Chapter 2

Literature Review

It is now apparent that global warming is a serious concern for the current century. With the United Nations Framework Convention on Climate Change (UNFCCC) Kyoto protocol [2] calling for a reduction in green house emissions to 92% of 1990 levels for the United Kingdom (U.K.) and 93% of 1990 levels for the United States of America (U.S.A.), other countries have been given similar targets (see reference [2]). The challenge facing the world is to reach or exceed these targets.

In the U.K., the global warming potential from CO_2 emissions in 2002 was greater that the potential for all other greenhouse gases summed together [6] making it the priority concern for any programme to reduce emissions. The report on U.K. emission of air pollutants 1970-2002 [6] also states that the greatest single contribution to CO_2 emissions comes from the public power sector at 29%. This is closely followed by road transport at 22% and these combine to form just over half of the U.K.'s CO_2 output. These two areas obviously have to be the primary targets for any programme to reduce emissions. One of the most promising long term solutions is to switch to alternative, non-polluting, primary energy sources. One way to do this would be to move away from a hydrocarbon based economy to a hydrogen economy to reduce emissions from the transport and industrial sectors.

A large source of radioactive material that has to be dealt with (apart from civilian nuclear power plants which will be discussed later) consists of highly enriched uranium and plutonium resulting from the dismantling of nuclear warheads under the international arms reduction treaties between the U.S.A. and Russia (START I [7], START II [8] and SORT [9]). There are multiple possibilities for this material which include, but are not limited to; processing to form UO_2 pellets for used in conventional nuclear reactors, using the plutonium in fast reactors or mixing it with uranium to form Mixed OXide (MOX) fuel [10]. The seemingly wasteful option is just to dispose of it in a geological repository.

2.1 Alternative Energy Sources

In the U.K. the majority of the electricity has been produced via the burning of fossil fuels which unavoidably releases large quantities of CO_2 into the atmosphere [6,11–13] (see Table 2.1 for a full breakdown of power generation in the U.K. in 2002). Previous cuts in CO_2 emissions have been made by the closure of old inefficient plants, greater use of nuclear power and more recently, the construction of combined cycle gas turbines (CCGT) [6]. These

Table 2.1: Energy generation in the U.K. in 2002 [12].

Generation Method	Percentage
Gas	38%
Coal	32%
Nuclear	23%
Renewables	3%
Oil and other	4%

cuts are likely to be counteracted soon as many of the current generation of nuclear power plants are approaching the end of their lifespan [12–14] and the drop in nuclear generation is most likely to be filled by new CCGT stations [11], unless new nuclear build is sanctioned by the government. To achieve a substantial drop in greenhouse emissions from power plants, it will be necessary to move away from conventional thermal plants that burn fossil fuels to renewable, nuclear power or other non polluting generation methods will be required [11, 13]. In the following few paragraphs a summary of the advantages and disadvantages of some of the possible generation methods is given.

Table 2.2: Advantages and disadvantages of power generation methods.

Generation Method	Advantages	Disadvantages
Fossil fuels	Small CO_2 reductions available by switching from coal and oil to gas CCTG stations. Cheap to run.	Still Produce large volumes of CO_2. Extracting and sequestering CO_2 is very expensive. Requires imports of gas.
Hydroelectric	No CO_2 emissions. Can vary power output according to demand.	Requires the damming of a suitable river valley.
Solar	Can provide some electricity and most of the hot water for a house during summer No CO_2 emissions.	Minimal benefit during winter months when it is needed most. Current Photovoltaic cells are inefficient.

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	Advantages	Disadvantages
Wind	Once constructed requires little maintainable and produces no CO_2.	Construction produces large quantities of CO_2 via the production of cement. Transient power source dependent on wind speed. Placement issues due to obstructions to low flying aircraft and social issues.
Biomass	Biodiesel can fuel cars and replace oil burners. Biodiesel is carbon neutral.	Biodiesel is more expensive than other sources of oil.
Geothermal	Provides heating and electricity with no CO_2 emissions.	Requires a hydrothermal vent
Tidal	Tidal mills and barrages produce no CO_2	Limited to 4 generating cycles per day with fluctuating output.

