1

Introduction

Throughout history, human society has generated huge quantities of waste materials through everyday living. This is particularly true of such periods as the industrial revolutions in Europe and elsewhere. In the past, the overall management of wastes has been poor, with a general disposition to dispose of these directly into the environment through dispersal, and with little thought given to the long term consequences of this action on the environment. Fortunately, this has not in general been the case for radioactive waste materials. After the discovery of radioactivity and radioactive materials in the late nineteenth century it soon became clear that these posed a special risk to humans and the environment. Consequently, radioactive wastes could not be treated in the same haphazard way as their nonradioactive counterparts but needed to be contained and excluded from the immediate environment. It is only relatively recently that serious efforts and a similar approach have been made in order to deal with nonradioactive toxic and hazardous waste materials through treatment, waste minimization, or recycling.

1.1 Categories of Waste and Waste Generation in the Modern World

Radioactive wastes are generated as a consequence of numerous processes and operations. These range from the reprocessing of spent nuclear fuel and plutonium production for weapon applications, to mining and refining of uranium ore, commercial research activities and use of isotopes, and medical, hospital and university activities. Unprocessed spent nuclear fuel itself has also been considered as a waste, although as discussed later this view is changing. Radioactive waste management practices vary worldwide but share the common interest of treating these wastes as highly hazardous materials from which the environment must be protected. Nonradioactive toxic and hazardous wastes are also generated by a host of industrial operations ranging from municipal incinerators to ferrous and nonferrous metal manufacture and processing, and these too are now attracting more serious attention.
**Introduction**

1.1.1 Radioactive Wastes from Nuclear Power and Defence Operations

Radioactive wastes are generally subdivided into a number of specific categories depending on their overall activity, as summarized in Table 1.1. These include very low level waste (VLLW), low level waste (LLW), intermediate level waste (ILW) and high level waste (HLW).

High level waste is heat generating and the temperature of this waste, at least in the shorter timescales, may rise significantly due to the result of radioactive decay processes. It has been defined as heat generating on a scale of >2 kW m\(^{-3}\) of material (IAEA, 1994; Dziewinska, 1998; Barton, 2003; UKAEA, 2003; Kim, 2004), although this figure has been questioned by Ojovan (Donald, 2007) and no international consensus on this power level currently exists. Sources of HLW include high level liquid waste (HLLW) produced during the reprocessing of spent nuclear fuel, which contains many short-lived fission products together with actinides and longer-lived fission products; another source of HLW arises from the production of plutonium metal and tritium for weapon applications.

Intermediate level waste may also be heat generating, but to a lesser degree than HLW, and consists primarily of items such as components inside nuclear reactors including graphite from reactor cores, fuel cladding and fuel element debris, together with radioactive sources used in medical equipment or experimental instruments, filters and chemical sludges. It is defined as waste with an activity of >4 × 10\(^8\) Bq\(\cdot\)t\(^{-1}\) α-radiation and >12 × 10\(^8\) Bq\(\cdot\)t\(^{-1}\) β- and γ-radiation. This type of waste is normally encased in concrete within steel containers and put into storage awaiting ultimate disposal. Other categories

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**Table 1.1 Categories of radioactive waste and definitions**

<table>
<thead>
<tr>
<th>Category of waste</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very Low Level Waste, VLLW</td>
<td>Waste &lt;0.4 × 10(^8) Bq m(^{-3}) β/γ</td>
</tr>
<tr>
<td>Low Level Waste, LLW</td>
<td>Waste &lt;4 × 10(^8) Bq t(^{-1}) α; &lt;12 × 10(^8) Bq t(^{-1}) β/γ</td>
</tr>
<tr>
<td>Intermediate Level Waste, ILW</td>
<td>Heat generating waste &lt;2 kW m(^{-3}) (but see text)</td>
</tr>
<tr>
<td>High Level Waste, HLW</td>
<td>Highly radioactive; heat generating &gt;2 kW m(^{-3}) (but see text)</td>
</tr>
<tr>
<td>Transuranic Waste, TRU</td>
<td>Transuranic elements with 100 nCi α-emitting TRUs with half lives &gt;20 years g(^{-1}) (USA)</td>
</tr>
<tr>
<td></td>
<td>Contacted handled TRU surface dose &lt;200 mRem h(^{-1}); remote handled TRU ≥200 mRem h(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Non-HLW generated from operation and dismantling of reprocessing facilities and MOX fuel fabrication facilities containing long-lived radionuclides such as TRU actinides. Also including non-HLW returned from BNG Sellafield and AREVA NC (Japan)</td>
</tr>
<tr>
<td>Mixed Waste, MW</td>
<td>Mixed waste is generally defined as wastes that contain a mixture of LLW together with nonradioactive toxic and hazardous wastes including heavy metals such as Pb and Cd</td>
</tr>
</tbody>
</table>

Sources: EPA; Knecht, 2001; Nirex, 2002; JAEA, 2007; Mallants et al., 2008.
of ILW which are not greatly heat producing include pyrochemical, electrorefining, and related wastes from the reprocessing of Pu metal for weapon applications, and these also require special treatment, as discussed in Chapter 9.

The activity of LLW, which is composed primarily of protective clothing and some equipment or materials used in radioactive facilities, together with contaminated soil and building materials and miscellaneous organic and inorganic materials, although relatively low, cannot be disposed of as ordinary waste. The activity of LLW is set at $<4 \times 10^9 \text{Bq t}^{-1}$ $\alpha$-radiation and $<12 \times 10^9 \text{Bq t}^{-1}$ $\beta$- and $\gamma$-radiation. It is currently compacted into steel drums that are placed inside large boxes and filled with concrete. In the case of VLLW the activity is so low that it can generally be disposed of as ordinary waste, either in domestic landfill sites or by incineration; it is normally defined as waste containing $<0.4 \times 10^9 \text{Bq m}^{-3}$ $\beta$- and $\gamma$-activity.

Another category of radioactive waste is defined by the USA for wastes of lower activity than HLW but which contains transuranic elements. These are known as transuranic waste (TRU) and contain $100 \text{nCi}$ of $\alpha$-emitting transuranic elements with half lives $>20$ years per gram of waste (Ewing, 1999).

A number of additional materials, including surplus uranium and plutonium from both civilian and military nuclear programmes, were at one stage during the 1990s considered as wastes and may at some future date be declared as wastes again although, as discussed later, this is now becoming increasingly unlikely. Spent nuclear fuel, which is currently being stored without reprocessing, has also been regarded as a nuclear waste, although the recently changing situation, brought about by the ever increasing worldwide demand for energy, and specifically for energy sources that do not emit substantial quantities of greenhouse gases, in particular carbon dioxide, is now leading to a worldwide drive to build new nuclear power stations, and this will require fuel recycling. This includes the UK, with the Government announcement in 2008 supporting in principle the building of new plants. It is reported that the total amount of nuclear power generated worldwide currently is of the order of 370 GW (Banks, 2007). This is forecast to increase to between 447 GW and 670 GW by 2030. China alone is planning to build 30 new reactors by 2020, whilst India is currently building seven new nuclear plants, and in Finland one is under construction at Olkiluoto. In the US many states have indicated an interest in building new nuclear power stations and it is estimated that three or four new plants would have to be built every year, starting in 2015, just to maintain the US’s current 20% nuclear power supply share (Sheppard, 2008). US electricity demand is forecast to grow by 30% by 2030. Thirty-five new reactors are in the planning stage, and although the projected cost of a new facility has increased to US$12–18 billion, the public are now mainly in favour of nuclear power (Grunwald, 2009). It is therefore very clear that nuclear power is indeed back on the agenda, with many articles also appearing in the popular press highlighting this change in political direction (Lauvergeon, 2008). This is creating a very serious problem for many countries that lack a sufficient pool of trained personnel and new graduates in the nuclear sciences, including waste management specialists.

In the longer term, the ever increasing demand for energy is also likely to lead to the development of a new generation of nuclear power stations, the so-called Generation IV (GenIV) nuclear energy systems. Due to the finite resource and future availability of uranium, these new energy systems will operate under closed fuel cycle conditions, requiring fuel recycling. The GenIV systems will also necessitate the development of advanced
wasteforms to deal with the more unusual or difficult waste products generated from fuel reprocessing operations. On 15 August 2008, DOE and NRC delivered to the US Congress the Next Generation Nuclear Plant (NGNP) Licensing Strategy Report which sets out the licensing approach, the R&D requirements, and the resources required to licence by 2017 an advanced reactor design under the GenIV umbrella, and with operation planned for 2021 (Anon, 2008). The new design would provide process heat, in addition to electricity, for numerous industrial applications including hydrogen production, coal-to-liquid fuel conversion, shale oil recovery, and many others. It has been noted by the US Assistant Secretary for Nuclear Energy that ‘DOE is committed to the development and commercial deployment of NGNP technology in a timely manner. Nuclear energy is vital to our nation’s energy security and NGNP has the potential to extend the benefits to bring nuclear technology to a whole new section of the US economy’. Advanced planning for these new systems is therefore already underway, and with it the need for advanced fuel reprocessing; accordingly, wasteform development to meet the new requirements is also becoming of paramount importance.

