 wt.% of U and Th oxides. Monazite deposits from Brazil are over two billion years old and still retain radionuclides and remain stable. Synthetic lanthanide phosphates exist in several crystalline forms, including hexagonal, monoclinic and tetragonal varieties.

Zircon is a silicate mineral (ZrSiO_4) , the principal source of Zr. Zircon is widespread as an accessory mineral in acid igneous rocks; it also occurs in metamorphic rocks and in beach sands and is a common heavy mineral in sedimentary rocks. Zircon contains U and Th oxides in concentrations up to 20 wt.%. Zircon is commonly employed in the dating of mineral samples (from the U/Pb ratio present) and consequently its mineralogy has been studied intensively. It has been noted that Pu can substitute directly for Zr and the pure end-compound PuSiO_4 has been successfully synthesised. Several processing operations have been demonstrated on a laboratory scale for the preparation of zircon and Pu-substituted zircon powders, including via sol-gel and hydroxide precipitation. Ceramics have been made by cold pressing and sintering or hot pressing (Fig. 18.1).

Hollandite has the general formula $\sim \text{A}_2\text{B}_8\text{O}_{16}$ where A is a monovalent or divalent atom, and B has a valence between 2 and 5. A range of natural

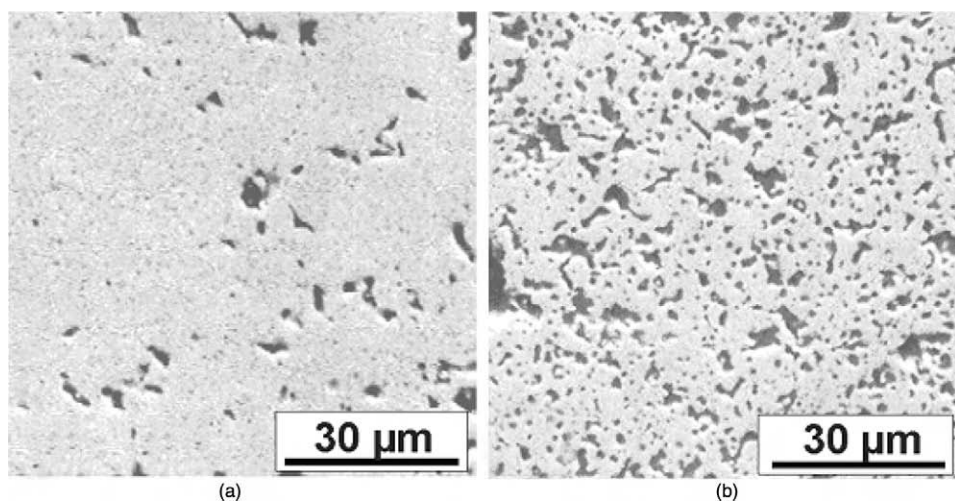


Figure 18.1: Backscattered electron SEM images of ceramics based on (a) zircon, $(\text{Zr}, \text{Pu})\text{SiO}_4$, doped with 6.1 wt.% Pu; (b) cubic zirconia, $(\text{Zr}, \text{Gd}, \text{Pu})\text{O}_2$, doped with 10.3 wt.% Pu. Courtesy B.E. Burakov, Radium Institute.

minerals crystallise with this structure. The difference between them lies in the chemical elements substituting for Ti on the B-site – e.g. hollandite (Mn totally substituted for Ti), priderite (Fe^{3+}), henrymeyerite (Fe^{2+}), redledgeite (Cr) and ankangite (Cr, V). Cs ions can fit into the channels parallel to the *c*-axis formed by octahedral chains $[(\text{Ti}, \text{Al})\text{O}_6]$ as occurs in $\text{BaCs}_{0.1}\text{Al}_{1.5}\text{Ti}_{6.5}\text{O}_{16}$. In this structure the A-site is occupied by Ba^{2+} and Cs^+ , and the B-site by Al^{3+} , Ti^{3+} , and Ti^{4+} . Hollandite powder can be synthesised by an alkoxide process and the ceramics densified by pressure-assisted sintering at 1200°C .

Zirconolite has the generic formulation $\text{CaZr}_x\text{Ti}_{(3-x)}\text{O}_7$ where $0.8 < x < 1.35$. Natural zirconolite contains up to 20 wt.% of ThO_2 and up to 14% UO_2 . Zirconolite is able to accommodate lanthanides, Hf and trivalent and tetravalent actinides by insertion into the Ca and Zr sites (several tens of per cent by mass of oxide). Charge compensation occurs by substituting trivalent cations (Al^{3+} , Ti^{3+}) in the Ti^{4+} site. Zirconolite is the main phase of Synroc (Section 18.3). Two synthetic processes have been developed for zirconolite. The first is a ceramiation process in which powders are synthesised by the alkoxide process and then air sintered at 1400°C . The second is an oxide melting process using high temperatures ($1700\text{--}1800^\circ\text{C}$) in a cold crucible.

Apatites comprise a family of chemical compounds with the formula $\text{Me}_{10}(\text{XO}_4)_6\text{Y}_2$, where Me is a divalent cation (Ca^{2+} , Pb^{2+} , Ba^{2+}), XO_4 is a trivalent anion (PO_4 , VO_4 , SiO_4), and Y is a monovalent anion (F^- , Cl^- , OH^- , Br^-). Apatites crystallise in the hexagonal system. Naturally occurring apatites, generally $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}, \text{OH}, \text{Cl})_2$, have high chemical, radiation and thermal durability. Iodine-apatite $\text{Pb}_{10}(\text{VO}_4)_{4.8}(\text{PO}_4)_{1.2}\text{I}_2$ is synthesised through solid-state reaction of PbI_2 and $\text{Pb}_3(\text{VO}_4)_{1.6}(\text{PO}_4)_{0.4}$. This iodine-rich core is then coated with a layer of $\text{Pb}_3(\text{VO}_4)_{1.6}(\text{PO}_4)_{0.4}$ during a sintering stage at a pressure of 25 MPa and a temperature of 700°C , to form a composite ceramic. Cs^+ has a strong affinity for fully phosphated apatites such as $\text{Ca}_8\text{NdCs}(\text{PO}_4)_6\text{F}_2$, and much less affinity for britholites (silicate apatite) with a nominal formula of $\text{Ca}_7\text{Nd}_2\text{Cs}(\text{PO}_4)_5(\text{SiO}_4)\text{F}_2$.

Britholite has been found in the vicinity of natural fission reactors, dating back more than one thousand million years, on the Oklo site in Gabon. This site has been exposed to intense internal irradiation doses due to alpha self-irradiation ($> 3 \times 10^{16} \text{cm}^{-3}$) and intense external doses induced by fission neutrons ($> 10^{21} \text{neutrons/cm}^2$). Britholite monosilicate $\text{Ca}_9\text{Nd}(\text{PO}_4)_5(\text{SiO}_4)\text{F}_2$, where Nd^{3+} simulates the presence of the minor actinides Am^{3+} and Cm^{3+} , is synthesised by solid–solid reaction and sintering in air at 1400°C .

NZP is a single phase sodium zirconium phosphate with the composition $\text{NaZr}_2(\text{PO}_4)_3$. The structure of NZP contains three types of crystallographic sites and exhibits great compositional flexibility. Waste loadings up to 20 wt.% have been incorporated into this structure using sol–gel and sintering techniques while maintaining a single phase material. For 20% waste loadings a

two-phase material is formed, with monazite as the second phase. Substitution of Ti for Zr yields NTP, which under suitable conditions can accommodate up to 60% waste loadings.

Pyrochlores are abundant in nature and over 500 synthetic compositions have been made, including zirconates, titanates and niobates. Pyrochlores occur in Synroc and have been examined as hosts for military Pu. Although many pyrochlore compositions, such as $\text{Gd}_2\text{Ti}_2\text{O}_7$ undergo a radiation-induced transformation from crystalline to amorphous state, radiation-resistant compositions e.g. $\text{Gd}_2\text{Zr}_2\text{O}_7$ and $\text{Er}_2\text{Zr}_2\text{O}_7$ have been discovered.

18.3. Polyphase Crystalline Waste-Forms: Synroc

Single-phase minerals can host a large number of nuclides and can be used as a monophasic waste-form. However, monophase ceramics are difficult to fabricate and polyphase compositions are more common. The composition of the polyphase ceramic is tailored to that of the waste composition to achieve complete and reliable immobilisation of the waste constituents. The most famous polyphase ceramic for nuclear waste immobilisation is Synroc. Synroc is short for “Synthetic Rock”, invented in 1978 by T. Ringwood of the Australian National University. Synroc is made of geochemically stable natural titanate minerals, which have immobilised uranium and thorium for billions of years. U/Th-containing natural analogues of the basic constituent of Synroc – zirconolites from Sri Lanka dating back 550 million years while amorphised, have nonetheless withstood the alteration processes of their natural environment.

Synroc is made via a chemical processing route involving Ti and Zr alkoxide hydrolysis in the presence of NaOH to form a sodium titanate/zirconate powder, which acts as a cation exchanger for Al, Ba and Ca waste nitrate solutions. This is dried and calcined under reducing conditions and hot pressed at 1100–1170°C, adding 2 wt.% Ti to lower the mobility of volatiles and keep Mo metallic thereby avoiding formation of water-soluble molybdates. Synroc can also be produced via an oxide-melting route in cold crucible melters (Section 17.13). Figure 18.2 illustrates the multi-phase microstructure of Synroc manufactured by melting.

Synroc can take various forms depending on its specific use and can be tailored to immobilise particular components in the HLW. The original form, *Synroc-C*, was intended mainly for the immobilisation of liquid HLW arising from the reprocessing of light water reactor fuel. The main minerals in Synroc-C are hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$), zirconolite ($\text{CaZrTi}_2\text{O}_7$) and perovskite (CaTiO_3). Zirconolite and perovskite are the major hosts for long-lived actinides such as plutonium (Pu), although perovskite principally hosts strontium (Sr) and barium (Ba). Hollandite principally immobilises caesium (Cs), along

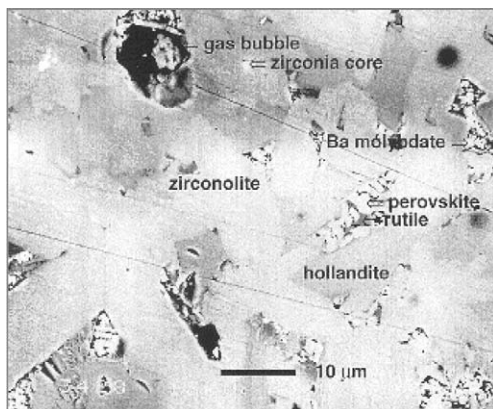


Figure 18.2: Microstructure of cold crucible melted Synroc-C containing 20 wt.% of HLW calcine: Courtesy S.V. Stefanovsky, SIA RADON.

with potassium (K), rubidium (Rb) and barium. Synroc-C can hold up to 30 wt.% HLW. *Synroc-D* contains nepheline – $(\text{Na}, \text{K})\text{AlSi}_3\text{O}_8$ instead of hollandite as host for Cs, Rb and Ba. *Synroc-F* is enriched in pyrochlores – $(\text{Ca}, \text{Gd}, \text{U}, \text{Pu}, \text{Hf})_2\text{Ti}_2\text{O}_7$, and has been developed for the disposal of un-reprocessed spent fuel from light water and CANDU reactors. *Zirconolite-rich Synroc* has been developed for immobilisation of excess plutonium. Zirconolite variants containing hollandite and rutile were produced either by sintering in air at 1375°C or by hot isostatic pressing of calcines at 1280°C and 150 MPa. Pyrochlore-rich Synroc was found to be more efficient for immobilising uranium contained in the waste. Pyrochlore is similar to zirconolite and can incorporate up to 50% by mass of PuO_2 and/or UO_2 .

A pilot plant to manufacture Synroc with non-radioactive simulants operates at Lucas Heights in Australia. In 1997 Synroc was tested with active HLW using technology developed jointly by ANSTO (Australian Nuclear Science and Technology Organisation), Australia and the Argonne National Laboratory, USA. Table 18.2 shows the durability parameters of HLW waste-forms.

18.4. Polyphase Waste-Forms: Composites

Two possible methods of immobilisation of radionuclides in crystalline matrices are: by incorporation into the crystalline structure of mineral phases as described in Section 18.2 (Fig. 18.3, left hand side) and by encapsulation within non-radioactive phases (Fig. 18.3, right hand side).