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	Advantages	Disadvantages
Wave	The U.K. has a huge coastline for the placement of wave generators	Fluctuating output. Stormy conditions can damage the generators making them expensive to maintain.
Burning waste	Methane can be produced from decomposing organic waste. Decreases the volume of waste going to landfill.	Plants are expensive to build. CO_2 is produced.

2.2 Nuclear Energy

2.2.1 Basic Nuclear Principals

Radioactivity and Nuclear Fission

Many elements exist in nature with a variety of isotopes. Chemically identical, the various isotopes only differ in the number of neutrons in their nuclei. The majority of the isotopes found on earth are stable but several, including uranium 238 (^{238}U), are not and these are termed radioactive elements. These can spontaneously naturally decay to form other elements by three processes; α , β and γ decay. During α-decay a helium nucleus is emitted, with β-decay a high energy electron is formed and γ decay results in the formation of a high energy photon [14, 15]. These will be discussed further in the radiation effects section.

Conversely to the above natural decay processes, a nucleus can be transformed through fission. This usually occurs in highly unstable nuclei, for example if a ^{235}U nucleus absorbs an extra neutron, it undergoes nuclear fission and splits into two or more fragments, which form atoms of other elements along with several other neutrons. The atoms remaining are termed fission products and examples include strontium and xenon. The neutrons produced in the fission process are able to be absorbed by other ^{235}U nuclei and the process can continue in a self sustaining chain reaction if the concentration of ^{235}U in the material is sufficiently high [14, 15].

Radiation Effects

Any material exposed to radioactive or fissile materials will experience some sort of interaction with the radiation. In a nuclear reactor, in addition to the three basic types of radiation, there is also neutron radiation to consider. The different types of radiation interact with materials differently as summarised here:

- Alpha radiation is the least penetrative form of radiation and can be stopped with light shielding such as a sheet of paper. It can, however, have a devastating effect on materials immediately surrounding the decay event such as nuclear fuel or cladding material. The damage is caused by the alpha particle itself and the recoil of the decaying atom. The alpha particle has a significant ionising effect and the recoil atom causes large displacement cascades in the material through both elastic and inelastic collisions with other atoms in the material. Any material designed to store alpha emitters (such as uranium and plutonium) will have to be able to withstand this constant damage. It is relatively straightforward to protect humans from α-particles, although inhalation or ingestion are a particular concern.

- Beta radiation is the result of a neutron decaying into a proton and a high energy electron. This form of radiation is ionising and more penetrative than alpha but less than gamma rays or neutrons.
- Neutron radiation is very penetrating, but less so than gamma [14]. Neutrons can be captured by stable nuclei making them radioactive and thus cause further decay processes. The absorption process itself can also release gamma rays. They can also interact with atoms in solids to produce elastic collisions if their energy is higher than the displacement energy.
- Gamma and X-ray radiation are the most penetrative forms of radiation and are effectively the same since they are both electromagnetic. They require a thick shield of lead or concrete to be stopped. Gamma rays are highly ionising as they can strip electrons off atoms in solids.

2.2.2 Nuclear Reactors

Nuclear plants operate in a very similar manner to conventional coal and oil plants in that fuel is “burnt” to turn water into high pressure steam which then drives a steam turbine to produce electricity. The only difference from the conventional power station is that nuclear fission is the source of heat. This introduces many challenges for which multiple reactor types have been developed. Those currently in use in the U.K. will be described later (Figure 2.1 shows the important parts of a nuclear reactor).