Coupled with the likely development of a new generation of nuclear energy systems, and in order to minimize the risk of nuclear proliferation, there is an additional drive to reprocess current spent nuclear fuel and to recover Pu in a form that is unsuitable for use in nuclear weapons. There are also additional special categories of radioactive waste arising from the pyrochemical reprocessing of Pu metal for weapon applications. This results in the generation of actinide- and halide-containing wastestreams and these are currently attracting considerable attention.

The quantities of radioactive wastes stored worldwide are substantial, with individual holdings varying widely from country to country, depending largely on their dependence on nuclear power or use of radioactive materials in weapon programmes. Some examples are summarized in Table 1.2. In the UK around 95% of radioactive waste is generated by the nuclear power industry and comes from nuclear fuel production and spent fuel reprocessing, in addition to wastes from the operation of nuclear reactors, research and development programmes, and decommissioning of old facilities. Decommissioning of the UK’s Magnox reactors is expected to produce large volumes of ILW, mainly concrete, building rubble, and redundant plant (Meehan et al., 2008). The remaining 5% is due to a combination of activities; for example, Ministry of Defence (MoD) operations including nuclear weapon production and nuclear submarine operation, together with medical, educational and research establishments, and certain non-nuclear facilities including the oil extraction industry. The 2004 inventory of the UK’s total radioactive waste holdings amounted to $2.27 \times 10^6 \text{m}^3$. This included $2.06 \times 10^6 \text{m}^3 \ (2.8 \times 10^6 \text{t})$ LLW, $217 \times 10^3 \text{m}^3 \ (250 \times 10^3 \text{t})$ ILW, and $1340 \text{m}^3 \ (3.6 \times 10^3 \text{t})$ HLW from a total of 37 waste producers ranging from the Dounreay nuclear site on the coast of Northern Scotland to the Devonport naval facility in Southern England (Nirex, 2005). Future waste arisings include around $260 \text{t}$ HLW from Magnox and oxide fuel reprocessing currently scheduled to end in 2013 and 2011, respectively, $150 \times 10^3 \text{t}$ ILW mainly from Sellafield, Magnox and AGR power stations, and $2.90 \times 10^6 \text{t}$ LLW mainly from remediation of contaminated ground at nuclear sites and the decommissioning of various facilities. The ILW inventory consists mainly of a variety of irradiated metals including steels, aluminium, lead, zircaloy and Magnox alloy, together with other inorganic materials including concrete, cement, sand, rubble, graphite, glass, ceramics, sludges, flocculants and zeolites, in addition to organics which include plastics, rubbers, complexing agents, bird guano, and ion-exchange resins (Abraitis
In the UK, treated LLW is disposed of at a purpose LLW site situated near Drigg in Cumbria which has been operating since 1959, although this site is likely to be filled to capacity by 2050 after which a new site will be required (King and Vande Putte, 2003; NDA, 2006). There are two main HLW wastestreams in the UK from the reprocessing of spent nuclear fuel and these are stored at the Sellafield nuclear plant. One is from the reprocessing of the older Magnox fuels, whilst the second has been generated by the reprocessing of uranium dioxide fuels. Currently, these wastestreams are combined in a one to three ratio of Magnox waste to oxide waste before vitrification, as discussed in Chapter 6. Approximately one-third of legacy HLLW has been vitrified and it is estimated that the remainder will be processed by 2016 (NDA, 2006).

There are considerable amounts of radioactive wastes in the USA, of the order of $232 \times 10^3$ m$^3$ of high level radioactive sludges at Hanford, $126 \times 10^3$ m$^3$ at SRS, and $2.5 \times 10^3$ m$^3$ at Oak Ridge, mainly generated by the US weapons programme (Bell, 2000). At Hanford, for example, the wastes, in the form of liquids and sludges generated through Pu production over the period 1944–1987, are kept in 177 underground waste tanks (Hrma and Kruger, 2008), as illustrated in Figure 1.1. At the Idaho National Laboratory around 4400 m$^3$ of calcined HLW from the reprocessing of irradiated defence nuclear fuel is currently stored (McGlinn et al., 2007), the composition of this waste consisting primarily of around 50 mass% CaF$_2$ together with oxides of Al, Zr and B; the radionuclide content is generally <1 mass%. It has not so far been general policy to reprocess commercial spent nuclear reactor fuel in the US.

### Table 1.2 Worldwide quantities of radioactive wastes

<table>
<thead>
<tr>
<th>Category of waste</th>
<th>Quantities (10$^3$ m$^3$)</th>
<th>Quantities (10$^3$ t)</th>
<th>Comments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLW</td>
<td>$2.06 \times 10^3$</td>
<td>$2.8 \times 10^3$</td>
<td>UK (2004 inventory)</td>
<td>Nirex, 2005</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>$2.9 \times 10^3$</td>
<td>UK (additional future projected for decommissioning of facilities)</td>
<td></td>
</tr>
<tr>
<td>ILW</td>
<td>217</td>
<td>250</td>
<td>UK (2004 inventory)</td>
<td>Nirex, 2005</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>150</td>
<td>UK (additional future projected from decommissioning)</td>
<td>Nirex, 2005</td>
</tr>
<tr>
<td>HLW</td>
<td>1.34</td>
<td>3.6</td>
<td>UK (2004 inventory)</td>
<td>Nirex, 2005</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>0.26</td>
<td>UK (future projected from Magnox and oxide fuel reprocessing)</td>
<td>Bell, 2000</td>
</tr>
<tr>
<td></td>
<td>232</td>
<td>—</td>
<td>USA (Hanford site)</td>
<td>Bell, 2000</td>
</tr>
<tr>
<td></td>
<td>126</td>
<td>—</td>
<td>USA (SRS)</td>
<td>Bell, 2000</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>—</td>
<td>USA (Oak Ridge)</td>
<td>McGlinn et al., 2007</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>—</td>
<td>Idaho National Laboratory</td>
<td>INEL</td>
</tr>
<tr>
<td>TRU</td>
<td>&gt;9</td>
<td>—</td>
<td>Idaho National Laboratory</td>
<td>INEL</td>
</tr>
<tr>
<td></td>
<td>152.8</td>
<td>—</td>
<td>Hanford contaminated soil</td>
<td>Pollett, 2004</td>
</tr>
<tr>
<td></td>
<td>175.6</td>
<td>—</td>
<td>WIPP licensed capacity</td>
<td>EPA, 2005</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>—</td>
<td>JAEA, Japan (projected to 2050)</td>
<td>JAEA, 2007</td>
</tr>
<tr>
<td>LILW-SL</td>
<td>70.5</td>
<td>—</td>
<td>Belgium (2003 inventory)</td>
<td>Mallants et al., 2008</td>
</tr>
</tbody>
</table>

Bell, 2000; NDA, 2006; Nirex, 2005; Pollett, 2004; McGlinn et al., 2007; INEL; EPA; JAEA; Mallants et al., 2008.
Figure 1.1 Hanford waste tanks under construction. [(a) Reproduced with permission from http://picturethis.pnl.gov/pictures.nsf/by+id.SMAA-496MJT, Use of images from PictureThis shall not claim any expressed or implied affiliation with, or endorsement by, Battelle Memorial Institute, Pacific Northwest National Laboratory or the US Department of Energy. PictureThis Photo credit: Courtesy of Pacific Northwest National Laboratory. (b) Reproduced from Privatization – A Report to the Secretary of Energy. Available online at http://www.osti.gov/privatization/report/chapt-5.htm. Copyright US Government]
The immobilization of highly radioactive waste materials in vitreous and ceramic hosts has been under investigation for many years (Donald et al., 1997; Ojovan and Lee, 2005, 2007; Donald, 2007; Caurant et al., 2009). Most of the available data relate to the development of hosts for the long term storage and ultimate disposal of high level nuclear waste materials, either from the reprocessing of spent commercial reactor fuels or from certain defence operations. As a consequence of these studies, the large volumes of legacy high level radioactive wastes from both civil and military nuclear programmes are currently being immobilized by vitrification employing borosilicate glasses, these glasses providing a suitable medium for the majority of the species present in these wastes. The decision to use borosilicate glass has resulted in the building and operation of many industrial scale vitrification plants throughout the world, using this glass as the first generation host for the immobilization of high level waste. As noted earlier, there are now many new categories of waste requiring treatment for which borosilicate glass is unsuitable; for example wastes containing halides. The solubility of halides, and particularly chlorides, in borosilicate glass is very low. Alternative candidate hosts and processes are therefore being sought for these additional categories of waste. These include both vitrification options and use of ceramic hosts, with various solutions being proposed, including the use of phosphate- rather than silicate-based glasses, together with the development of novel glass/ceramic hybrid systems, as reviewed in Chapter 9.