Table 18.2: Comparison of Synroc matrix parameters with nuclear waste glasses

Parameter	Phosphate glass	Borosilicate glass	Synroc	
			Sintered	Melted
Density (g/cm ³)	2.6	2.6	4.35	3.8–4.4
Thermal conductivity (W/mK)	0.74	1.1	2.1	1.7
Thermal expansion coefficient (×10 ⁻⁶)(K ⁻¹)	1.5	8.1	10.5	8–10
Heat capacity (J/gK)	0.96	0.9	0.55	0.5–0.7
Compressive strength (MPa)	10	80	547	500–600
Micro-hardness (GPa)		7.2	8.4	8.0–8.5
NR (g/cm ² day)				
Cs	$1.1 \times 10^{-6*}$	10^{-4}	$<3 \times 10^{-6}$	5×10^{-5}
Sr	$4 \times 10^{-7*}$	7×10^{-6}	6.5×10^{-7}	10^{-6}
An		10^{-5}	10^{-7} – 10^{-8}	10^{-7} – 10^{-8}

* At room temperature.

Crystalline phases can form a ceramic waste-form or they can be encapsulated into a vitreous matrix forming a glass composite material or GCM as described in Section 17.11. This option is currently being considered in many countries including the USA, France, Australia and Russia. The processing, compositions, phase assemblages and microstructures of GCMs (including glass ceramics, see section 18.5) may be tailored to achieve the necessary parameters. GCMs may be used to immobilise long-lived radionuclides (such as actinides, An) by incorporating them into the more durable crystalline phases, whereas the short-lived radionuclides may be accommodated in the less durable vitreous phase. An example of such a glass composite is the so-called Synroc-glass, which is a GCM with Synroc crystalline phases in a vitreous matrix.

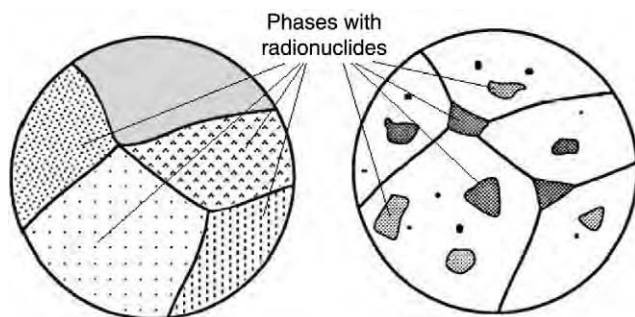


Figure 18.3: Schematic of radionuclide immobilisation by crystalline hosts.

18.5. New Technological Approaches

A number of technological processes have been developed to produce crystalline and composite waste immobilising materials. Some of them have been used with real waste streams, some have been tested in laboratory conditions although most have been limited to experiments with simulants. Interesting new technological methods of synthesis are: melting, sintering and thermochemical techniques.

New melting techniques follow the traditional vitrification approach but extend its capabilities to new or difficult waste streams. Melting (Table 18.3) can be used to synthesise minerals that can be formed from melts, e.g. zirconolite, pyrochlore, garnet, perovskite, zirconia (cubic stabilised) and murataite. Zircon, however, cannot be obtained through direct melting of batch mixtures. A novel melting route comprises preparation of a batch of waste and mineral-forming additives followed by melting in a cold crucible melter (Section 17.13).

Melting is also used to produce GCM (Section 17.11). Glass ceramics are produced by melting suitable parent glasses and subsequent controlled crystallisation. Glass ceramics containing basalt-like crystalline phases are obtained by controlled cooling of basaltic rocks or blast furnace slag melts. GCMs for immobilising refractory components of nuclear waste are produced by dispersing small refractory particles into the glass melt. Yellow phase may be immobilised by emulsification into glass melt prior to pouring from the melter into steel canisters.

Simple ceramiation comprises preliminary preparation of precursors sometimes using chemical routes such as sol-gel. The powders are then cold pressed followed by sintering of compacted precursors. Sintering may also be done using hot uniaxial or isostatic pressing. The sintering mechanisms usually involve generating small amounts of liquid (liquid phase sintering) especially when waste is incorporated. A concern is that this liquid will cool to a less durable grain boundary glassy phase. Figure 18.4 illustrates the sintering process used to produce Synroc at ANSTO.

Some generic data on sintering processes utilised to produce immobilising minerals are summarised in Table 18.4.

In situ sintering of waste-forms in a very deep repository may be used to create geochemically stable materials in equilibrium with the disposal

Table 18.3: Melting temperatures for some host ceramics

Mineral	Zirconolite	Murataite	Zirconia	Synroc B and C
Temperature (°C)	1530	1400–1500	2500	1400–1550

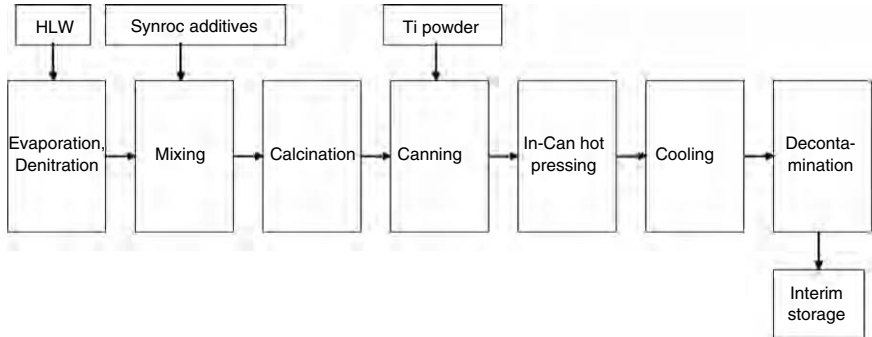


Figure 18.4: Schematic of Synroc production.

Table 18.4: Sintering parameters for some host ceramics

Mineral	Monazite	Zircon	Zirconolite	Zirconia	Apatite	Synroc
Temperature (°C)	900–1200	1450	1300–1800	1400–1600	700	1100–1300
Pressure (MPa)	29		150	80	25	14–21

environment ensuring a higher degree of safety compared to existing approaches. Moreover, *in situ* immobilisation significantly diminishes the costs and hazards associated with predisposal immobilisation. A schematic of this approach is illustrated in Fig. 18.5.

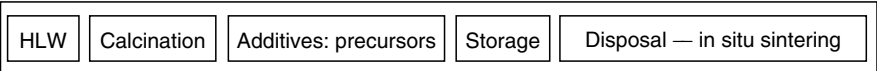


Figure 18.5: Schematic of *in situ* sintering approach.

Mixtures of waste and matrix-forming precursors may be placed in a very deep underground repository where the lithostatic pressure P acting on waste packages is proportional to disposal depth H and average density of overlying deposits ρ :

$$P = \rho g H \tag{18.1}$$

Pressures above 25–30 MPa are typical at $H = 1$ km. Once in place, the mixtures are exposed to continuous high pressures and temperatures caused by the decay of radionuclides and the natural high temperature of the rocks at this depth. These contribute to viscous and diffusion sintering process resulting in consolidated and durable waste-forms. *In situ* sintering is similar to the natural

mechanisms of formation of metamorphic rocks but occurs at relatively shorter times due to the self-heating of HLW and resulting higher temperatures.

Low temperature ceramics lie at the boundary between room temperature cements (Chapter 15) and the high temperature ceramics discussed here. In particular a range of CSA (calcium sulpho aluminate) cements, geopolymers (alkali activated aluminosilicates) and chemically-bonded phosphate ceramics offer the potential for immobilising ILW and possibly HLW in matrices made at low (and thus inexpensive) temperatures. VRFs are likely to be low so these systems, if successfully developed, are likely to find use only for some difficult and legacy wastes for which immobilising matrices are not currently available.

Thermochemical methods include self-sustaining high-temperature synthesis (SHS) and self-sustaining immobilisation (SSI). In SHS, precursors are prepared to participate in self-sustaining exothermic reactions. Figure 18.6 illustrates SHS of corundum-carbide ($\text{Al}_2\text{O}_3\text{-TiC}$) ceramics to immobilise long-lived ^{14}C from irradiated reactor graphite. SHS requires proper control of precursor concentrations within limited ranges and typically produces porous ceramics.

SSI uses self-sustaining exothermic reactions provided by powder metal fuels (PMF) and radionuclide confining additives (RCA). SSI is similar to SHS, but it uses additional RCA to immobilise waste contaminants. RCA are selected for their affinity to waste radionuclides, e.g. natural zircon can be used to immobilise uranium and plutonium. PMF provide sufficiently high temperatures to facilitate the chemical reactions that bind radionuclides in the final product, which can be a mineral-like material or GCM. Moreover, the SSI occurs

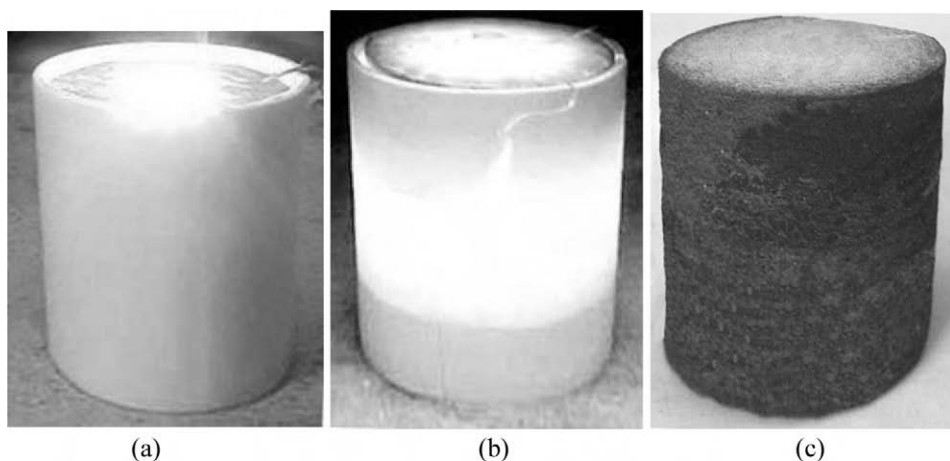


Figure 18.6: SHS (self-sustaining high-temperature synthesis) of corundum-carbide ceramic immobilising long-lived ^{14}C from irradiated graphite:
(a) SHS ignition, (b) SHS reaction and (c) final product.

through formation of melts and produces monolith waste-forms. SSI chemical reactions can be described by



SSI uses exothermic reactions to obtain high temperatures, and RCA to retain radionuclides in the resulting waste-form. Both SHS and SSI use the energy released during exothermic chemical reactions, which makes them similar to the well-known thermite reaction. However, chemical reactions in SHS and SSI are carried out within carefully selected, stable and controlled regimes. These are determined using thermodynamic modelling and simulant trials. SSI is controlled by the parameters of the initial mixture (waste + PMF + RCA). Unlike in thermite compositions, SSI compositions ensure efficient immobilisation of hazardous components into the final waste-form. In addition during the SSI the release of contaminants due to volatilisation or through emission of contaminated aerosols is minimised. Figure 18.7a shows a GCM block immobilising ash residues after incineration of solid radioactive waste. Advantages and drawbacks of these novel synthesis methods are summarised in Table 18.5.

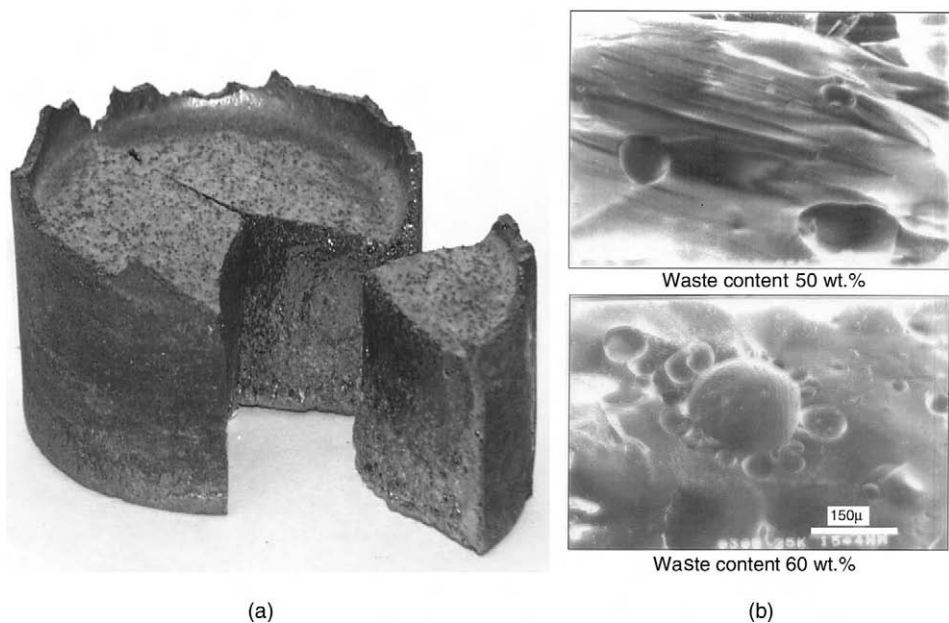


Figure 18.7: GCM obtained via self-sustaining exothermic reactions in a mixture of incineration ash with PMF and glass-forming RCA: (a) a view of GCM block and (b) GCM microstructure with 50 wt% waste (top) and 60 wt% (bottom) added.