There are two types of fission reactor, which are classified in terms of the speed of the neutrons in the core. Thermal reactors use a moderator to slow the neutrons down close to thermal motion in order to allow ^{235}U atoms to absorb them more easily. Fast reactors dispense with the moderator and utilise the neutrons at the speed they are released. Fast reactors produce more neutrons than are absorbed and these “spare” neutrons can be used to convert a fertile non-fissile fuel such as ^{238}U into plutonium, which is fissile [15]. Such a system can theoretically generate 50 times the energy per kilogramme than a thermal reactor and therefore highly efficient in terms of fuel. Fast reactors are currently at the prototype stage and would be significantly more expensive to construct and thus are uneconomic to build. This is unlikely to change unless the price of uranium climbs [14], and as such all current commercial reactors use thermal neutrons.

There are many designs for nuclear reactors and for brevity, only designs currently operating in the U.K. are considered. For information on other reactor designs see references [14] and [15]. All of the following reactor designs feature a separate coolant and boiler system. This is because the coolant inevitably becomes contaminated with radionuclides and keeping this contained within the reactor core and steam generator limits the amount of contaminated material at the end of plant life. It also means that maintenance can be carried out on the turbines without radiological protection, and that this section does not require shielding. Another common feature with these designs is that the control rods enter from the top of the reactor and are designed to fall into the core in the unlikely event that the control rod drive system fails.

Magnox Reactor

The Magnox design is one of the earliest commercial reactors and is unique to the U.K.. It uses a graphite moderator and CO_2 is blown across the fuel pins to cool them and transfer the heat to the steam generator. The fuel elements are made from natural uranium metal enclosed in Magnox cans. Magnox is a magnesium alloy designed with corrosion resistance in mind and after which the reactor is named. The fuel elements are loaded vertically in a core constructed of graphite blocks and other vertical channels containing withdrawable carbon rods that absorb neutrons and thus are able to control the reaction. Early designs used a steel pressure vessel enclosed in a concrete radiation shield but later designs utilised a combined concrete pressure vessel and shield. Magnox reactors operate at about 400 °C and have a thermal efficiency of 31% [14]. Power stations based on this design had peak electrical outputs between 200 MW and 950 MW [14].

Advanced Gas-Cooled Reactor

Advanced Gas-Cooled Reactors (AGR) are an improvement on the Magnox design. AGRs operate at higher temperatures than Magnox reactors (gas temperatures of up to 650 °C) in order to improve the thermal efficiency and increase the power density. To achieve this, the cooling gas pressure had to be increased, the cladding material was changed to stainless steel and the fuel changed from natural uranium metal to uranium dioxide (UO_2) pellets. This allows higher enrichments to be used and corresponding higher core temperatures. Like the Magnox reactors, AGRs use graphite moderators and a concrete pressure vessel and radiation shield. AGRs have a thermal efficiency of about 42% and current reactors in the U.K. produce between 1110 MW and 1250 MW [14].

Pressurised Water Reactor

About 60% of the world's nuclear reactors are Pressurised Water Reactors (PWR). Like the AGR, they use UO_2 pellets as the fuel. In a PWR, these are contained within a zirconium alloy fuel can to form a fuel rod and these are interspersed with carbon control rods. The reactor is cooled and moderated by high pressure water, to prevent boiling, and is contained in a steel pressure vessel. The high pressure water is pumped through a heat exchanger to boil water at lower pressure and produce steam. The hot water temperature arriving at the heat exchangers is approximately 325 °C [14]. The pressure vessel and steam generation are both enclose in a concrete radiation shield. Sizewell B is the only PWR in the U.K. and it has a thermal efficiency of