1.1.2 Toxic and Hazardous Wastes

In addition to the key requirement to immobilize both conventional and unusual categories of radioactive wastes, and to render these passively safe, it is becoming increasingly essential environmentally, as land-fill sites become full and/or become more expensive, that more be done to address problems associated with the ever increasing quantities of nonradioactive wastes. These include toxic and hazardous wastes, in addition to very large volumes of less hazardous materials, all of which increasingly threaten the environment and which will continue do so at an escalating level well into the foreseeable future. Vitrification offers a possible solution for some of these nonradioactive wastes by simultaneously reducing or eliminating their hazardous nature and reducing the volume of the final wasteform. An added advantage of vitrifying these wastes is that some of the vitrified products may even find useful commercial applications, rather than simply being disposed of.

There are numerous descriptions and definitions of nonradioactive toxic and hazardous wastes. In general, a waste is considered hazardous if it possesses any one of a number of undesirable characteristics including toxicity, corrosive behaviour, reactivity or flammability. Wastes that contain significant quantities of heavy metals are one example. Many industries such as ferrous and nonferrous metal foundries and facilities, chemical and petroleum facilities, electrical and electronic component manufacturers, textile mills, automobile manufacturing plants, and glass and ceramics manufacturers, to name but a few, produce hazardous wastes. Categories of toxic and hazardous wastes range from municipal incinerator ashes and coal and fly ash from thermal power stations, to sewage and dredging sludges, blast furnace slags and metal processing wastes, medical and electronic wastes, and asbestos products. Hazard waste categories and some examples are summarized in Table 1.3.
### Table 1.3 Hazardous waste categories and examples

<table>
<thead>
<tr>
<th>Code</th>
<th>Category</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Wastes resulting from exploration, mining, quarrying, and physical and chemical treatment of minerals</td>
<td>Metal excavation; processing of metals; drilling muds</td>
</tr>
<tr>
<td>02</td>
<td>Wastes from agriculture, horticulture, aquaculture, forestry, hunting and fishing, food preparation and processing</td>
<td>Sludges; waste metal</td>
</tr>
<tr>
<td>03</td>
<td>Wastes from wood processing and the production of panels and furniture, pulp, paper and cardboard</td>
<td>Inorganic wood preservatives; sludges</td>
</tr>
<tr>
<td>04</td>
<td>Wastes from the leather, fur and textiles industries</td>
<td>Tanning liquor containing Cr; sludges</td>
</tr>
<tr>
<td>05</td>
<td>Wastes from petroleum refining, natural gas purification and pyrolytic treatment of coal</td>
<td>Sludges; spent filters; wastes containing Hg or S</td>
</tr>
<tr>
<td>06</td>
<td>Wastes form inorganic chemical processes</td>
<td>Solid salts and solutions containing heavy metals; heavy metal oxides; wastes containing sulphides, As, Hg and other heavy metals; sludges; wastes containing asbestos from electrolysis; barium sulphate sludge containing Hg; phosphorus slag; calcium-based reaction wastes from TiO₂ production; wastes from asbestos processing; soot</td>
</tr>
<tr>
<td>08</td>
<td>Wastes from the manufacture, formulation, supply and use of coatings</td>
<td>Sludges; waste coating powders; aqueous sludges containing ceramic materials</td>
</tr>
<tr>
<td>09</td>
<td>Wastes from the photographic industry</td>
<td>Wastes containing Ag</td>
</tr>
<tr>
<td>10</td>
<td>Wastes from thermal processes</td>
<td>Wastes from power stations and other combustion plants, e.g., bottom and fly ashes, slags and sludges; wastes from the iron and steel industry, e.g. slags, scales, sludges and filter cakes; wastes from aluminium, lead, zinc copper, precious metal processes, e.g. slags, flue dusts, sludges and filter cakes; wastes from metal casting operations; wastes from the manufacture of glass, ceramic, and glass and ceramic products; wastes from the manufacture or use of cement, lime and plaster products</td>
</tr>
<tr>
<td>11</td>
<td>Wastes from chemical surface treatment and coating of metals and other materials; nonferrous hydrometallurgy</td>
<td>Sludges; filter cakes; zinc hydrometallurgical sludges (jarosite, goethite); copper hydrometallurgical wastes; wastes from hot galvanizing processes</td>
</tr>
<tr>
<td>12</td>
<td>Wastes from shaping and physical and mechanical surface treatment of metals and plastics</td>
<td>Metal filings and turnings; metal dusts; welding wastes; machining sludges; waste blasting materials</td>
</tr>
</tbody>
</table>
The quantities of nonradioactive wastes produced are considerably higher than for radioactive wastes, as summarized in Table 1.4 and discussed in detail in Chapter 12. It is estimated, for example, that around $550 \times 10^6$ t of coal ash is produced worldwide every year, together with $>25 \times 10^6$ t of fly ash from municipal waste incineration (Reijnders, 2005). This includes over $12 \times 10^6$ t of incinerator ashes annually in Europe, $2 \times 10^6$ t in Taiwan, and $6 \times 10^6$ t in Japan. In Italy, $31.7 \times 10^6$ t of municipal solid waste were produced in 2005, of which $3.2 \times 10^6$ t were incinerated (Andreola et al., 2008). Additional hazardous wastes include over $5 \times 10^6$ t annually worldwide of electric arc furnace dusts, and $>10^6$ t of galvanic wastes. It is only relatively recently that the controlled management of toxic and hazardous wastes has become a serious issue, driven in part by the increasing volume of such wastes generated each year.

### 1.1.3 Other Sources of Waste Material

There are additional categories of radioactive wastes for which the borosilicate glasses are not suitable hosts; for example, with the ending of the Cold War, interest was initially expressed in the immobilization of surplus stocks of weapons grade Pu and U from dismantled nuclear weapons. Also, due partly to public concerns over the safety of nuclear power plants, particularly since the accidents at Three Mile Island in 1979 and Chernobyl in 1986, many governments abandoned or severely limited their plans for future nuclear power plants. Consequently, materials that would have been employed in new nuclear facilities were considered less likely to be required, and this also led to a substantial effort during the 1990s in the development of routes for immobilizing and disposing of excess commercial stocks of U and Pu. These new categories of ‘waste’ presented a problem in so far as the borosilicate glasses employed in the vitrification of conventional HLW were
not suitable for immobilizing this class of material due to the low solubility of actinide elements in borosilicate glass. Many novel hosts were developed during this period, some of which continue today to attract interest for alternative applications. The situation which led to these initiatives, and which provided the incentive for the development of many new hosts for dealing with these materials has, of course, changed again with the worldwide drive to curb greenhouse gas emissions, resulting in nuclear power again beginning to reappear on the energy agendas of many countries.