Table 18.5: Comparison of novel synthesis methods

Synthesis method	Advantages	Drawbacks
Melting		
Ceramics	Simple, pre-treatment not required, high capacity	Often coarse inhomogeneous final product; high temperatures
GCM	Simple, pre-treatment not required, high waste loading, high capacity	Additional mixing tool in the melter
Glass ceramics	Simple, pre-treatment not required	Additional heat-treatment procedure
Ceramication	High quality product	Powders; complex pre-treatment, e.g. sol-gel; good homogenisation required; potentially glassy secondary phases
Thermo-chemical		
SSI	Autonomous process; power supply and melters not required	Powders; calcination required
SHS	Autonomous process; power supply and melters not required	Powders, pre-treatment required, e.g. calcination; poor quality of final product; composition limitations

18.6. Metal Matrix Immobilisation

Metal matrix immobilisation was invented in the 1970s at Mol, Belgium as part of the Pamela HLW vitrification programme. Vitromet is a composite material made of beads of nuclear waste glass dispersed in a metallic host matrix made of lead. It has superior retention properties for radionuclides and an excellent heat transfer by the metallic host from the decaying radionuclides. The slow corrosion rate of lead (less than 1 μm per year) ensures a very low radionuclide leaching rate as well as an absence of environmental contamination. The IAEA recommends metal matrix immobilisation for spent sealed radioactive sources (SRS), as other immobilising materials including glasses are not able to withstand the enhanced radiation doses and heat generation from such highly radioactive sources. In addition, metal matrix immobilisation is an excellent method of isolating long-lived SRS for safe storage and disposal. Metal matrix

immobilisation technology was deployed in the mid-1980s to ensure safe SRS disposal in borehole-type repositories in the former USSR and studied to immobilise damaged SNF rods from Russian channel-type nuclear reactors (RBMK). Lead is a suitable immobilising matrix due to its high radiation stability, ability to withstand deformation without loss of integrity, high corrosion resistance, high heat conductivity, effective filling of free space between sources and compatibility with other construction materials. Lead also does not contaminate ground water due to its high passivity and slow corrosion. Figure 18.8 shows waste-forms produced via metal matrix immobilisation. SRS immobilisation involves two steps. In the first stage a large volume of molten metal is poured over the sources in an underground repository vessel. Owing to their lower density the sources rise to the surface of the melt, and once it solidifies they are fixed in the metal. In the second stage of the technological process a thin layer of melt is poured on the surface of the metal block.

Mobile facilities may be used to immobilise SRS directly in underground vessels in repositories. Matrix metal melts are prepared outside of the repository in a special technological unit so that the duration of thermal impact on spent SRS is minimised. The prepared melt is fed into the repository by a flexible heat-resistant hose lowered through the SRS loading channel of the borehole. The existing biological protection of the repository functions as an ionising radiation shield, ensuring an enhanced degree of operational safety. Figure 18.9 illustrates the metal matrix immobilisation technique.

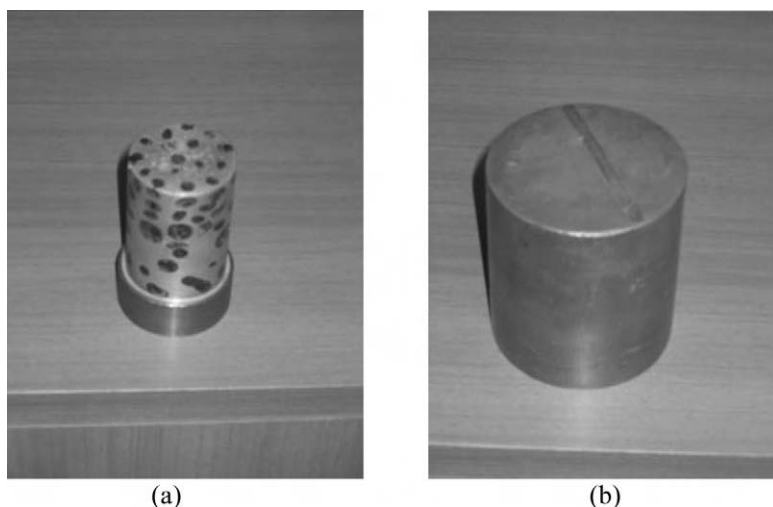


Figure 18.8: Metallic waste-forms: (a) a simulant sample of HLW immobilising vitromet, (b) a lead block of simulant SRS. Authors' photo.

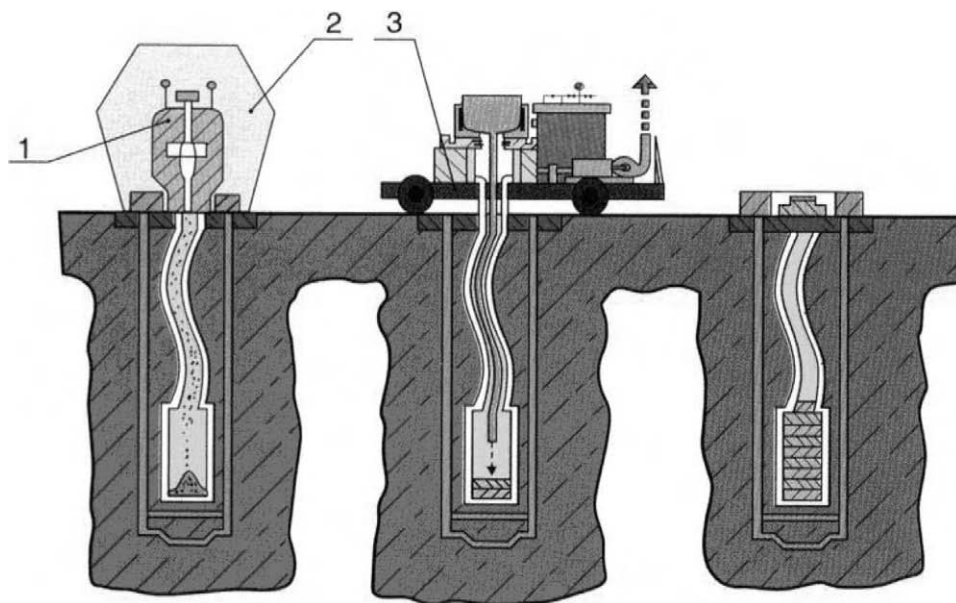


Figure 18.9: Schematic of *in situ* metal matrix immobilisation of SRS.
1 – transport container, 2 – gas purification unit, 3 – encapsulating unit.

Metal matrix immobilisation technology has been used since 1986 to immobilise spent SRS in Russia and this technique is currently being employed in other countries.

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Chapter 19

Nuclear Waste Disposal

19.1. Disposal/Storage Concepts

Waste disposal is the final step of waste management and ideally comprises placing radioactive waste in a dedicated disposal facility although discharging of effluents into the environment within permitted limits is also a disposal option. The first “disposal” of radioactive waste was carried out in 1944 at Oak Ridge, Tennessee, USA when a site was selected for disposal of contaminated materials not intended for subsequent use. This disposal facility (capacity 6700 m³) was a simple earthen trench located on the Oak Ridge site and filled with unconditioned waste. Similar approaches were adopted by other nuclear facilities and waste generators during the early stages of nuclear power’s development in many countries. Concepts for radioactive waste disposal have however developed considerably since that time and great consideration is now given to the necessary retention times and retention capacities for different types of waste resulting in much improved repositories and planned disposal facilities.

19.2. Retention Times

All types of radioactive waste need to be carefully managed to keep the public safe, protect the environment and ensure security from accidental or deliberate intrusion. Disposal of radioactive wastes in a disposal facility is intended to isolate the waste both from human activity and from natural dynamic processes. As was mentioned in Chapter 12 it is important to distinguish between disposal (permanent and irretrievable removal of waste) and storage (temporary residence with waste retrievability). Unfortunately, the nuclear industry has got into the habit of talking about disposal in a repository. This is further confused by many *de facto* plans for repositories to become permanent disposal facilities. Whatever the terminology, eventual release of radionuclides from a repository

or disposal facility must be at such low concentrations that they do not pose a hazard to human health and the natural environment.

The necessary time t_{ret} for the isolated retention of nuclear waste (disposal or storage) is calculated based on the requirement for an absence of potential radiotoxicity after t_{ret} : $I_p(t > t_{\text{ret}}) < 1$. The index of potential radiotoxicity of nuclear waste is the sum over all radionuclides of waste (Section 3.3): $I_p(t) = \sum_i C_i(0) \exp(-\lambda_i t) / \text{MPC}_i$, where $C_i(0)$ is the initial concentration of the i th radionuclide, MPC_i is the maximum permitted concentration or the intervention level IL_i and λ_i is the decay constant. After t_{ret} the nuclear waste becomes “safe”, as the concentration of any radionuclide is below the maximum permitted. From this equation an assessment of retention time t_{ret} (year) can be found:

$$t_{\text{ret}} = \max_i 1.44 T_{1/2,i} \ln \left(\frac{C_{0,i}}{C_{\text{ex},i}} \right) \quad (19.1)$$

where $T_{1/2,i}$ are the half-lives of waste radionuclides, $C_{0,i}$ (Bq/g) are the initial concentrations of radionuclides in the waste and $C_{\text{ex},i}$ (Bq/g) are their exemption levels. MPC_i or IL_i have been replaced by the exemption levels in this assessment as the waste is not considered to be radioactive when the radionuclide content becomes lower than exemption levels.

19.3. Multibarrier Concept

Repositories for the storage/disposal of radioactive waste generally rely on a multi-barrier system to isolate the waste from the biosphere (Fig. 12.4). This multi-barrier system typically comprises the natural geological barrier provided by the host rock and an engineered barrier system (EBS) illustrated in Fig. 19.1.

The EBS consists of a number of components such as the waste matrix, container or over-pack, buffer or backfill, repository walls and wall linings. The various barriers act in concert, initially to contain the radionuclides and then to limit their release to the accessible environment. The key functions of a geological repository are: (a) isolating waste from near-surface processes and human activities, (b) protecting the biosphere, (c) limiting release from the progressively degrading EBS and (d) dispersing and diluting the flux of long-lived radionuclides. The overall safety and acceptability of such a system is achieved through a sensible balance of these functions.

It is important to realise that for HLW all hierarchies or levels of immobilisation are significant from the atomic level incorporation of radionuclides in the glass or ceramic structure through the microstructure, packaging to the near-field repository environment including the EBS, to the far-field geosphere.

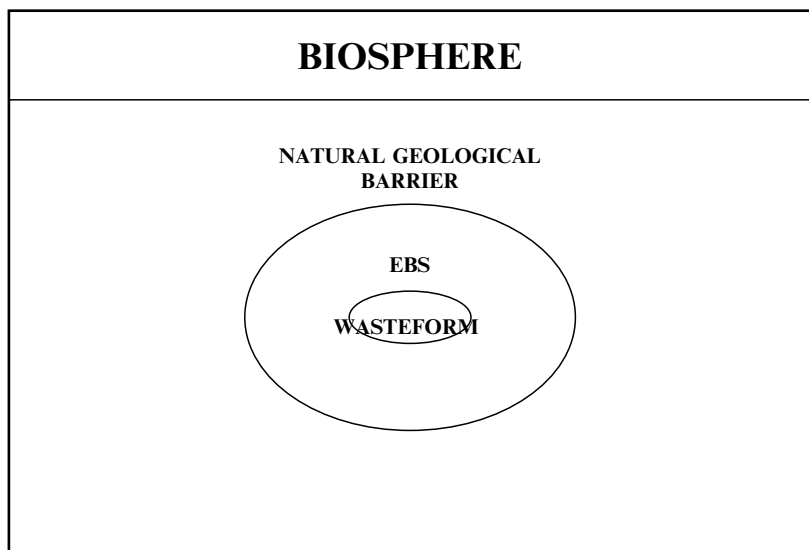


Figure 19.1: Schematic of two basic barriers of a multi-barrier system in a nuclear waste repository.

19.4. Disposal/Storage Options

The IAEA radioactive waste classification system (see Chapter 9) identifies potential disposal options for various waste categories based on their specific characteristics, with specific activity and longevity of radioactive components being the key characteristics. Near-surface disposal is considered a suitable option for disposal of short-lived LILW-containing radionuclides, which decay to insignificant radiation levels within a few decades or centuries. According to IAEA terminology, near-surface disposal can include different types of disposal facilities such as disposal units with or without different types of EBSs located on the surface, at depths of a few metres, as well as facilities where the waste is emplaced as deep as tens of metres in rock cavities and boreholes (Fig. 19.2).