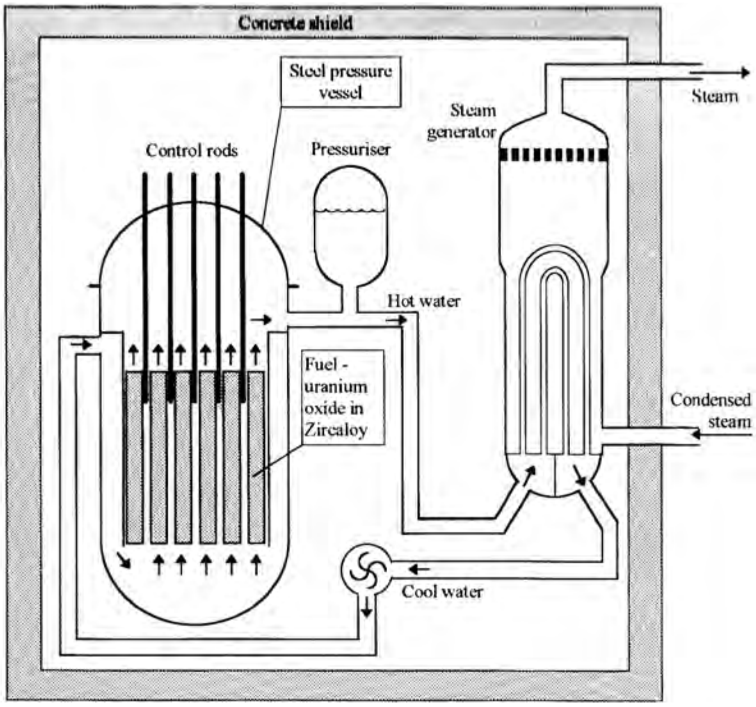

Figure 2.1: Schematic of a PWR reproduced from [15]

32% and provides 1188 MW to the grid [14]. Figure 2.1 shows the design of a PWR.

2.2.3 Fission Products

As mentioned earlier, fission products are the nuclear fragments from the fission of uranium or plutonium atoms in nuclear fuel. Fission products can cause deterioration of fuel properties and gaseous species can be produced that cause high pressure in the fuel pin. Under extreme circumstances a high buildup of these could cause the protective cladding to burst, releasing highly radioactive material into the core, or if the fuel has been removed from the reactor, the environment.

Fission products consist of a wide range of elements between copper and europium [15–17] but most fission products are symmetrically clustered in two broad peaks around elements with mass numbers of 95 and 135. Some of these elements have neutron absorbing properties and the build-up of these elements in the fuel limits the lifespan of the fuel as there are fewer neutrons to cause fission of uranium atoms. This is not the only concern as fission products can have very different chemical and physical properties to that of the fuel matrix [18]. This causes changes in the physical properties of the fuel itself, for example, the thermal conductivity is decreased by the formation of oxides of zirconium, strontium and some of the rare earth elements [16]. This is important as under operating conditions the temperature at the centre of the fuel pin can reach 1500 K and any decrease in the thermal conductivity will cause this to increase further with significant increases able to cause fuel melting. The accumulation of fission products can cause swelling in the fuel which can also increase pressure in the fuel pin and eventually lead to cladding failure [19].

Most primary fission products are unstable due to the difference in proton to neutron ratio between elements with high atomic number and those with small atomic numbers. Uranium has 1.56 times as many neutrons as protons whereas the stable isotopes of fission products, which are much smaller, have neutron to proton ratios much closer to 1. This means that fission products have too many neutrons and they tend to decay quickly by emission of β particles until they are stable. This decay occurs even after the fuel has been removed from the reactor and ^{235}U fission no longer occurs. This means that fuel that has been removed from the reactor needs to be cooled as the process still generates ”quite a lot” of heat [15].

Even though most unstable fission products decay quickly, there are some with half lives from tens to thousands of years, two in particular, iodine-129 and technetium-99, have half lives of 15.7 million years and 212,000 years respectively. Of these two, iodine is more of a concern if it is released into the environment as the human body will tend to concentrate it in the thyroid gland and this will cause tissue damage leading to cancer. For more in-depth discussion of fission products see references [15–21].