As a result of the Chernobyl and related nuclear incidents, building of new nuclear power stations declined throughout the 1980s and 1990s. This decline initially resulted in Table 1.4 Examples of nonradioactive hazardous wastes and summary of worldwide quantities

<table>
<thead>
<tr>
<th>Waste</th>
<th>Quantities (t year(^{-1}))</th>
<th>Comments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Municipal solid waste incinerator ashes</td>
<td>25 × 10(^6)</td>
<td>Worldwide</td>
<td>Reijnders, 2005</td>
</tr>
<tr>
<td></td>
<td>12 × 10(^6)</td>
<td>Europe</td>
<td>Eighmy et al., 1998</td>
</tr>
<tr>
<td></td>
<td>2.8 × 10(^6)</td>
<td>UK</td>
<td>Tanaka and Johnson, 2005</td>
</tr>
<tr>
<td></td>
<td>5.2 × 10(^3)</td>
<td>Netherlands</td>
<td>Xiao et al., 2008</td>
</tr>
<tr>
<td></td>
<td>2 × 10(^6)</td>
<td>Taiwan</td>
<td>Eighmy et al., 1998</td>
</tr>
<tr>
<td></td>
<td>5.2 × 10(^6)</td>
<td>Japan</td>
<td>Tanaka and Johnson, 2005</td>
</tr>
<tr>
<td>Sewage and dredging sludges</td>
<td>3.8 × 10(^6)</td>
<td>Catalonia, Spain</td>
<td>Garcia-Valles, 2007</td>
</tr>
<tr>
<td>Zinc hydrometallurgical wastes – red mud</td>
<td>5.5 × 10(^6)</td>
<td>Worldwide</td>
<td>Sushil and Batra, 2008</td>
</tr>
<tr>
<td>Blast furnace slags and electric arc furnace dusts</td>
<td>5 × 10(^6)</td>
<td>Electric arc furnace dusts, worldwide</td>
<td>Kavouras et al., 2007</td>
</tr>
<tr>
<td></td>
<td>700 × 10(^3)</td>
<td>Electric arc furnace dusts, USA</td>
<td>Pelino et al., 2002; Mikhail et al., 1996; Kavouras et al., 2007</td>
</tr>
<tr>
<td></td>
<td>15 × 10(^3)</td>
<td>Electric arc furnace dusts, Greece</td>
<td>Rawlings et al., 2006</td>
</tr>
<tr>
<td></td>
<td>10(^6)</td>
<td>Electric arc furnace dusts, Europe</td>
<td></td>
</tr>
<tr>
<td>Alternative metallurgical wastes and slags</td>
<td>24.6 × 10(^6)</td>
<td>Cu floatation wastes worldwide</td>
<td>Çoruh and Ergun, 2006</td>
</tr>
<tr>
<td></td>
<td>150 × 10(^3)</td>
<td>Wastes from the refining of Cu, Turkey</td>
<td>Karamanov et al., 2007</td>
</tr>
<tr>
<td>Metal finishing and plating wastes</td>
<td>10(^6)</td>
<td>Galvanic wastes, worldwide</td>
<td>Silva et al., 2008</td>
</tr>
<tr>
<td></td>
<td>550 × 10(^6)</td>
<td>Worldwide</td>
<td>Reijnders, 2005</td>
</tr>
<tr>
<td>Medical wastes</td>
<td>455.6 × 10(^3)</td>
<td>Regulated medical waste, USA</td>
<td>Lee and Huffman, 1996</td>
</tr>
<tr>
<td></td>
<td>1.65 × 10(^6)</td>
<td>Hospital wastes, China</td>
<td>Zhao et al., 2008</td>
</tr>
<tr>
<td>Electrical and electronic wastes</td>
<td>7.5 × 10(^6)</td>
<td>Europe</td>
<td>Bernardo et al., 2005</td>
</tr>
</tbody>
</table>
in surplus stocks of reactor grade U for power plant operation. A similar situation arose with excess stocks of reactor grade Pu. With the ending of the Cold War, the USA and Russia were also left with surplus stocks of weapons grade Pu and U. Various steps were therefore taken to deal with these perceived excesses, and one possible solution was immobilization either by vitrification or use of a ceramic host, as described in Chapter 9. Other nuclear weapon countries have not at the present time declared any Pu or U that they may currently hold as surplus. In the case of the UK, neither commercial nor military stocks of Pu and U are considered surplus, although contingency plans have been formulated in the event that at some future date some stocks may be declared so (King, 2002; King and Vande Putte 2003). In the case of nuclear fuel, many countries do not currently reprocess spent fuel, and therefore this has been regarded as a separate type of waste. This situation is now changing with the recognition that new energy sources are required in order to meet the ever increasing worldwide demand for additional energy, coupled with the drive toward more environmentally friendly energy sources that do not generate large quantities of greenhouse gases.

1.2 General Disposal Options

As noted, various categories of radioactive wastes are produced as the result of the operation of commercial nuclear power stations and the production of Pu and tritium for military applications. The problem is what to do with all these wastes, legacy as well as current and future, from both nuclear power and defence operations going back over 50 years to the 1950s. Many different options have been considered in the past, some more outrageous than others; the following are some examples:

- Store indefinitely in secure facilities, with regular repackaging as necessary.
- Disposal in sealed drums at sea.
- Burial between tectonic plates.
- Burial under Antarctic ice sheets.
- Disposal in space (e.g. transport to the sun).
- Partitioning and transmutation of long- to short-lived nuclides.
- Monitored retrievable storage either above or below ground (‘nuclear priesthood’).
- Geological disposal, which may be subdivided into the following:
  - Immobilize and make passively safe in a suitable host awaiting permanent nonretrievable disposal in a deep underground repository.
  - Very deep underground disposal (e.g. >4 km).
  - Direct injection of liquid waste into geological rock formations.

Many of these options are either not technically feasible or they are now considered environmentally unacceptable and have been banned by international agreement (Nirex, 2002). In the case of LLW and ILW, disposal at sea was carried out by a number of countries including the USA, Japan, Belgium, France, Sweden, Finland, Spain, Germany, the Netherlands, Switzerland, Italy, South Korea and the UK over the period 1949 to 1982. This method of disposal is now environmentally unacceptable and is internationally banned.

Burial between tectonic plates or under Antarctic ice sheets has also been seriously considered, primarily by the USA, but again has been rejected as a viable and
Introduction

environmentally acceptable method by most countries, as has disposal in space. In the case of disposal in space, firing into the sun would present an ideal solution, but the cost, together with the prospect of space vehicles carrying waste failing and returning to the ground, make this a totally unacceptable route at the present time. Similarly, for burial between tectonic plates the possibility arises that the waste constituents might be expelled through volcanic action at some other site on the earth, as depicted in Figure 1.2, again making this an unacceptable solution (Nirex, 2002). In the case of burial under ice sheets it has been proposed that containers of heat-generating HLW be placed in stable ice sheets in Greenland or the Antarctic. The heat would melt the ice, and the containers would progressively sink into the ice sheets with the ice reforming above them creating a thick solid barrier layer. Although seriously considered as a viable method (but never imple-
mented) the disposal of radioactive waste within the Antarctic was banned after the Antarctic came under international control through the Antarctic Treaty of 1959. A similar ban was implemented by Greenland.

Use of very long term monitored retrievable storage, although reasonable in principle and with one advantage being that the integrity of the storage facility could readily and regularly be observed and confirmed, suffers from the major disadvantage that it would rely on the long term stability and security of society. There is no guarantee that social order, as we know it, will survive over a period of hundreds of thousands or even thousands of years. Such a facility would also be open to more intermediate term social unrest and natural disasters including war, meteor impact, earthquake damage, flooding, and even terrorist attack.

Partitioning and transmutation of long- to short-lived radionuclides has also been proposed as a method of dealing with HLW (Bowman and Venneri, 1993; Beller et al., 2001; King, 2002; Van Tuyle et al., 2002; Chwaszczeński and Słowiński, 2003). This would rely on the separation or partitioning of the long-lived isotopes present in HLW, including the minor actinides, together with fission products such as $^{129}$I and $^{99}$Tc. After chemical separation, these would be transmuted in a nuclear reactor by bombardment with neutrons to produce shorter lived isotopes, thereby alleviating their longer term hazard; these could then be vitrified with other wastes, leading to less of a long term impact. This is undoubtedly a technology for the future, aimed at the management of spent fuel rather than existing HLW from reprocessing, and with many countries actively engaged in research in this area, including the USA, Russia, France, Japan, Spain, Germany, China, Belgium, the Netherlands, Italy and South Korea.

It was ultimately agreed that wastes must be treated before disposal in order to render them passively safe. To be passively safe requires that safety be assured without dependence on active systems, maintenance, monitoring, or human intervention. The radioactive material should be in a form that is physically and chemically stable and the waste package should be acceptable for final disposal. The question then arises as to what form the passively safe wasteform package should take. There are a number of intrinsic wasteform possibilities; these include a vitrified wasteform where glass is employed as a solvent for the waste; a ceramic wasteform where a ceramic is employed as a solvent, with different ceramic mineral phases acting as hosts for specific waste constituents; encapsulation in a suitable matrix which may be metal, glass, ceramic, cement, polymer, or other ‘inert’ medium; or a hybrid system in which the advantages of different materials are combined to form a composite solution to the problem. The different options are illustrated in Figure 1.3. Encapsulation of waste is normally only employed for LLW or certain categories of ILW as, strictly speaking, the resultant wasteform is not passively safe. This is because damage or disintegration of the matrix surrounding the waste particles will release the waste constituents into the surroundings. To be passively safe the waste elements must be chemically incorporated into a stable host lattice and must be highly leach resistant.