The main contaminant of short-lived LILW, ^{137}Cs , has $C_{\text{ex}} = 10 \text{ Bq/g}$ (see Table 7.1) while the highest possible C_0 for LILW is 10^7 Bq/g giving $t_{\text{ret}} \sim 600$ years. Moreover, at typical concentrations of ^{137}Cs in the LILW $C_0 = 3.7 \times 10^3 \text{ Bq/g}$ (e.g. 10^{-4} Ci/kg), so the retention time becomes ~ 250 years. Thus the retention (storage – disposal) time of short-lived LILW ranges from tens to hundreds of years. For such time frames the evolution of the EBS in near-surface conditions can be assessed with a high degree of confidence. LILW, which contains limited concentrations of long-lived radionuclides, may also be disposed of in near-surface facilities. Figure 19.3 shows the UK's Drigg

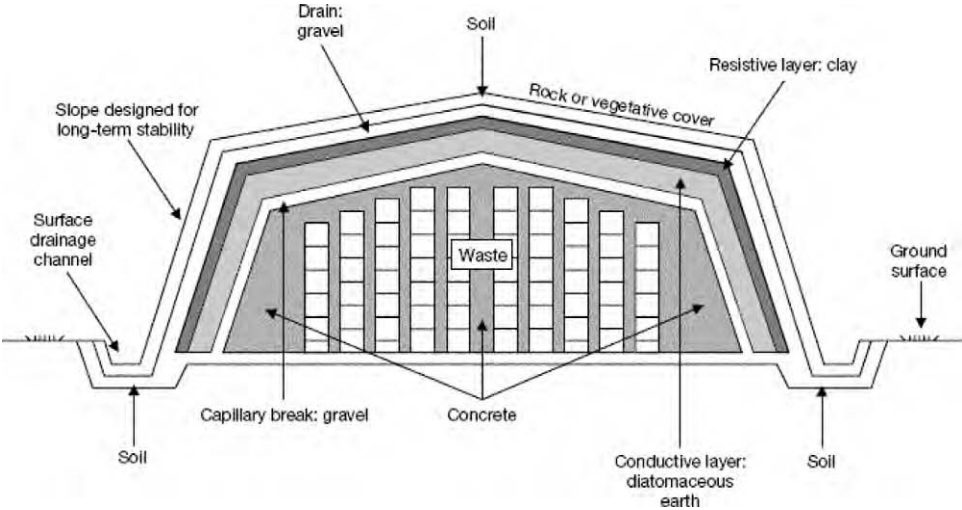


Figure 19.2: Schematic of a surface repository.



Figure 19.3: The UK's Drigg near-surface site for disposal of LLW.
Picture courtesy of BNFL.

LLW facility, which now contains hundreds of containers of LLW of the sort illustrated in Fig. 15.4 in addition to older trenches where waste was directly buried. This will eventually be covered with soil and vegetation as illustrated in Fig. 19.2.

Geological disposal/storage is the most likely option for HLW, SNF, SRS and long-lived LILW. The three main concepts of geological disposal are wet, dry and very deep disposal. The wet option is a mined and engineered repository located at a depth of about 500 m so that eventual water ingress and saturation is inevitable. Various types of host rock being considered are governed largely by the local geology including hard rock (e.g. granite as in the Swedish KBS-3 concept, Fig. 19.4) and soft rocks (e.g. shales in France and clay in Belgium).

The dry mined and engineered repository concept is favoured in the USA including high and dry (Yucca Mountain, Nevada) and shallow and dry (the Waste Isolation Pilot Plant [WIPP] located in salt in Carlsbad, New Mexico, Fig. 19.5).

Another concept is that of very deep (permanent) disposal. In this concept the waste is located at depths of 3 km or more and as such any transport of radionuclides through the geosphere is extremely limited. Further, if located in suitable (granitic) rock the radiogenic heat from HLW can cause reaction with the surrounding rock and lead to creation of a sarcophagus or granite coffin, which seals the waste in for good (Fig. 19.6).

The retention time for HLW, SNF and SRS in such repositories/disposal facilities must be longer because of the much higher initial radionuclide concentration. In addition these wastes may contain significant amounts of radionuclides with longer half-lives $T_{1/2,i}$ and lower $C_{ex,i}$. For example, ^{237}Np has a half-life of 2.1×10^6 years and exemption level 1 Bq/g. Thus, ^{237}Np -containing waste must be kept isolated for millions of years. Such timescales are termed geological because they are characteristic of geological changes on the earth. Uncertainties in the environment and the evolution of the EBS under near-surface conditions become unacceptably high over geological times. Therefore for the HLW, SNF, SRS and long-lived waste, geological disposal is the only acceptable option. Table 19.1 summarises features and limitations of some of the available options.

Alternative disposal options, such as disposal in subduction zones along the boundaries of the earth's tectonic plates, in Antarctica/Greenland ice caps or in outer space, have been rejected on the basis of generic assessments. Geological disposal of waste packages in the clay-rich sediments underlying the ocean floor, despite the extremely promising results of international studies carried out in the 1980s, is presently not considered a realistic disposal option and is prohibited by the London Convention.

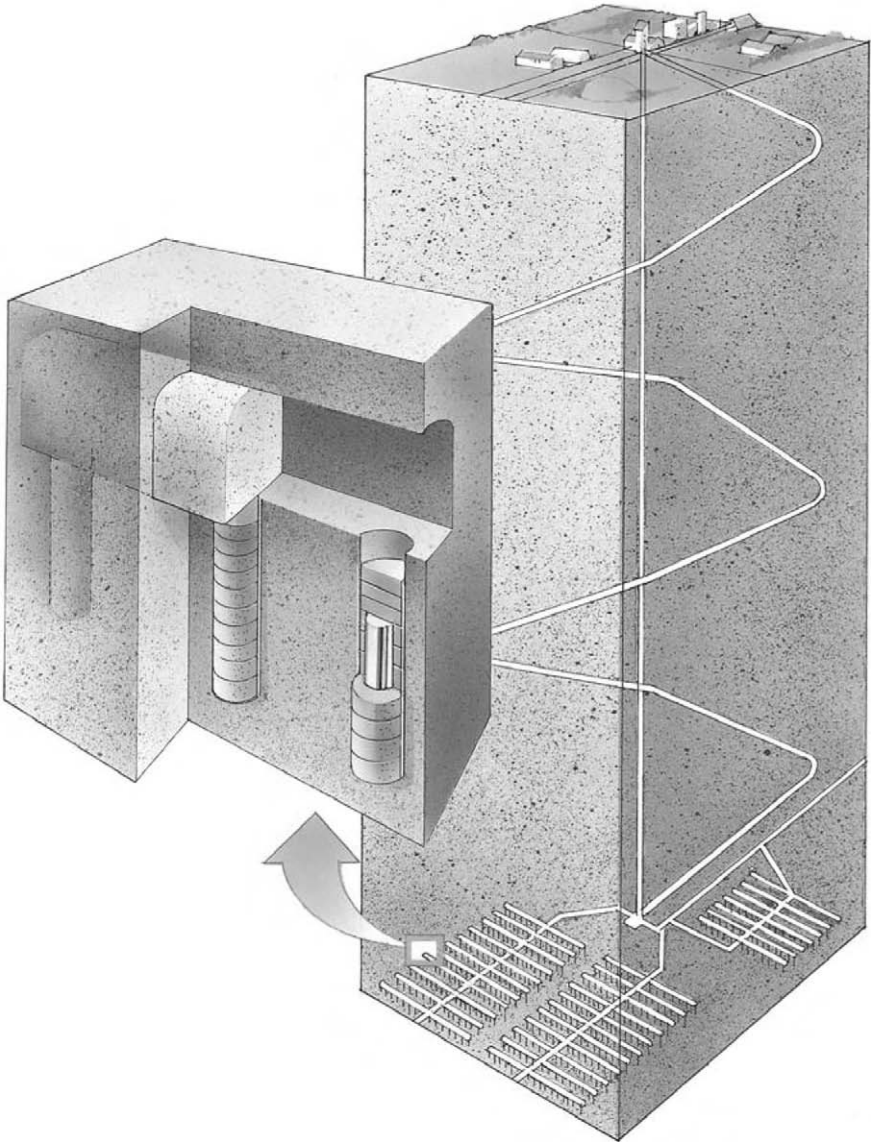


Figure 19.4: Schematic of a geological repository. Courtesy L. Werme, SKB, Sweden.

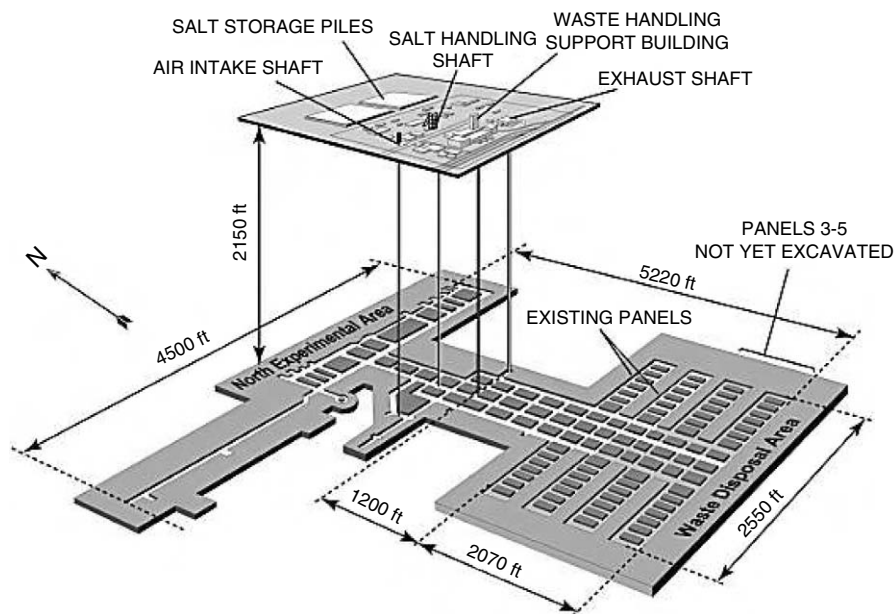


Figure 19.5: WIPP facility in Carlsbad, USA which has been operational since 1999.

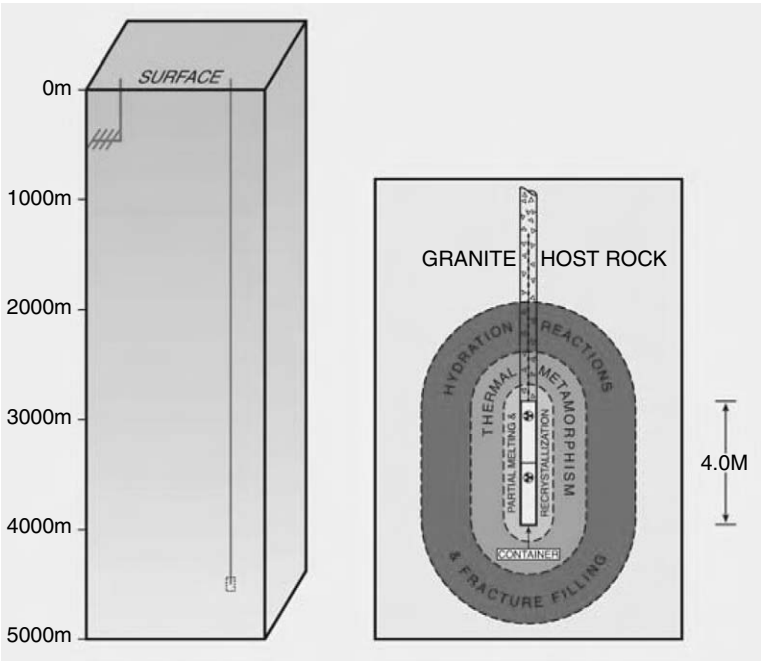


Figure 19.6: High-temperature very deep borehole disposal concept (courtesy of FGF Gibb, ISL, University of Sheffield).

Table 19.1: Features and limitations of some disposal/storage options

Disposal option	Features	Limitations
Near-surface without engineered barrier systems	Excavated trenches covered with a layer of soil. Simple and inexpensive.	Suitable only for short-lived and LLW. Erosion, intrusion and percolation of rainwater may affect performance.
Near-surface with EBS	Multi-barrier approach to enhance the safety of disposal. Suitable for most LILW. Long experience of operation.	Limited amount of long-lived waste. Erosion, intrusion and percolation of rainwater may affect performance.
Borehole and cavities at intermediate depth	The depth is adequate to eliminate the risk of erosion, intrusion and rain water percolation. Possibility to use existing disused cavities, mines. Simple and not expensive (boreholes).	Geological barriers are site dependent.
Geological disposal (including borehole)	Suitable for all waste categories. Enhanced confinement.	Site dependent geological formations. High cost. Complex technology involved. Extensive safety and performance analyses needed.