2.2.4 The Nuclear Fuel Cycle

The fuel cycle for a nuclear power station is much more complicated than for a traditional fossil fuel power plant. For a coal power station, the fuel is extracted, transported to the plant where it is burnt and any ash is either sold to the construction industry or disposed of. The fuel cycle for a nuclear plant can include all of the steps shown in figure 2.2. When fuel reaches the end of its usable life, it is removed from the reactor and can be reprocessed to reclaim the “unburnt” uranium and plutonium. This process is sometimes called “closing the back end of the fuel cycle” and reduces the amount of fresh uranium that has to be purchased.

Mining

The U.K. has no uranium reserves and most of the supply comes from Australia and Canada. The impurities are removed at the site in order to save

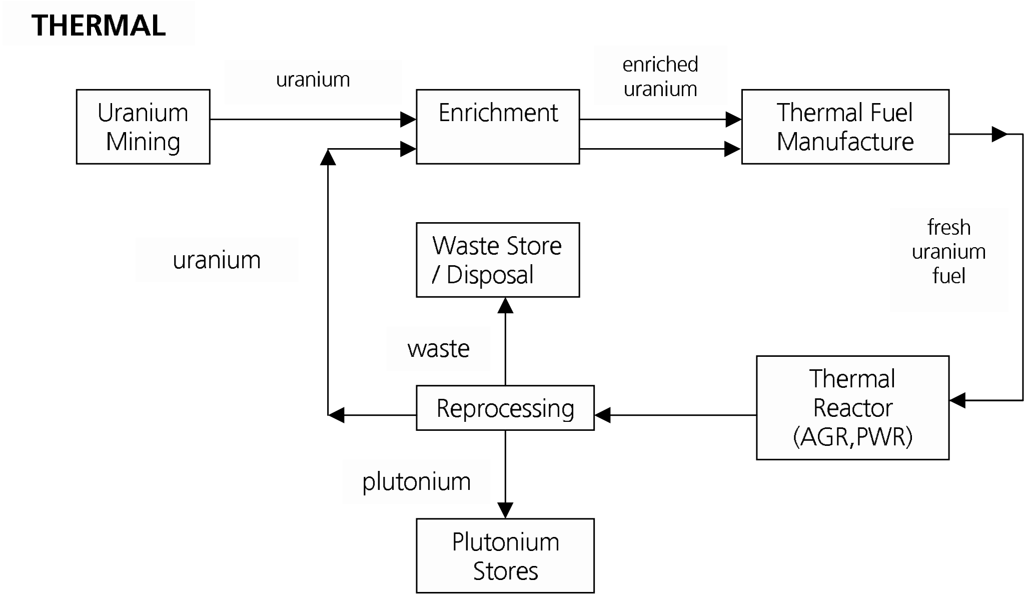

Figure 2.2: The Nuclear Fuel Cycle [14].

on transport costs and the uranium ore concentrate or “yellow cake” is taken to be processed into uranium metal or enriched UO_2 pellets. At this point the levels of radiation are still very low [14].

Processing and Enrichment

If the fuel is to be used in an AGR or PWR reactor, the fuel must be enriched from the natural 0.7% ^{235}U to the operating level for the reactor, normally between 2% and 3.5% ^{235}U. The same effect can also be achieved by mixing with plutonium gained from the reprocessing step, discussed later, to form a mixed oxide fuel.

Once purification is complete, the yellow-cake is converted to uranium hexafluoride (UF_6). This process has several stages and is discussed in depth in reference [15]. Uranium hexafluoride is gaseous, and is spun in a very high speed centrifuge to partially separate the lighter ^{235}U from the heavier ^{238}U. If purification had not been carried out other light gases would exist in the centrifuge and contaminate the enriched product. In France and the U.S.A. a different process is used in which they exploit the different rates at which the two uranium isotopes diffuse through a porous metal membrane [14]. The enrichment process yields large quantities of uranium in which the level of ^{235}U is reduced to about 0.2-0.25%, this is termed depleted uranium. This material is currently stored but it may be used in future fast reactors as a fertile fuel.

Fabrication

The next step in the process is to convert the enriched UF_6 into uranium dioxide for used in AGRs and PWRs. Alternatively, the unenriched uranium ore is converted into uranium metal rods for the use in Magnox reactors see [15] for further details.