Most countries that have stock piles of HLW, TRU waste and certain categories of long-lived ILW, are investigating the feasibility of underground repositories in stable geological surroundings for the long term storage and ultimate disposal of these wastes. There have been many studies over the years aimed at identifying the criteria and quantifying the requirements necessary for ensuring satisfactory site selection (Miller et al.,
Ewing reaches the conclusion that ‘because of the uncertainties in performance assessments of geological repositories, it is misleading to identify a performance or risk assessment as quantitative’. He concedes that such assessments are, however, an absolutely necessary part of the political and regulatory process, but that a performance assessment in itself is not a sufficient basis for determining whether or not a given site is or will be safe. In the case of the proposed Yucca Mountain repository in the USA the near-field environment consists of the host rock, together with dust and water through seepage and pores. The geochemistry of these surroundings has been extensively studied in order to assess the likely impact they may have on the long term properties of nuclear wasteforms, in addition to the impact that the wasteforms themselves may have on the surroundings.
The surrounding rock mass has been studied at a number of sites (Hadgu et al., 2007). It is recognized that after the drifts are sealed temperatures will rise and create a dried out zone in the rock mass. As the waste cools and the temperature decreases humidity will increase to around 100% after $10^4$–$10^6$ years. Analyses of solutes in pore and seepage water indicate concentrations of many elements including $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{K}^+$, $\text{Na}^+$, $\text{NH}_4^+$, $\text{SiO}_2$, $\text{Cl}^-$, $\text{Br}^-$, $\text{F}^-$, $\text{HCO}_3^-$, $\text{NO}_3^-$, $\text{SO}_4^{2-}$ and $\text{PO}_4^{3-}$. As noted by Hadgu et al. (2007) and Peterman and Oliver (2007), radioactive waste canisters will generate significant quantities of heat, and it is important that this generated heat be taken into account in considering the suitability of a repository site. Such a study has been undertaken to determine how this heat will affect the thermal hydrology of the Yucca Mountain site and also how possible mineralogical reactions between repository components may affect overall performance. Some concerns have also been raised over the possibility that cement used in the construction of a repository may react with the silica in host rocks to form colloidal silica which could subsequently affect the migration of radionuclides (Chida et al., 2004); this is an additional factor that must be taken into account, as covered in Chapter 10.

The only country currently with a working underground repository is the USA with the Waste Isolation Pilot Plant (WIPP) at Carlsbad in New Mexico. This is situated 658 m below the surface within a salt deposit, and is employed for TRU wastes (Matthews, 2003). These ILW/TRU waste systems are cemented into steel drums with magnesium oxide surrounding the containers. Containment of radionuclides relies on a complete absence of water flow in these salt deposits, together with a gradual self-sealing of the repository due to creep of the salt. As noted earlier, the USA is also developing a site at Yucca Mountain in Nevada as a deep underground repository for HLW. This is situated adjacent to the underground nuclear weapons test site, as shown in Figure 1.4, and is believed to be a geologically stable area, although some doubts have been raised as to the areas very long term suitability (Dublyansky and Smirnov, 2005), with the possibility of volcanic activity in geological timescales and the presence of a fault zone. Approval for submission of an application for construction of the Yucca Mountain repository site was given by President Bush in July 2002. Later that year the US Congress ratified the recommendation despite objection by the Governor of Nevada. A licence application was subsequently prepared by the DOE for submission in December 2004. It was originally anticipated that the site could be operational as early as 2010. In fact, it was announced by the new administration of President Obama in 2009 that funding for the project has been cut and alternatives will be sought (Doggett, 2009). This is despite the US$13.5 billion spent so far. It is proposed that the estimated 600,000 t of spent reactor fuel will remain at the various nuclear power plants awaiting a new disposal option. Other areas worldwide under investigation as potential repository sites include Grimsel in Switzerland (Kickmaier et al., 2001), Åspö in Sweden, Mol in Belgium, Bure in France, Eurajoki and more recently Olkiluoto in Finland (Vaittinen et al., 2004), the Mont Terri underground research laboratory and Zürcher Weinland (Kuhlmann and Marschall, 2004) in Switzerland, the Asse salt mine in Germany, and regions around Woomera in South Australia (Perkins et al., 2001). In addition, Italy, Holland and Japan are actively seeking out potential sites (Tsuchi et al., 2004). Commissioning of a disposal facility in France is proposed for 2025 (Toulhoat, 2007). However, other nuclear countries including the UK, Spain and Canada have yet to commence detailed programmes in this area, although some studies are in progress (Lodha...
et al., 2004). The UK Government, for example, has recently put out a request for information aimed at the selection of potential disposal sites. The environmental issues relevant to the sighting of such sites cannot, of course, be over emphasized, and these have been covered in a number of publications (Nirex, 2001; Patton et al., 2001).

Figure 1.4 Yucca Mountain, Nevada, repository site. [Reprinted with permission from Scientific Basis for Nuclear Waste Management Proceedings XXIV, Vol. 663, Warrendale, PA, Insights to repository performance through study of a nuclear test site by D. K. Smith et al. Copyright (2001) Materials Research Society]
Alternative geological disposal options that have been or still are being considered include the original concept of very deep geological disposal (Sizgek, 2001). This involves the placement of HLW containers in boreholes several kilometres deep (typically 4–6 km), rather than the few hundred metres depth characteristic of conventional underground repositories, where the intrinsic heat of the surrounding rock combined with decay heat generated by the waste package may melt the rock and dissolve the HLW constituents (Nirex, 2002). As the heat generating fission products cool, the surrounding rock would solidify thus immobilizing the waste in a natural wasteform formed *in situ* at this great depth. One advantage of this method would be that the waste would not need to be immobilized before disposal; however, this is offset by the fact that reliance on melting rock to immobilize the waste successfully could not be easily confirmed, and the waste might simply be dispersed without being rendered passively safe. A related concept involves placing waste that has been immobilized first in containers in very deep boreholes where the temperature would be sufficient to melt the rock but not the containers themselves (Gibb, 1999). On cooling, the rock would solidify around the containers, thus forming a natural barrier. Disadvantages associated with this method include high anticipated cost, identification of a suitable container material, being able to confirm that the containers had been successfully sealed into the rock, and the effect of interactions at the high temperatures involved between the wasteform, the container, and the rock itself, i.e. would interaction of the surroundings with the wasteform degrade its properties, particularly in terms of long term chemical durability, or would the geological environment itself be damaged. Some of these questions have been addressed more recently and possible solutions proposed. For example, Attrill and Gibb (2003) and Gibb *et al.* (2008b) have proposed encapsulation of Pu-containing wastes in granite prior to burial in boreholes 5–6 km deep. Prior encapsulation would be accomplished by mixing waste, which had probably already been immobilized in a ceramic matrix such as zircon or zirconolite, with powdered granite to form granite cylinders. Under borehole conditions the granite matrix would at first melt but later solidify to provide a granite-to-granite seal with the borehole rock itself. Alternatively, *in situ* sintering has been proposed whereby mixtures of waste and matrix constituents would be placed in a deep borehole where the temperature and pressure was sufficient to instigate sintering and consolidation of the mixture to yield a geochemically stable wasteform in equilibrium with the surroundings (Ojovan *et al.*, 2004).

Direct injection of radioactive and hazardous wastes in liquid form into rock formations deep underground has also been proposed (Apps and Tsang, 1996; Rumynin *et al.*, 2005; Tsang and Apps, 2005). This has been implemented to some degree both by the USA and Russia. In Russia, liquid LLW, ILW and HLW has been injected into porous sandstone formations overlaid with clay at depths of up to 1400 m. Liquid LLW was also injected at a depth of 300 m into shale formations at the Oak Ridge National Laboratory (ORNL) in the USA in the 1970s, but further injection was later abandoned due to concerns over possible migration of waste constituents.

Spent fuel has itself been considered as the wasteform, destined ultimately for final disposal. This does present certain advantages; for example, the cost of reprocessing is eliminated and new reprocessing wastes are not generated. An added advantage is that should the need to reprocess become necessary at some later time due to fuel shortages, the shorter lived fission products will have progressively decayed, leaving a somewhat
safer material to deal with. This, of course, relies on the spent fuel being retained in secure and accessible facilities. Disposal concepts to deal with spent fuel have been considered and include the placing of fuel assemblies directly into steel-lined copper canisters which may or may not be back-filled with lead or glass, and ultimately storing/disposing of these in underground repositories. Gibb et al. (2008a) have suggested an alternative disposal route for spent fuel elements utilizing a variant of the very deep borehole disposal concept in which fine lead alloy shot would be introduced into the 4–5 km deep borehole along with the fuel rod containers. The lead alloy would be expected to melt under the initial borehole conditions and fill in any gaps and fissures between the surrounding rock and the containers. As the containers would in effect be floating in a liquid medium it would not be necessary for individual containers to support and survive the weight of overlying containers or back-fill. Eventually, the lead would cool and solidify and encase the containers in a solid lead sarcophagus sealed into the rock.