19.5. Role of the EBS

The role of the EBS in the disposal/storage system is to ensure complete containment of short-lived radionuclides. Hence in a near-surface repository the EBS is the most important barrier protecting the environment and humans. Waste-forms such as cement, bitumen and glass contain and significantly limit radionuclide release via leaching into ground water. Backfill material should not react with the (usually metal) waste container and must delay the radionuclide release into the environment. The container as well as preventing escape of radionuclides also facilitates waste handling. In a geological disposal/

storage system the combined natural and engineered barriers should contain the short-lived, highly active radionuclides completely, i.e. until their radioactivity has decayed to insignificant levels. This period can be of the order of a few hundred to a few thousand years. There is broad agreement that the majority of repository concepts cannot be relied on to contain completely all the long-lived radionuclides present in the wastes. Therefore geological repositories rely, in large part, on geologically stable formations. However, in several planned disposal/storage facilities (Finland, Japan, Sweden, Switzerland and the USA) the EBS plays a major role in providing the required performance for geological disposal/storage. Table 19.2 shows the major EBS components of several geological systems while Table 19.3 gives information on their functions and expected lifetimes.

Backfilling is used to fill the bulk of void spaces in a repository in order to limit water ingress and stabilise the disposal/storage system. Drainage backfilling with materials, which will transport water around the repository is also considered sensible. Some backfill materials are likely to contain deliberate additions of well distributed oxide or silicate particles designed to preferentially sorb and thus prevent release of any radionuclides which have escaped from the waste in future millennia.

19.6. Importance of Geology

The geological formation (host rock), in which the waste is placed, constitutes an important isolation barrier in a repository. Geological formations selected for siting nuclear waste repositories must contribute to the isolation of the waste and limit radionuclide release to minimise potential adverse effects on environment. Factors considered when selecting suitable formations include the:

- (a) Stability: the site is expected to possess a stable geology with overall predictability of site evolution.
- (b) Acceptable hydrogeology: limited contact between waste and ground water is preferred to minimise the mobilisation and transport of radionuclides.
- (c) Suitable geochemistry: characteristics minimising the potential for radionuclide migration, for example reducing conditions are preferred (see Table 3.2).
- (d) Low seismicity: the potential of earthquakes to affect the site must be considered.

For geological disposal of radioactive waste the geological formation may be the main and most reliable barrier. For example, the Morsleben (Germany) and WIPP (USA) repositories do not consider EBS to be important and rely instead

Table 19.2: Engineered barrier system (EBS) components of actual or planned geological disposal/storage facilities

Country	Waste	Matrix	Container	Backfill	Others
Belgium	HLW	Glass	Stainless steel	Clay, bentonite, quartz sand, graphite	Disposal tube, tunnel lining
	SNF	—	—		—
Canada	SNF		Carbon steel, copper	Bentonite, sand, clay, crashed rock	Tunnel and shaft seals
Czech Republic	ILW HLW SNF	Concrete Glass	Steel	Bentonite	Clay seals
Finland	SNF		Copper, iron	Bentonite, crushed host rock	Bentonite, concrete
France	ILW	Various	Stainless steel, concrete	Concrete lining	Bentonite, concrete
	HLW	Glass	Stainless steel, steel	Bentonite	Bentonite, concrete seals
	SNF		Stainless steel	Bentonite, disposal tube	Bentonite seals

Germany (Morsleben)	LILW, SRS	Not considered as EBS	Not considered as EBS	Salt concrete	Seals
Japan	HLW	Glass	Carbon steel	Bentonite, sand	Tunnel sealing and grout
Korea	SNF		Steel, copper	Bentonite, sand	
Russia	HLW	Glass	Stainless steel	Bentonite, concrete	Bentonite, concrete
Spain	SNF		Carbon steel	Bentonite	Concrete, bentonite
Sweden	SNF		Copper, iron	Bentonite	Tunnel backfill
Switzerland	HLW	Glass	Steel	Bentonite	
UK	LILW	Cement	Steel, concrete	Cement based	Seals
USA	TRU ¹ /WIPP ² SNF/YMP ³	Various	Steel Stainless steel, Ni- based alloy	MgO –	Concrete, shaft seals
	HLW/YMP	Glass	–		

¹Transuranic waste, ²Waste Isolation Pilot Plant, ³Yucca Mountain Plant.

Table 19.3: Functions of the matrix and container as EBS

Country	Matrix function	Container function
Belgium	10000 years resistance to leaching	Facilitate handling
Canada	10000 years radionuclide retention	100000 years containment
Czech Republic	10000 years radionuclide retention	500–1000 years containment
Finland	Slow rate of release	100000 years containment
France	100000 years resistance	Facilitate handling
Germany (Morsleben)	Not part of EBS	Not part of EBS
Japan	>10000 years containment and slow release	1000 years containment, creating reducing conditions
Korea	Resistance to leaching	1000 years containment
Spain	Slow rate of release	1000 years containment
Sweden (KBS-3)	Slow rate of release	1000000 isolation
Switzerland	150000 years low release	Initial period complete containment
UK/Nirex	300–500 years limit release	300–500 years physical integrity, limit release
USA	WIPP: not part of EBS; YMP: reduce release rate	WIPP: not part of EBS; YMP: >10000 years resistance to corrosion

Table 19.4: Geological formations for deep underground disposal of nuclear waste

Host rock	Rock characteristics	Radionuclide transport mechanisms	Country
Granite, gneiss	Fractured, ground water flow in open fractures	Advection and some diffusion	Canada, China, Finland, Russia, Sweden
Salt bedded, dome	No open fractures, no ground water	No transport	Germany, USA (WIPP)
Volcanic tuffs and lavas	Fractures and pores, unsaturated	Percolating water	USA (YMP), UK (Longlands Farm)
Clays and mudrocks consolidated, plastic	No open fractures, stagnant pore water	Diffusion	Belgium, Hungary, France, Russia, Switzerland

on the isolation properties of the geological formation. Table 19.4 gives examples of geological formations selected or considered for geological disposal of nuclear wastes.

19.7. Transport of Radionuclides

One of the most important parameters [implicit in (b), Section 19.6] is the flow rate/throughput of water through/around the repository, which must be as low as possible. Equally important is the predictable stability of this in terms of, e.g. climate change arising from global warming. The most likely source of radionuclide reintroduction to the biosphere is via water. The subsurface transport of water contaminants has been the subject of intense investigation prompted by understandable public interest in protecting water supplies. The interstitial velocity of water in porous media, v (cm/s), is determined by the gradient of the hydraulic head ∇H (cm/cm), the hydraulic conductivity (or permeability) K (cm/s) and effective porosity n_e of the medium according to Darcy's law:

$$v = -\frac{K}{n_e} \nabla H \quad (19.2)$$

The higher the water conductivity and the lower the rock's porosity, the higher the interstitial velocity of water in a rock. Figure 19.7 illustrates the bulk conductivity of water in soils and rocks. It is important to note that, e.g. in

granites and basalts and most metamorphic rocks the hydraulic conductivities (of the actual rock) are very low. However, because they tend to be traversed by cracks and fissures, the “bulk” conductivity of a given volume of rock is much greater due to the flow of water through the fissures.

Clays and shale rocks have the advantage of very low water conductivity and are capable of significantly delaying water transport.

Transport of contaminants in porous media is described by the diffusivity equation for the concentration of particular species C_i :

$$\frac{\partial C_i}{\partial t} = \frac{1}{B_i} \frac{\partial}{\partial x_m} D_{m,n} \frac{\partial C_i}{\partial x_n} - \frac{1}{B_i} \nu_m \frac{\partial C_i}{\partial x_m} - \lambda_i C_i + \lambda_{s,i} C_s \quad (19.3)$$

where m and n refers to the three Cartesian coordinates and are summed when repeated. Here D is the coefficient of convective dispersion, which in practice is invariably assumed to have its principal axis aligned in the direction of the water velocity ν . λ_i is the radioactive decay constant and $\lambda_{s,i}$ is the production rate of nuclide i from decay of nuclide s . The retardation factor B_i accounts for species adsorbed on the rock:

$$B_i = 1 + \frac{\rho_b K_{d,i}}{n_e} \quad (19.4)$$

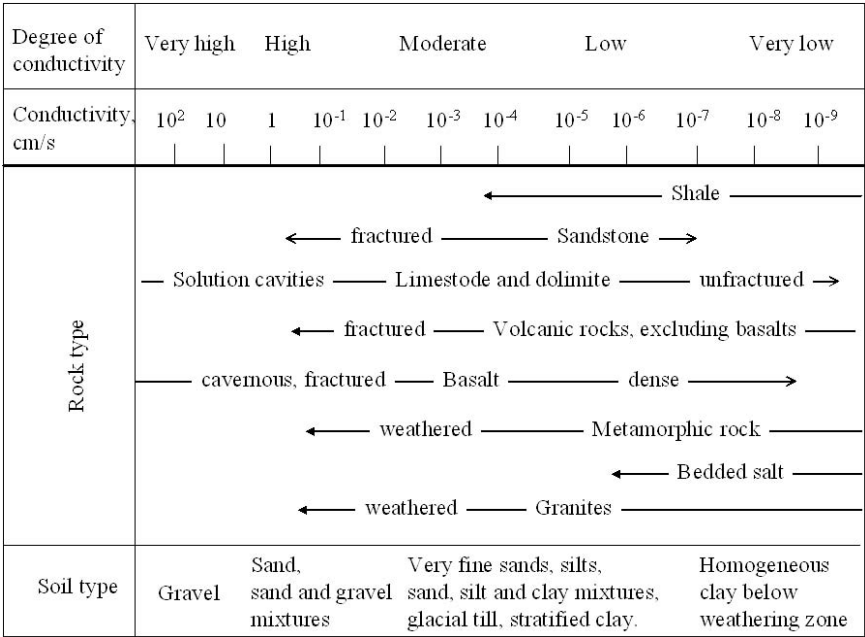


Figure. 19.7: Bulk water conductivity of soils and rocks at 20°C.

where ρ_b is the rock bulk density (g/cm^3), $K_{d,i}$ is the distribution coefficient of the species i (cm^3/g), and the effective porosity n_e gives the volumetric water content in rock (cm^3/cm^3). As most radionuclides have relatively high sorption affinity to some materials of the soils and rocks (see Chapters 10 and 11) they migrate more slowly than the ground water. The extent of the retardation of the contaminant front is given by B_i , hence with higher $K_{d,i}$ the contaminants move more slowly.

Table 19.5 shows the sorption capabilities of some potential host rocks indicating the high retaining capacities of clayey formations in addition to their self-healing capabilities and very low water permeability. These characteristics make argillous formations among the most prominent host rocks for geological disposal.

19.8. Disposal/Storage Experience

Considerable experience in the disposal and storage of radioactive waste is currently being amassed. Disposal sites for LILW range from near-surface facilities to engineered geological repositories. More than 100 LILW disposal/storage facilities are, or have been, operating, and more than 42 repositories are under some stage of development. Concepts for radioactive waste disposal have developed considerably over the past 50 years, with most experience being gained for near-surface facilities. The lessons learned from experience in repository performance have led to the development and adoption of improved disposal/storage concepts and technologies employed at the currently operating near-surface facilities such as Dukovany in the Czech Republic, the Centre de l'Aube in France, Rokkasho-mura in Japan, Vaalputs in South Africa, El Cabril in Spain, Drigg in the United Kingdom (Fig. 19.2), and Barnwell and Richland in the USA. Table 19.6 gives some data on these facilities.

Significant progress has been achieved in developing and validating geological repositories for high-level and long-lived waste. The use of vitrification to convert unstable liquid slurries and sludges to stable solids has enhanced the safety of interim storage, thus enabling time for improved understanding of disposal issues for this waste. The transuranic (TRU) waste repository WIPP in the US has been certified and operating since 1999. Approximately 20 000 drums of TRU waste have already been disposed of there. The Yucca Mountain storage facility in the USA is under consideration as a potential site for a repository for HLW, the construction being planned for 2008 and the first placement of wastes is expected in 2010 although delays currently seem inevitable.

Table 19.5: Average distribution coefficients of elements in some materials at 22 °C

Material	$K_{d,i}(\text{cm}^3/\text{g})$								
	Sr	Tc(VII)	Cs	Ba	Ce	Eu	U(VI)	Pu	Am
Quartz monzonite	20	<80	440	160	740	960	9	1300	2600
Argillite	130	<40	2500	1900	$> 4 \times 10^4$	$> 5 \times 10^4$			
Alluvium	200		7000	5000	$> 2 \times 10^4$	$> 2 \times 10^4$	10	>1000	
Tuff vitrified	1.3×10^4		1.5×10^4	5000	40	30		170	170
Tuff devitrified	60		120	400	80	90		110	110
Tuff + zeolites	240		600	750		6000		280	590

Table 19.6: Status of some LLW near-surface facilities

Repository, country	Type	Operation period	Capacity (m^3)
Dukovany, Czech Republic	Near-surface engineered	Since 1995	5.52×10^4
Centre de l'Aube, France	Near-surface engineered	Since 1992	1×10^6
Rokkasho, Japan	Near-surface engineered	Since 1992	4×10^4
SIA Radon, Russia	Near-surface engineered	Since 1961	1.9×10^5
El-Cabril, Spain	Near-surface engineered	Since 1992	5×10^4
Drigg, UK	Near-surface engineered	Since 1959	1.8×10^6

19.9. Acceptance Criteria

Waste accepted for disposal into a disposal facility must conform to criteria that are consistent with the operational and post-closure safety cases. Acceptance criteria of disposal facilities are site specific. A general requirement is that the waste must be in a solid form with stable chemical and physical properties, and compatible with the engineered and natural barriers. The waste acceptance criteria usually specify radionuclide or radioactivity limits and waste matrix or encapsulation requirements and container properties. Table 19.7 gives an example of some of the waste acceptance criteria for the WIPP repository in the USA.

A significant technical challenge of a disposal facility is that of record keeping. Data on the disposed wastes are important components of overall safety. These need to be stored in a retrievable and future comprehensible form for millennia, a non-trivial undertaking.

Table 19.7: Some important acceptance criteria for the WIPP repository, USA

Parameter	Acceptance limits
Container	Type A
Container vent	HEPA filtered
Immobilisation	Must be stabilised: <10 μm diameter particles >1 wt.%, <200 μm diameter particles >15 wt.%
Liquids	<1 vol.% of container
Materials: corrosive, ignitable, reactive, pyrophoric and explosive; Compressed gases	Prohibited
Hydrogen and other explosive gases	<50% of the lower explosive limit during storage and transport
Specific activity	<100 nCi/g TRU
Fissile materials	<200 ²³⁹ Pu fissile gram equivalent (FGE) per 208 L drum
Surface dose rate	Contact handled drums: <2 mSv/h at surface and <0.1 Sv/h at 2 m; otherwise requires packaging in remote-handle cask
Compatibility	Incompatible chemicals prohibited
Labelling	Required

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Chapter 20

Performance Assessment

20.1. Safety and Performance Assessments

The final evaluation of any waste management concept is done using safety assessment (SA) and performance assessment (PA) cases. SA of nuclear waste disposal evaluates the repository performance and its radiological impact on the environment and humans. SA results in data demonstrating either compliance with safety standards or unacceptability of the proposed concept. PA provides data on the performance of all repository subsystems and the repository itself. PA results in data which are used to improve the overall safety and to demonstrate compliance with safety standards and performance targets. PA comprises scenario development and potential impact calculations. As a rule, the impact is characterised by the most probable doses arising from radionuclides which may be released and interact with the biosphere. Scenarios considered are not limited to the most probable but also include abnormal events. Mathematical models are key components of the SA and PA of waste disposal. A chain of mathematical models is used to describe the long-term degradation of the engineered barriers and the eventual release of radionuclides into ground water and their transport to the biosphere. All studies to date have shown that disposal of radioactive waste including geological disposal, can be safe; adequate isolation from the environment can be assured for hundreds of thousands of years and, thereafter, radionuclide releases are negligible in comparison to natural radiation exposures.

20.2. Safety Requirements

A fundamental requirement of all disposal practices is that they comply with the IAEA principles of radioactive waste management (see Chapter 8). The adequacy of the safety of a disposal system is judged by comparing the results of

the SA with the appropriate national criteria, which are generally set on the basis of internationally agreed standards. The main emphasis is generally on radiological criteria such as:

- 1. limiting exposure doses ($\mu\text{Sv}/\text{year}$) or risks (relative),
- 2. achieving levels of radiological protection for future generations comparable to those currently achieved,
- 3. ensuring that the additive impact of the disposal system on the natural radiation background is limited.

The International Commission on Radiological Protection (ICRP) 1998 publication on disposal of radioactive waste recommends the control of public exposure from waste disposal through the use of the constrained optimisation of protection. Estimated doses and risks should be compared with a dose constraint of no more than about $0.3 \mu\text{Sv}/\text{year}$ or its risk equivalent. Figure 20.1 shows an assessment of maximum radionuclide concentration and doses caused by radionuclide release near an SRS borehole repository after 100 years under conditions of potential flooding.

The ICRP 2000 recommendation for assessing long-lived radionuclides differentiates between natural processes causing release (with dose constraint

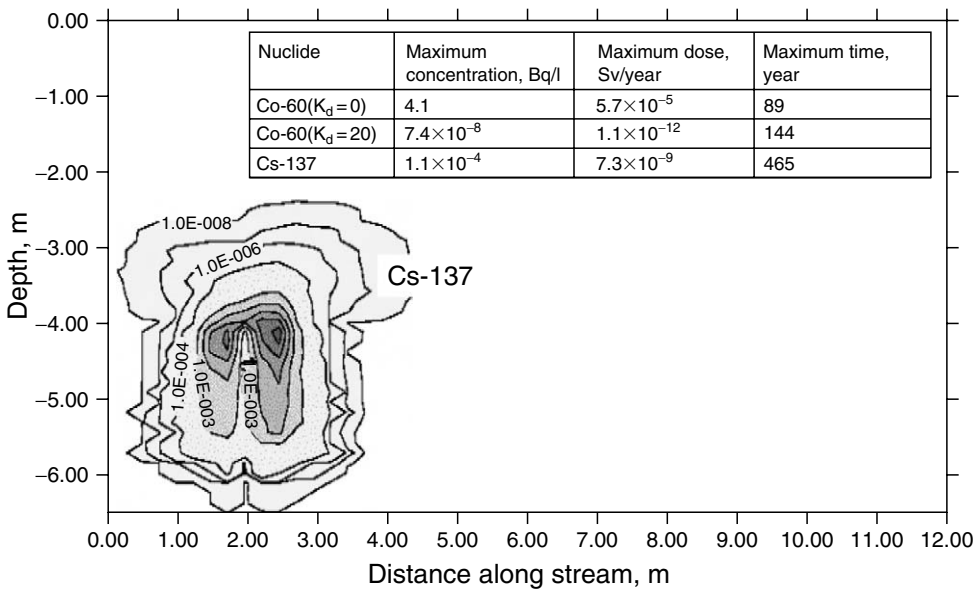


Figure 20.1: Concentration of radionuclides (Ci/m^3) after 100 years for an infiltrating water stream flowing through a borehole SRS repository.

0.3 $\mu\text{Sv}/\text{year}$) and those due to human intrusion. If the assessed dose of a disposal system is lower than 10 $\mu\text{Sv}/\text{year}$, the radiological consequences of human intrusion can be considered to be broadly tolerable provided there are no straightforward means for their reduction. If the assessed doses are higher than 10 $\mu\text{Sv}/\text{year}$, the design of the repository is reconsidered to reduce either the probability of intrusion (e.g. by locating the repository at a greater depth) or its consequences (e.g. by dilution of the radionuclides in water).

20.3. Safety Case Content

Safety cases address the logic and soundness of the overall disposal system design and a range of aspects, which provide confidence in the design and the quantitative aspects of safety impact assessment. Safety cases usually contain descriptions of the:

- robustness of the design explaining the passive safety features adopted,
- mechanisms that provide for waste containment and its isolation from the environment,
- reliability of the various natural and engineered design features and their assessed performance.

The safety case explains how the multi-barrier system is employed and what features provide multiple barriers or levels of safety. It also addresses the safety margins designed into the facility. The integrated PA of the repository (as part of the safety case) includes some uncertainties. Table 20.1 shows the content of an SA report as recommended by the OECD/Nuclear Energy Agency.

Important issues are the adequacy, appropriateness and validation of the modelled processes and the models used. The level of confidence associated with the safety of the repository at particular stages of its development should be addressed. In certain cases models can be tested by comparison with natural analogues – similar processes occurring in natural systems even though over the relevant long timescales the available analogue data are limited. One example is the movement of radioactive elements from the nuclear reactors that occurred spontaneously in rich uranium ores at Okla in the Gabon, Africa, starting about 2000 million years ago. The transport of these radionuclides matched predictions made in safety assessments of model repositories. Another example is the 1300 million-year-old uranium deposit near Cigar Lake in Canada. This extremely rich ore body lies at a depth of 430 m and is surrounded by a layer of clay 5–30 m thick, which has isolated the ore. The

Table 20.1: Content of a safety case

Topic	Description
1. Programme context	Historical perspective, regulatory context, brief description of the waste disposal concept
2. Regulatory criteria	Criteria of guidance, quantitative and qualitative
3. Objectives and scope of the assessment	Related to the programme context
4. Description of the system at the conceptual level	Required level of safety, e.g. multi-barrier concept, safety functions
5. Statement of the constraints	Long timescale, uncertainties
6. Approach to safety assessment	Treatment of uncertainties, model using traceability
7. Detailed description of the disposal system	Waste-form, EBS, site characteristics
8. Interpretation and elicitation of databases	Methods description, use of experts to elicit data
9. Scenario development	Methodology, description, assumptions, justification
10. Description of models	Conceptual and mathematical, spatial and temporal
11. Results and interpretation	For individual subsystems and total system, sensitivity uncertainties
12. Confidence in key arguments	Key processes, model, data and assumptions revisited and their basis examined
13. Compliance with regulatory criteria	Overall compliance with regulatory criteria
14. Conclusions	Indication of areas in which further development is required, which goals have been reached

deposit is, in many ways, similar to several designs for repositories for the final disposal of used fuel. More quantitative tests of models can be derived from process specific analogues such as of canister corrosion (e.g. studies of metal archaeological artefacts), of backfill degradation (e.g. natural hydrothermally altered bentonite clays) and of solute transport (movement of natural series radionuclides).

20.4. Cement Performance

The fraction of radionuclide released from the waste-form Φ_i is defined as

$$\Phi_i = \frac{A_i(t)}{A_i(0)} \quad (20.1)$$

where $A_i(0)$ and $A_i(t)$ are the initial radioactivity and the radioactivity of radionuclides leached from the waste-form at time t .

Cementitious waste-forms are used for immobilisation of short-lived radionuclides and are assumed to retain radionuclides for a few hundred years. Existing experimental data allow assessment of the behaviour of cements over these time spans. Water degradation of cement-based structures is represented by two mechanisms. The first mechanism results from the concentration gradient and is controlled by diffusion. The second one results from dissolution of the surface layers in contact with water. This dissolution causes shrinkage of the interface, thereby compromising the cement structure (Fig. 20.2). In practice, these two mechanisms are coupled.