On a final note, it is worth mentioning the Pangea proposal. This is a privately funded project that has not yet been fully endorsed by any government. At present there is a clear international understanding that each nuclear country is responsible for the storage/disposal of its own radioactive wastes. It may make longer term sense, however, to consider a multinational approach to the management and disposal of radioactive waste including spent fuel, as noted by the Director-General of the IAEA in 2003, who also observed that there would be considerable advantages in terms of cost, safety, security and nonproliferation gained from international cooperation in this area. The issue of an international repository had already been addressed earlier, initially in the 1990s, by Pangea Resources International and Pangea Resources Australia, a consortium of companies including BNFL, EHL and Nagra, who identified a number of international sites with appropriate geological conditions for locating a common deep underground repository (Kurzeme, 1999; Black and Chapman, 2001; Hill and Gunton, 2001; Mccombe and Kurzeme, 2001; Mccombe & Chapman, 2002). These sites were based on meeting a number of specific criteria in addition to stable geology, including a stable and arid climate with little erosion, flat topography and low permeability host rock to reduce groundwater movement, old and saline groundwater indicating negligible groundwater movement, reducing geochemical conditions to minimize the solubility of radionuclides, a low population density, an absence of conflicts in terms of resources, and economic and political viability. On this basis, areas within Argentina, South Africa, Russia, China, Mongolia and Australia were selected for more detailed evaluation. Of these, the desert basin area of Western Australia was highlighted as one of the most suitable on geological, economic and political grounds, and pilot feasibility studies are currently underway. The overall proposal envisages a dedicated port and rail linkages to an inland repository aimed at nuclear waste disposal from most countries other than the USA. Unfortunately, at the present time, there is only limited political support in Australia for this concept, with the Nuclear Waste Storage Facility (Prohibition) Bill passed in the Australian Parliament in 1999. There is some evidence to suggest that objections to such a facility are relaxing in Australia, and the concept of an international site may therefore be more favourably received in future years. There is no doubt that such a project does indeed offer a number of significant advantages in addition to those already outlined. These include the fact that there is a need for economically viable commercial waste disposal options for small countries where suitable disposal sites may be difficult or impossible to identify, and there are political, economic
and security benefits associated with international cooperation. Transport of radioactive waste around the world to such an international site is a cause for some concern, but this issue has been treated comprehensively with reference to public safety (Tunaboylu et al., 2001).

### 1.3 Radiation Issues

There are many public concerns regarding radioactivity and radioactive wastes, as noted in Table 1.5. Radioactive materials and radiation are perceived as highly dangerous, and there are concerns that the wastes generated by nuclear power stations will be released into the environment. Radiation is, of course, a natural phenomenon and can, with proper safeguards, be handled safely. The major causes of natural radiation include U, Th and $^{40}$K that are present in the earth’s crust, together with their decay products, one of the most important of which is radon gas (Hart, 2005). There are many sources of background ionizing radiation to which everyone is normally exposed. The highest levels occur in geological areas where granite or mineralized sands are predominant, and are due to traces of naturally occurring radioactive materials including U and Th minerals and the decay product radon gas. Living at high altitudes also increases the level of cosmic radiation received. Medical and dental use of X-rays may also increase exposure. Background radiation comprises around 87% natural radiation together with 13% from artificial sources which include, in order of severity, medicinal uses, various miscellaneous sources, fallout from early atmospheric nuclear weapons tests, occupational exposure, and radiation due to nuclear discharges, as illustrated in Figure 1.5. It should be noted that there are no differences in effect on materials, including biological systems, between natural and artificial radiation (Hall, 2002).

The radiation effects on humans are measured in Sieverts (Sv) which is a measure of the effective dose received (1Sv = 100rem). It is known that the minimum dose received by everyone on the earth comprises the typical natural background level of around 2mSv year$^{-1}$. There is no scientific evidence of risk (for example, of developing cancers) at doses below 50mSv in the short term or 100mSv per year in the longer term.

### Table 1.5 Concerns over radioactivity and radioactive waste

<table>
<thead>
<tr>
<th>Concern</th>
<th>Negative Image</th>
<th>Reality</th>
<th>Positive Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation is dangerous</td>
<td>• Cancer • Birth deformities • Pollution</td>
<td>• Radiation is natural • Radiation can be handled safely</td>
<td>• Morro do Ferro, Brazil • Ramsar, Iran; • Kerala &amp; Madras, India</td>
</tr>
<tr>
<td>Geological disposal is not safe</td>
<td>• Leaking waste dumps</td>
<td>• Engineered repositories</td>
<td>• Oklo, Gabon, was a natural nuclear reactor where radioactivity has not migrated • Natural analogues</td>
</tr>
<tr>
<td>The barriers will not last</td>
<td>• Release into the environment</td>
<td>• Natural materials can last for millions of years</td>
<td></td>
</tr>
</tbody>
</table>
However, it is known that a short term dose of $>1000$ mSv is sufficient to cause immediate radiation sickness, whilst a dose of $10000$ mSv would normally result in death within a few weeks.

Notably, there are many examples worldwide of where relatively high natural background radiation levels ($>50$ mSv year$^{-1}$) have not apparently caused significant health related problems. For example, the Morro do Ferro region in Brazil, Ramsar in Iran, and Kerala and Madras in India (Hart, 2005). The Morro do Ferro region, a pleasant natural environment, depicted in Figure 1.6, also known as the ‘Mount of Iron’, is situated 34 km from the town of Oliveira, with an estimated 30000t of Th near the summit, this giving rise to a high background radiation level, whilst in Ramsar, a city in northern Iran near the Caspian Sea, a dose of 260 mSv year$^{-1}$ has been estimated. The radiation source in Ramsar arises from the many hot springs in the area, these containing the $^{226}$Ra isotope. Apparently, none of these sites show evidence for increased ill health effects in animals or humans. In fact, a limited number of studies, as reviewed by Cameron (2001), tend to indicate that some degree of background radiation may in fact be good for the immune system, although it is apparent that many more studies are required before definitive conclusions can be drawn. In general, exposure to radiation should always be kept as low as is reasonably practicable, and avoided where possible.

Figure 1.5  Pie chart illustrating composition of background radiation. [Reprinted from schoolphysics.co.uk. With kind permission from Keith Gibbs. http://www.schoolphysics.co.uk/teachers/OHT%20sheets/Nuclear/Background_pie_chart/index.html.]
There are general concerns that geological disposal will not be safe, with the perception of leaking waste dumps and barriers that will not last. The reality is that disposal will inevitably involve carefully engineered repositories and the wasteforms produced will be designed to be stable as far as is possible over geological timescales. On this issue there are informative lessons to be learnt from nature.

For example, a series of natural nuclear fission reactors have been discovered at various sites within the Franceville basin in south-eastern Gabon, this region having been mined for U since 1961. These sites include Oklo (The ‘Oklo Fossil Reactors’), where the first reactor was found in 1972, and Bangombé, with these reactors running for around 600–800×10³ years. This region of Gabon, believed to be 2×10⁹ years old, has contained the radioactive products in the surrounding granite, sandstone and clay, with no major release into the environment. ‘Nature showed that it could effectively contain the radioactive wastes created by the reactions; for example, Pu has migrated <1 m from where it was formed two billion years ago’ (DOE, 2004; Horie et al., 2004). The reactors at Oklo have now been extensively mined and the remaining parts of the reactors are at this time inaccessible, whilst the single reactor at Bangombé has been spared for further scientific study. The region consists of sedimentary deposits with sandstones, shales and clay. The conditions necessary for fission reactions to occur at these sites included a high U content with high fissionable isotope concentration which enabled critical mass to be reached (the great age of the U deposits in these reactors gave a ²³⁵U content of around 3.7%), a low concentration of neutron poisons, including boron and rare earth elements in the immediate geological environment, and a high concentration of light elements, for example hydrogen in water which acted as a neutron moderator to control the nuclear reaction. Criticality occurred due to groundwater permeating these U-rich mineral deposits. The Oklo site, illustrated in Figure 1.7(a), is composed of 16 natural reactor cores with the
Figure 1.7  (a) Illustration of Oklo natural reactor region and (b) section through geological environment of a reactor. [Reproduced from Geochimica et Cosmochimica Acta, Redistribution of fissionogenic and non-fissionogenic REE, Th and U in and around natural fission reactors at Oklo and Bangombe, Gabon by H. Hidaka and F. Gauthier-Lafaye, 64, 12, 2093–2108. Copyright (2000) Elsevier Ltd]
individual cores typically a few metres long and wide by a few tens of centimetres thick and ranging in depth from around 3000 m for many of the Oklo reactors to only 12 m for the Bangombé reactor, as illustrated in Figure 1.7(b) which shows a section through the geological environment of a representative reactor. A photograph of the imprint of a fission reactor core at Oklo is shown in Figure 1.8.