The rate of dissolution depends on the difference between actual and equilibrium concentrations of cement constituents. When the cement surface layer is not in thermodynamic equilibrium, the kinetics of its dissolution determine the degradation, which is greater if the surface layer is more soluble and the contacting water takes up ionic species from the interstitial pore solution of the cement paste. As calcium solubility is generally the highest, its dissolution results in enrichment of the paste with trivalent iron. Its incorporation into

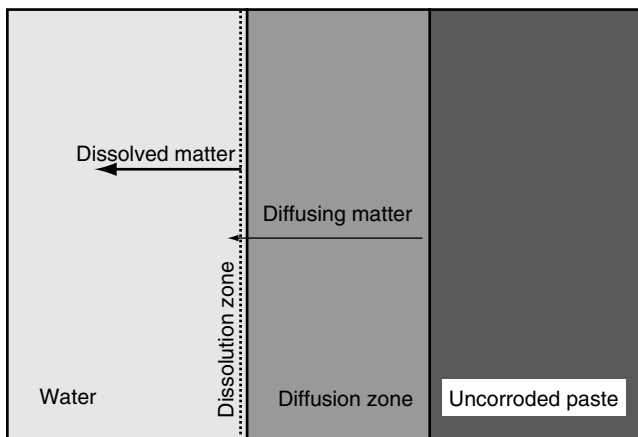


Figure 20.2: Schematic of degradation of a cement waste-form.

surface layer CSH gel reduces the calcium solubility. The surface layer then reaches thermodynamic equilibrium and does not dissolve. In this case diffusion-controlled processes govern cement corrosion and the release of radionuclides from cemented waste can be described as an effective diffusion of radionuclides through the cement matrix. The normalised leaching rate $NR_i(\text{g}/\text{cm}^2\text{day})$ of a radionuclide (i) from the cementitious waste-form can be represented as

$$NR_i = \rho \sqrt{\frac{D_i}{\pi t}} \quad (20.2)$$

where $\rho(\text{g}/\text{cm}^3)$ is the waste-form density, $D_i(\text{cm}^2/\text{day})$ is the effective diffusion coefficient. D_i can be found by plotting normalised leaching losses $NL_i(\text{g}/\text{cm}^2)$ versus square root of leaching time $t^{1/2}(\text{day}^{1/2})$. The total amount of radionuclides $A_i(t)$ (Bq) released from a cement waste-form with a contacting surface area $S(\text{cm}^2)$ at a time t (days) in the future will be given by

$$A_i(t) = \frac{A_i(0)S}{\rho V} \int_0^t NR_i \exp(-\lambda_i t) dt \quad (20.3)$$

where $A_i(0)$ (Bq) is the initial radionuclide activity, $V(\text{cm}^3)$ is the volume and $\lambda_i(\text{day}^{-1})$ is the decay constant. Hence, for a cementitious waste-form the fraction of radionuclides released is given by

$$\Phi_i = \frac{S}{V} \sqrt{\frac{D_i}{\lambda_i}} \phi(\sqrt{\lambda_i t}) \quad (20.4)$$

where $\phi(z)$ is the error integral:

$$\phi(\sqrt{\lambda t}) = \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{\lambda t}} \exp(-x^2) dx \quad (20.5)$$

At times much longer than the decay half-life $t \gg T_{1/2,i} = (\ln 2)/\lambda_i$, the error integral tends to unity, hence the maximum possible fraction of released radionuclides from a cementitious waste-form can be assessed as (see also Chapter 3):

$$(\Phi_i)_{\max} = \frac{S}{V} \sqrt{1.44 D_i T_{1/2,i}} \quad (20.6)$$

Experimental tests done on cements under wet disposal conditions show a low leaching rate of the order of $10^{-6} \text{ g}/\text{cm}^2\text{day}$ after $\tau \sim 10$ years of disposal demonstrating that $\Phi(10 \text{ years}) < 0.04\%$.

20.5. Bitumen Performance

The release of radionuclides from bituminised waste can be described as an effective diffusion of radionuclides through the bitumen matrix (similar to that from a cementitious waste-form) with a diffusion coefficient which usually is several orders of magnitude lower than that of cement. Hence, the fraction of released radionuclides is given by

$$\Phi_i = \frac{S}{V} \sqrt{\frac{D_i}{\lambda_i}} \phi(\sqrt{\lambda_i t}) \quad (20.7)$$

and

$$(\Phi_i)_{\max} = \frac{S}{V} \sqrt{1.44 D_i T_{1/2,i}} \quad (20.8)$$

where D_i is the effective diffusion coefficient of radionuclides in the bitumen. Figure 20.3 shows the percentage (f) of radionuclides released from bituminised radioactive waste measured and calculated using similar form equations, demonstrating that $\Phi_{\max}(\infty) < 0.001\%$.

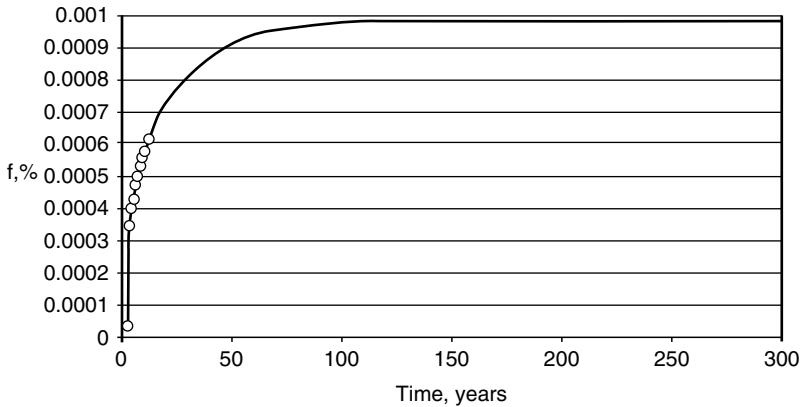


Figure 20.3: Calculated (line) and measured (circles) percentage (f) of radionuclides released from bituminised radioactive waste with time under conditions of near-surface disposal.

20.6. Glass Performance

Since glasses are already used to immobilise HLW and it is planned to locate them in a geological repository, their interaction with the likely environment has been more extensively studied than that of cements and bitumen described

in the previous sections. Figure 20.4 illustrates schematically the changes that are likely to occur in a packaged HLW glass waste-form over time in a repository environment with eventual water saturation. Note that the glass is cracked from its initial processing. In the first few hundred years significant radiogenic heat will maintain the waste-form at temperatures of several hundred degrees Celsius and significant radiation damage will occur (Section 20.7). After this period and once the metal canister material has corroded, water in contact with the glass will alter it leading eventually to radionuclide escape.

Once water (and the canister corrosion product) contacts the glass, quite rapid changes will occur to its surface which will lead to formation of surface layers different in composition and morphology to the bulk glass (Fig. 20.5). Initially, this is expected to be in the form of a gel layer, which later may form alteration products or secondary phases, likely to be clay-like aluminosilicates (Fig. 20.6).

The two basic mechanisms of glass corrosion are leaching (e.g. ion exchange) and dissolution. Leaching is incongruent so that different species are removed from the glass at different rates whereas dissolution occurs congruently, so that glass species are found in the water at the same ratio as in the glass. The leaching of glasses occurs via diffusion-controlled ion exchange and is characterised by the normalised rate:

$$\text{NR}_{X,i} = \rho \left(\frac{D_i}{\pi t} \right)^{1/2} = \rho \times 10^{-\text{pH}/2} \left(\frac{\kappa D_{0\text{H}}}{C_i(0)\pi t} \right)^{1/2} \exp\left(\frac{-E_{\text{di}}}{2RT}\right) \quad (20.9)$$

where $\rho(\text{g}/\text{cm}^3)$ is the glass density, $D_i(\text{cm}^2/\text{day})$ is the effective interdiffusion coefficient, $E_{\text{di}}(\text{J}/\text{mol})$ is the activation energy of interdiffusion, $D_{0\text{H}}(\text{cm}^2/\text{day})$ is the pre-exponential term in the diffusion coefficient of protons in glass, $C_i(0)(\text{mol}/\text{L})$ is the cation concentration at the glass boundary and κ is a constant relating the concentration of protons in the glass with concentration

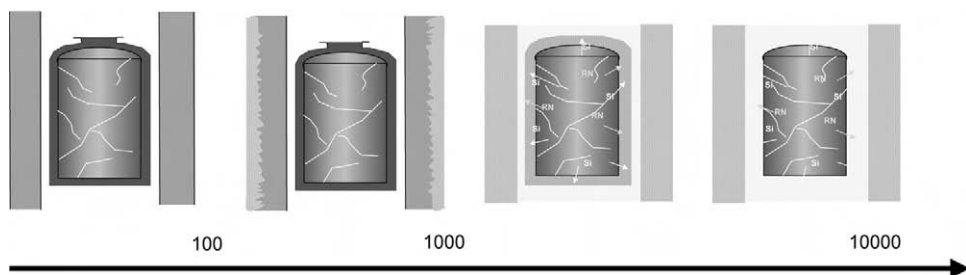


Figure 20.4: Schematic of alteration to packaged glass waste-form in wet repository environment with time (in years). Courtesy Stephane Gin, CEA France.

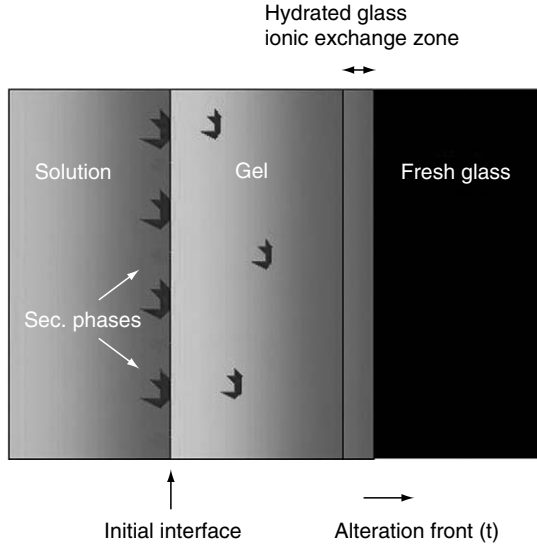


Figure 20.5: Schematic of changes to glass on contact with water, formation of gel layer and growth of secondary phases. Courtesy of Stephane Gin, CEA France.

of protons in the water, e.g. with the pH. The dissolution of glass occurs via hydrolysis and is characterised by the normalised rate:

$$NR_H = \rho r_c = \rho k a_{H^+}^{-\eta} \left[1 - \left(\frac{Q}{K} \right)^\sigma \right] \exp \left(\frac{-E_a}{RT} \right) \quad (20.10)$$

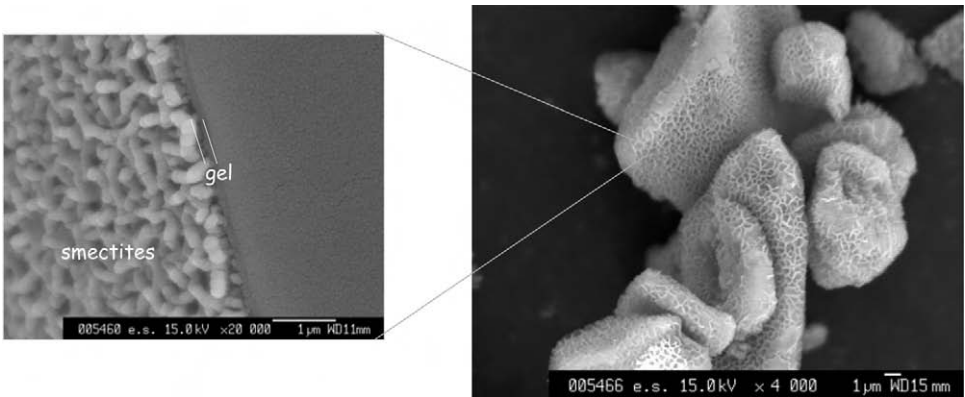


Figure 20.6: Clay-like (smectite) alteration products on the surface of simulant radwaste glasses after extended contact with water. Courtesy of Stephane Gin, CEA France.

where r_c is the normalised leaching rate measured in units of cm/day, k is the intrinsic rate constant, a_{H^+} is the hydrogen ion activity, η is the pH power-law coefficient, E_a is the activation energy, Q is the ion activity product of the rate-controlling reaction, K is the equilibrium constant of this reaction and σ is the net reaction order. The affinity term characterises the decrease in solution aggressiveness with respect to the glass as it becomes increasingly concentrated in dissolved elements and as the ion activity product Q of the reactive species approaches the material solubility product K . The normalised corrosion rate of glass NR_i is given by the sum of two contributions from both mechanisms:

$$NR_i = NR_{X,i} + NR_H \quad (20.11)$$

Leaching is characteristic of the initial stages of corrosion while dissolution is characteristic of the later stages. The parameters that control glass corrosion can be found by applying standard testing procedures such as SPFT (Section 17.3). The time required for the transition from one mechanism (ion exchange) to another (hydrolysis) depends on the glass composition and environmental conditions such as pH and temperature. Figure 20.7 shows corrosion mechanisms for a Russian alkali-borosilicate glass (K-26) as a function of exposure time and temperature along with experimental data on the transition from leaching to dissolution for Na₂O–SiO₂ glasses in water (exposure time 1 h) at different temperatures.

The fraction of radionuclides released from the glass at time t is given by

$$\Phi_i = \frac{S}{V} \sqrt{\frac{D_i}{\lambda_i}} \phi(\sqrt{\lambda_i t}) + \frac{Sr_c}{V\lambda_i} [1 - \exp(-\lambda_i t)] \quad (20.12)$$

At times much longer than the decay half-life ($t \gg T_{1/2,i} = \ln 2/\lambda_i$) the maximum possible fraction of radionuclides released from a glass waste-form can be assessed as (see also Chapter 3):

$$(\Phi_i)_{\max} = \frac{S}{V} \sqrt{1.44 D_i T_{1/2,i}} + \frac{1.44 \times Sr_c T_{1/2,i}}{V} \quad (20.13)$$

Figure 20.8 shows an example of calculated and measured data on radionuclides released from glass K-26 in conditions of near-surface disposal.