These reactors have been considered as excellent analogues for the disposal of radioactive wastes in geological repositories, and it has been noted that they have provided a unique opportunity to study actinide and fission product migration in an extremely old natural system (Gauthier-Lafaye et al., 1996; Touhoat et al., 1996; Pourcelot and Gauthier-Lafaye, 1998; Fernández-Diaz et al., 2000; Hidaka and Gauthier-Lafaye, 2000; Gauthier-Lafaye, 2002; Bros et al., 2003; Gurban et al., 2003; Stille et al., 2003; Horie et al., 2004). In addition, the shallow depth of the Bangombé reactor has rendered it susceptible to near-surface weathering effects, from which lessons have been learnt. Uranium is present in the reactor cores mainly as the mineral uraninite with some coffinite, USiO₄·xH₂O. Actinides and fission products including Np, Pu, Am, Cm, Ru, Rh, Pd, Te, Y, Nb, Tc, Bi, Th, rare earth elements and Zr have mainly been retained within the uraninite structure. Exceptions include the noble gases Xe and Kr, together with I, Br, Cd, Rb, Cs, Sr, Ba, Te, Pb, Mo, Sn and Ag. Many of these elements have been found within or close to the core of the reactors within a hydrothermal alteration region or halo as metallic aggregates and crystals of galena (Bros et al., 2003). Also present within these
regions have been found phosphate phases, in particular apatites, containing nuclides such as Nd, Sm, Gd, Pb, Sr and Rb (Horie et al., 2004). Aluminium phosphate mineral phases containing Zr, Ce, Nd and Sm nuclides have also been discovered. In addition, chlorite and calcite minerals have been detected in the clays associated with some of the reactors. It has been stressed (Gauthier-Lafaye et al., 1996) that the Oklo reactors represent the only occurrence in the world where actinides and fission products have been retained in a geological environment for very long periods of time. The analogy between Oklo and proposed deep underground nuclear waste repositories is therefore very relevant. Studies that have been conducted are providing invaluable data on the geological, mineralogical and geochemical parameters responsible for the retention or migration of actinide and fission products in a geological system. The presence of clay and phosphate minerals at Oklo has also been shown to be important in playing a role in the retention of fission products, demonstrating clearly the importance that secondary barriers will play in an engineered repository design, making it very clear therefore that engineered barriers can be extremely successful. In addition to Oklo, there are numerous other natural sites containing radioactive minerals where the radioactivity has not migrated during geological timescales. For example, the Morro do Ferro region of Brazil, where the Th and its decay products have weathered millions of years without migrating, and similarly the Koongarra U ore deposit in Australia where groundwaters have been flowing and the U and its decay products have migrated only a few metres away from the main site (Warf and Plotkin, 1996). A report by Nirex (2001) outlines some of the main criteria that are important in the understanding and design of a deep underground repository.

It has also been possible to monitor radionuclide migration under analogue repository conditions by analysing the environment at the Nevada nuclear test site in the USA (Bowen et al., 2001; Smith et al., 2001). Over 800 underground nuclear tests were carried out at this site at a depth of between 600 m and 1200 m over the period 1951–1992, with around 300 being performed at or below the static water level. Radioactive elements produced during these tests have been incorporated into silicate glass produced under the extreme temperatures and pressures of a nuclear explosion (>10^6 K and 1 Mbar). It is estimated that during an underground nuclear explosion around 700 t of glass is produced per kiloton of nuclear yield (Olsen, 1967). The composition of the glass produced at the Nevada test site has been identified as 13.7Al_2O_3 - 2.3CaO - 3.1Fe_2O_3 - 2.9K_2O - 0.9MgO - 1.1Na_2O - 75.9SiO_2 (mass%), with smaller additions of Am_2O_3, Cs_2O, Eu_2O_3, PuO_2, SrO and P_2O_5 (Tompson et al., 1999). These tests have provided the opportunity to monitor radionuclide solubility and release as a function of groundwater flow in the absence of specific repository engineered multibarrier systems. The proposed Yucca Mountain repository will be situated above the water table, analogous to the underground tests carried out at this level. Data from underground tests under worst scenario conditions below the water table where water flow is estimated to be of the order of 76 m year^{-1}, have provided the most useful statistics and are providing information relevant to the design of the Yucca Mountain repository with its engineered barriers. This in turn is promoting confidence that this site will offer a safe and effective disposal environment.

In addition to the environments at the natural reactors and the Nevada test site, there are also many naturally occurring mineral phases and volcanic glasses containing high concentrations of radioactive elements that have been noted to have weathered well over geological timescales, showing that stable and remarkably durable wasteforms are indeed
possible. This is coupled with comprehensive experimental studies of the radiation effects in many different materials (Ewing et al., 1998), discussed in detail in Chapter 10.

1.5 Nuclear Accidents and the Lessons Learnt

There have been a number of incidents involving nuclear facilities, some more serious than others, from which lessons have been learnt. It is important to stress that the majority of reports involving radiation-related incidents and accidents have usually been caused by poor power or research reactor design, often coupled with human error, and significant lessons have indeed been learnt from these. It is important, nevertheless, not to forget these incidents and why they occurred. The worst nuclear incident in the history of nuclear power occurred at Chernobyl in Ukraine, then part of the former Soviet Union, on 26 April 1986, and was caused by a combination of an unauthorized experiment and defective reactor design, as highlighted later; however, the first major reactor accident and publicised release of radioactivity into the environment occurred between 10 and 11 October 1957 at the Windscale plant (Sellafield) in Cumbria in the UK, resulting in contamination falling in England and parts of Western and Northern Europe including Holland, Belgium, Germany and Norway (Arnold, 2007; Garland and Wakefield, 2007; Bergan et al., 2008).

It is important to stress that the Windscale reactor was not a commercial reactor for power generation, but rather a reactor for producing Pu, and later tritium, for the UK’s very early nuclear weapons programme. Two piles were built at Windscale, shown in Figure 1.9, both relatively low temperature graphite-moderated reactors fuelled with natural U (and later some slightly enriched U to increase the reactivity of the pile). The reactors were air cooled with fans blowing air through the reactor cores. The cooling air was discharged to the atmosphere via 125 m high stacks fitted with filters. Each pile contained 180 t of U rods encased in a total of around 70000 finned aluminium fuel cans. These were located in batches of 21 in 3440 horizontal channels within 1966 t of precisely machined graphite blocks in an octagonal stack, the graphite acting both as moderator and pile structure. The power level of the reactors was controlled by 24 horizontal rods of boron steel. Twelve additional vertical rods were incorporated to facilitate rapid emergency shut down. Each reactor core was enclosed in a reinforced concrete radiation shield just over 2 m thick. Neutron irradiation of $^{238}$U and a lithium alloy produced $^{239}$Pu and $^3$H, respectively. A particular known problem associated with the use of a graphite moderator was Wigner growth, radiation damage causing graphite to change dimensions, and this had to be taken into account in the reactor design. A less well known effect at that time was Wigner energy, whereby energy is stored in the graphite on irradiation over time. This may subsequently be released spontaneously, leading to a potentially catastrophic rise in temperature. It was therefore necessary to anneal the graphite periodically by controlled heating to remove the stress. This was not a standard operation, and had no detailed set procedure, as Wigner releases tended to be unpredictable, and therefore the knowledge of the operators and experience of past anneals had to be relied on. It is believed that the incident was precipitated due to a combination of localized Wigner energy release coupled with a burst U or Li-Mg can. This initiated a fire in the reactor core of Pile Number One during just such an annealing operation. The much localized
fire in the reactor core rapidly became a runaway event, and exceptional measures had to be taken to bring it under control and prevent the whole pile catching fire. The fire resulted in the release of some quantities of radionuclides via the reactor stack into the environment, with the main contaminant being radioactive $^{131}$I, together with minor quantities of a number of volatile radioisotopes including $^{137}$Cs, $^{210}$Po, $^{89}$Sr and $^{90}$Sr. The overall cause of the accident at this time seems to have been due to a combination of factors. These included insufficient knowledge of the behaviour of irradiated graphite, weaknesses in reactor instrumentation for monitoring Wigner releases, and intense pressure on staff to deliver to very tight timescales. In hindsight it has been argued that the accident had been inevitable. It was certainly not the fault of any one individual and the Windscale staff acted with outstanding courage, resourcefulness and devotion to duty in combating the event (Arnold, 2007). This accident demonstrated the importance and need for adequate R&D coupled with very close coordination with those responsible for operational requirements, and the incident yielded timely and important information on nuclear safety.