20.7. Radiation Effects

As glasses are used to immobilise HLW, potentially adverse radiation effects need to be taken into account. The principal sources of radiation in HLW are decaying fission products such as ¹³⁷Cs and ⁹⁰Sr and actinide elements such as U, Np, Pu, Am and Cm (see Chapter 2). Beta decay of fission products generates

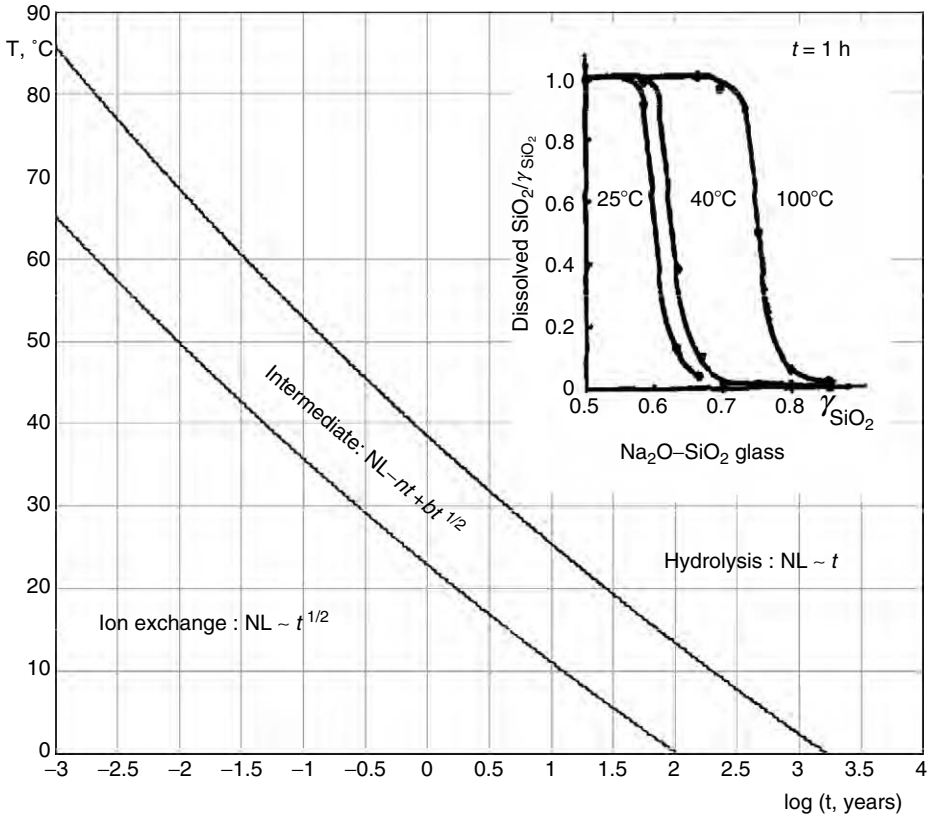


Figure 20.7: Corrosion mechanisms of alkali-borosilicate glasses. The insert shows the transition from leaching to dissolution for $\text{Na}_2\text{O-SiO}_2$ glasses at different temperatures.

energetic β particles, very low-energy recoil nuclei and γ -rays (see Chapter 10). Alpha decay of actinides produces energetic α particles (4.5–5.5 MeV), energetic recoil nuclei (70–100 keV) and some γ -rays (see Chapter 11).

Beta and alpha decay affect glass waste-forms through interactions of the β particles, α particles, recoil nuclei and γ -rays with the glass. Absorbed doses for non-US commercial HLW glass are assessed to be about 10^{10} Gy for beta decay and about 2×10^{10} Gy for alpha decay. Absorbed doses for defence HLW glass in the US are assessed at about 7×10^8 Gy for beta decay and about 8×10^8 Gy for alpha decay (Fig. 20.9).

The most obvious result of irradiation is self-heating of the glass (see Q -values in Table 2.1). In the case of non-US commercial HLW glass in a repository, self-heating from α -decay of the fission products can result in initial storage temperatures greater than 200°C , with temperatures falling below

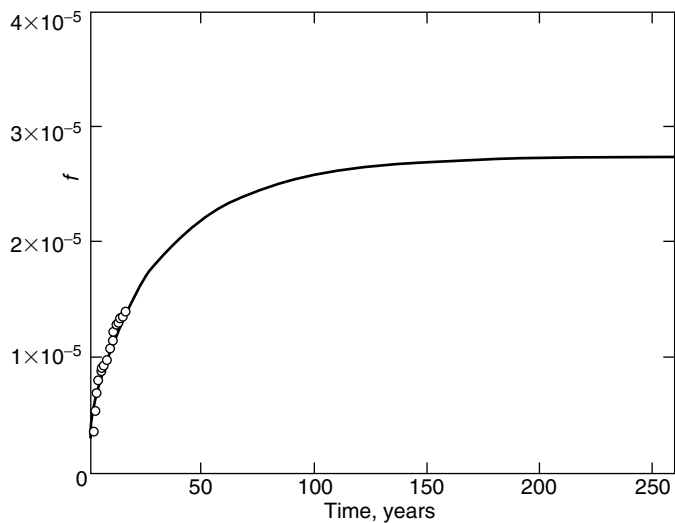


Figure 20.8: Calculated (line) and measured (circles) fraction (f) of radionuclides released from glass K-26 in conditions of near-surface disposal.

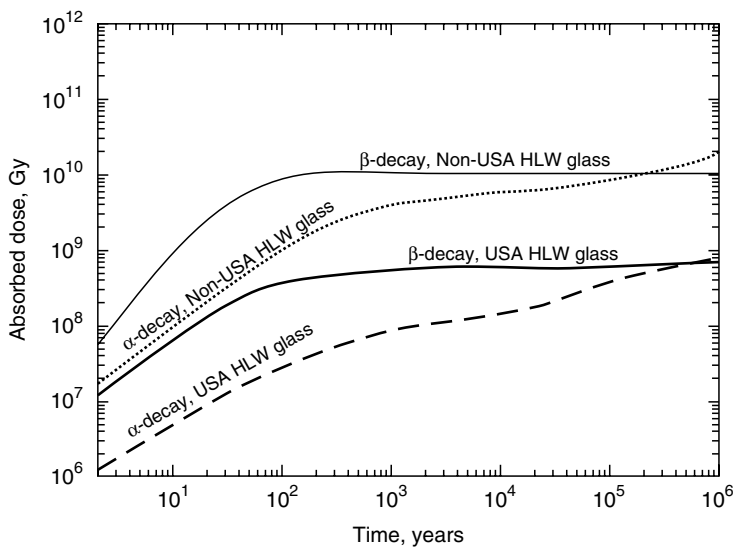


Figure 20.9: Cumulative absorbed doses for nuclear waste glasses.

150°C several hundred years after emplacement. For defence HLW glass in the US, initial temperatures in the Yucca Mountain repository may be as high 250°C, but will decrease to less than 100°C after several hundred years.

In addition to self-heating, ionisation and electronic excitations produce a large number of point defects in the glass structure and electron-hole pairs and can result in covalent and ionic bond rupture and enhanced diffusion. Bond ruptures and localised electronic excitations can lead to the formation of NBO defects and local glass decomposition (radiolysis). Irradiation results in progressive accumulation of defects and broken network linkages and affects the release rate of radionuclides from waste glasses, initially by increasing the rate of ion exchange, then by increasing the potential surface area for radionuclide release (microfracturing) and by changing the dissolution rate of the glass due to radiation-induced changes in chemistry, microstructure and network bonding. Figure 20.10 illustrates the effect of irradiation on leaching of alkali elements from glasses as a function of exposure temperature and cumulative irradiation dose. Irradiation can result in enhanced leaching at high doses provided the exposure temperatures are not too high.

Radiation-induced changes in HLW glass structure are not expected to increase the leach rate by more than a factor of 10 provided there is no radiation-induced phase separation. *In situ* experiments such as those carried out at Mol, Belgium support the assumption that irradiation does not cause a large increase of radionuclide leaching rates. However, the effects of irradiation on glass durability need further systematic investigation.

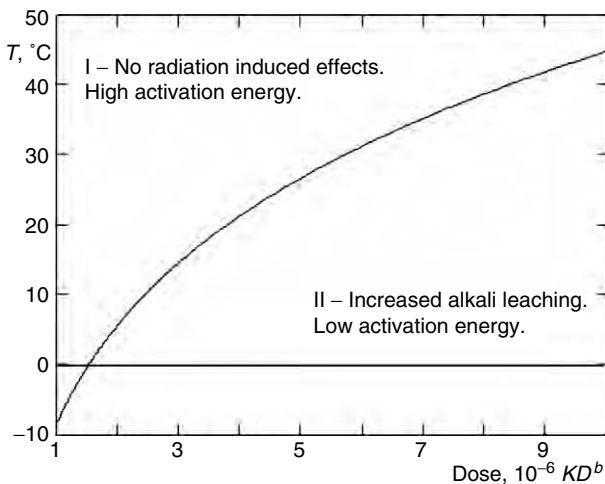


Figure 20.10: Radiation-induced increase of leaching of alkalis from irradiated glasses.

The effects of radiation damage in cement and ceramic hosts are also significant. In particular in ceramics for HLW (including Pu) disposition, generation of displacement cascades by alpha recoils and resulting formation of dislocations and voids or direct amorphisation will lead to extensive swelling impacting on waste-form longevity.

20.8. Research Laboratories

The timescales for nuclear waste repositories are enormous, covering hundreds to thousands and millions of years. Predictive possibilities diminish with time, as new uncertainties appear which may substantially change the evolution scenario. Table 20.2 compares the timescales for important events in nuclear waste repositories.

Important results increasing our confidence in PA are provided by natural (or field) tests of simulant and real waste-forms. Many countries carry out such tests, including Belgium, Canada, Finland, France, Germany, Japan, Russia, Spain, Sweden, Switzerland, the UK and the USA. Russia, for example, has carried out field tests of cemented, bituminised and vitrified wastes since the late 1960s (SIA “Radon”, Moscow Region). Moreover, countries currently developing geological repositories for HLW disposal have adopted a stepwise approach that includes a period of intensive underground investigation and testing. Table 20.3 provides a list of the principal existing underground research facilities.

20.9. Conclusion

This book has illustrated that the world currently has large amounts of nuclear waste but that we have the ability to immobilise, contain, store and finally dispose of it in an environmentally sensible manner. We are optimistic about our ability to

Table 20.2: Timescales of processes

Process	Timescale (year)
Radioactivity of SNF, HLW, long-lived SRS	10 ⁶
Climatic cycles (glaciations)	10 ⁴
Passive institutional control (markers)	10 ³
Radioactivity of short-lived SRS, ILW	10 ³
Active institutional control	10 ²
Radioactivity of short-lived LILW	10 ²

Table 20.3: Main underground research facilities related to geological disposal of nuclear waste

Country	Location	Name, type	Rock	Time period
Belgium	Mol	HADES, PRACLAY	Plastic clay	Since 1980
Canada	Lac du Bonnet, Manitoba	URL	Granite	Since 1984
Finland	Olkiluoto	Research tunnel	Granite	Since 1993
France	Fanay, Augeres/Tenelles	Galleries in U mines	Granite	1980–1990
	Amelie	Galleries in K mines	Bedded salt	1986–1994
	Tournemire	Test galleries	Shale	Since 1990
Germany	Asse	Test galleries in K/salt mine	Dome salt	1977–1980
	Gorleben	URL	Dome salt	Since 1997, halted
	Konrad	Test galleries in Fe mine	Shale	Since 1980
Japan	Tono	Galleries in U mine	Sandstone	Since 1986
	Kamaishi	Galleries in Fe–Cu mine	Granite	1988–1998
Sweden	Stripa	Galleries in Fe mine	Granite	1976–1992
	Aspo	HRL	Granite	Since 1990
Switzerland	Grimsel	GTS at dam tunnel	Granite	Since 1983
	Mont Terri	Galleries at road tunnel	Shale	Since 1995
USA	Nevada test site	CLIMAX	Granite	1978–1983
	Nevada test site	G-tunnel	Tuffs	1979–1990
	Carlsbad	WIPP	Bedded salt	Since 1982
	Yucca Mountain	ESF	Tuffs	Since 1993
	Yucca Mountain	Busted Butte	Tuffs	Since 1997



Figure 20.11: Hanford Low Activity Waste Vitrification Plant under construction (August 2004). Courtesy of B.P. McGrail, PNNL, USA.

take care of the “waste problem” and Fig. 20.11 illustrates construction of the clean-up operation underway at the Hanford site in the USA. As we have described, plans for such facilities and suitable repositories for waste are well advanced and construction is ongoing. While we cannot afford to be complacent, it at last appears that the worst period of our misuse of nuclear material is behind us.

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