In the case of the Chernobyl incident, the reactors at Chernobyl are based on the RBMK-1000 design which is a graphite moderated boiling light-water-cooled facility illustrated in Figure 1.10 (OECD, 2002). This type of reactor is quite different from most power reactor designs in use around the world as it was intended for both power generation and production of Pu, and the combination of water coolant and graphite moderator is not now found in any other power reactor design. At the time in 1986 there were four nuclear reactors in operation at Chernobyl, with two more RBMK designs under construction. The RBMK reactors use slightly enriched U fuel (2% $^{235}$U) in the form of uranium
dioxide. Water is passed through pressure tubes containing the uranium dioxide fuel encased in zirconium alloy fuel rods, the water acting as coolant and producing steam which is used directly to power two 500 MW turbines. Graphite blocks surround the pressure tubes, acting as moderator. Heat distribution is improved through the core by circulation of a nitrogen-helium mix that also prevents oxidation of the graphite. Boron carbide control rods are used to control the rate of fission. The core of these reactors is around 7 m high by 12 m in diameter and is located within a concrete lined cavity that acts as a radiation shield. The reactor cover plate, or upper radiation shield, is made of steel and also supports the fuel assemblies. A number of safety features were used in this design including emergency core cooling and the requirement for at least 30 control rods to be inserted at any given time. The overall characteristics of the RBMK design mean that if the power increases or the flow of water decreases then more steam is produced in the pressure channels. This has the effect of increasing fission, but as the power increases so does the fuel temperature and this leads to a reduction in neutron flux. These opposing characteristics vary according to the power level. At high power levels during normal reactor operation power excursions which would lead to fuel overheating do not occur, but at lower power levels the reactor becomes unstable and the likelihood of sudden power surges increases.

On 25 April 1986 the Unit 4 reactor was to be shut down for routine maintenance and it was decided to take this opportunity to establish whether or not, faced with a loss of station power, the turbine, as it slowed down, could provide enough power to operate emergency equipment, in addition to the core cooling pumps, until a back-up diesel generator came on line. This test was not, however, apparently carried out with the knowledge

![Diagram of RBMK reactor](Diagrammatic)
of the team responsible for reactor operation and safety. This led to a series of catastrophic events in which control rods were removed leaving less than the 30 rods considered necessary for safe operation, with the reactor subsequently becoming unstable. At the same time the slowing turbines could no longer provide sufficient power to maintain cooling water pressure. The result was a tremendous power surge. The subsequent rise in core temperature ruptured the fuel cans allowing hot fuel to react with water causing a steam explosion followed by a second, possibly hydrogen explosion, powerful enough to blow off the 1000t reactor cover plate and the roof of the building, thus exposing the reactor core to the atmosphere. Exposure to air caused the graphite core to catch fire discharging U fuel, fission products and noble gases into the environment, with a plume rising over 1 km in height into the atmosphere. The core continued to burn for 10 days, ending in another explosion. It is reported that after fighting the resulting fires a total of 31 firemen died due to the radiation. The resulting long-range release of radionuclides, composed mainly of $^{137}$Cs and $^{134}$Cs particulates and gaseous $^{131}$I, but also containing many more fission products with both short and longer half lives, contaminated many parts of Central and Northern Europe, reaching as far away as the UK (Bell and Shaw, 2005), and with the short-term consequences for agriculture ultimately proving more serious than originally predicted. After the event, the reactor building, shown before and after the explosion in Figure 1.11, contained large quantities of melted fuel rods and vitrified products resulting from reaction of sand used in the clean-up process with reactor constituents. This yielded a ‘lava’ like substance which contained up to around 3 mass% U. Solidified melted products are illustrated in Figure 1.12. It was subsequently agreed that the Chernobyl incident was due to a lack of an effective safety culture coupled with poor reactor design. Since this incident and the experiences gained from it, numerous improvements have been made in all aspects relating to nuclear safety, and cooperation between nations regarding nuclear accidents has been substantially improved. In addition, many new safety features have been introduced into the existing larger RBMK-1500 reactor facilities (Ušpuras et al., 2006, 2007).

Another reactor accident, albeit with far less serious consequences, occurred at the Three Mile Island nuclear power plant in the USA on 29 March 1979, and was a consequence of the plant operating system being unable to cope successfully with a series of unusual events (Le Bot, 2004). This led to exposure of the reactor core and the release of radionuclides into the containment building which, unlike the incident at Chernobyl, successfully prevented the release of major radioactive products into the environment. To put these incidents into context, it was estimated that 16 Ci of $^{131}$I was released into the atmosphere at Three Mile Island, compared with $20 \times 10^3 \text{Ci}\) at Windscale (this was the only major fission product to be released), whilst up to $50 \times 10^6 \text{Ci}\) of fission products were released at Chernobyl (Arnold, 2007).

There have been a number of additional reported accidents involving nuclear facilities or materials that warrant consideration from an historical perspective. On 11 March 1997, for example, a fire and explosion occurred at the low level waste facility of the Power Reactor and Nuclear Fuel Development Corporation (PNC) in Tokai, Japan, which resulted in a minor release of radioactivity into the surrounding environment (Igarashi et al., 1999; Sun et al., 2005). Another, more serious, incident occurred at the JCO Company’s U fuel facility in Tokai-mura, Japan on 30 September 1999. This resulted in a criticality event in a precipitation tank with the release of a number of fission products
Figure 1.11 Chernobyl before and after the explosion. [Reproduced from http://insp.pnl.gov/-library-uk_ch_1-1.htm with kind permission from PNL]

and neutron-induced radionuclides including $^{131}$I, $^{133}$I, $^{135}$I, $^{24}$Na, $^{56}$Mn, $^{91}$Sr, $^{46}$Sc, $^{59}$Fe, $^{60}$Co, $^{140}$La, $^{137}$Cs and $^{138}$Cs into the immediate locality, but with no significant release outside. The main danger came from neutron and $\gamma$-radiation released by the criticality event, with radiation levels as high as 4.5 mSv h$^{-1}$ being recorded 90 m from the building over a period of around 20 h (Koide et al., 2000; Komura et al., 2000; Takada and Hoshi, 2000). Again, both these incidents occurred during a deviation from standard procedures. Additional events include the dispersal of U and Pu as a result of accidents involving military aircraft carrying nuclear bombs (Lind et al., 2007). In one accident on 17 January 1966 a B52 bomber collided with an airborne fuel tanker over southern Spain, resulting in release of the bombs and causing radioactive contamination over a 2.3 km$^2$ area around Palomares. In another incident in 1968, a B52 bomber crashed at Bylot Sound in Greenland
Figure 1.12 Chernobyl fused nuclear fuel/glass: (a) ‘stalactite’ emerging from the roof of a corridor; (b) issuing from a steam distribution header. [Reproduced from http://insp.pnl.gov/-library-uk_ch_1-1.htm with kind permission from PNL, The Kurchalov Institute (Russia) and the ISTC Shelter (Ukraine)]
releasing radioactivity over a distance of a few kilometres. Lessons have been learnt, and it is highly unlikely that incidents such as these could be repeated today.

A study of the contribution of design to accidents in the aircraft and nuclear industries has concluded that as many as 50–60% of all accidents have root causes in the actual design of the facility (Kinnersley and Roelen, 2007). Societal factors may also play an important role in creating conditions favourable for the occurrence of major accidents, as highlighted by Britkov and Sergeev (1998) in relation to Chernobyl and Three Mile Island. Today, much more in depth consideration is given to all new engineering projects, including nuclear plants, with exhaustive safety and risk assessment procedures in place. It must therefore be stressed that it is far less likely that such incidents could occur today. Past events must not, of course, be forgotten, and it is important that experiences gained are retained and acted upon.

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