The production of oxide fuel from the enriched UF_6 can be performed via two methods, a dry route and a wet route. The dry fabrication process is the most common route so that will be the method explained here, for information of the wet fabrication route see reference [15].

In dry conversion the UF_6 is decomposed by steam to produce UO_2F_2 which is a solid. This is then reduced to UO_2 using either a fluidised bed technology, a two step process using a rotary kiln or a one step process using flame reaction technology [15]. The UO_2 powder produced at the end of this process is then uniaxially pressed into pellets. The shape and size of the pellets differs for different reactors but in the U.K. there are only 2 different designs. Solid pellets are used in most PWRs and annular pellets are used in AGRs. Annular pellets have a cylindrical hole running through the centre of the pellet and thus require a retractable pin in the press. The purpose of this hole is to accommodate distortions in the fuel and fission gasses formed in the reactor. Once the pellets have been pressed, they are sintered at 1750 °C in a reducing atmosphere of hydrogen or a mixture of hydrogen and nitrogen to prevent oxidation and the formation of U_3O_8. This process increases the density of the pellets and gives them the physical properties they require to withstand the high temperature conditions in the reactor.

The pellets are then assembled into fuel pins or elements. These differ wildly amongst the different reactors but a similar process is used for both AGR and PWR fuel elements. In both of these, the fuel pellets are stacked and weighed and then inserted into the cladding. Once this is complete, the cladding is then filled with helium gas and the ends are sealed, welded and tested.

The fuel is then transported and installed into the reactor where it is used until the build-up of neutron absorbing fission products and other detrimental effects, such as fuel swelling, require the fuel to be removed and either disposed of or reprocessed. This completes the front-end of the fuel cycle.

Reprocessing and Recycling or Disposal

After the fuel has been removed from the reactor, it enters the back-end of the fuel cycle. At this point the fuel is highly radioactive due to the presence of fission products. This fuel must be stored and cooled until the level of radioactivity is low enough to allow transport to the reprocessing site or the interim storage facility. The fuel is normally stored in ponds at the reactor site. These ponds are sealed reinforced concrete structures filled with water. This acts as an effective radiation shield and also provides cooling to the fuel which may otherwise heat to the point where the fuel or the cladding becomes damaged enough to release contaminated material into the local environment.

Once the material has cooled sufficiently it is either taken to a storage site or to a reprocessing plant. Reprocessing has several advantages over storage for later disposal and these are listed here:

- Security of Supply: Security of supply is a concern for the U.K. as there are no natural uranium deposits. This means reprocessed uranium is a valuable resource that should not be wasted. Some countries choose to store the spent fuel and leave the reprocessing for later but corrosion of the fuel and cladding materials can be a problem if it is to be stored for long periods.
- Waste Management: The recovery of useful material means that the volume of high level waste that must be disposed of is reduced by a factor of 9 [15]. The radioactive content is also reduced as the alterna-

tive, direct disposal, adds approximately 250kg of plutonium per year to the fuel awaiting burial. Since the medium to long term radioactivity is dominated by plutonium isotopes and daughter products, the radioactivity over 10,000 years can be reduced by over 30%.

- Improved Proliferation Resistance: Proliferation is the unlawful diversion of fissile material. In particular, plutonium is potentially attractive to terrorist organisations. While considerable effort is made to keep this material safe, converting this material into MOX fuel makes it much less attractive as the organisation would not only have to move the bulky material but to chemically separate it before it could be used.

While it is true that reprocessing does substantially reduce the volume of HLW, it does increase the volume of intermediate and low level waste produced [22]. It was estimated by Webster [23] that by 2030 26% of the volume (only 6% by activity) of all radioactive waste in the U.K. will be ILW and a substantial proportion of it will have come from reprocessing. Arm *et al.* [22] propose several concepts to reduce these volumes, one of these is the elimination of one of the solvent extraction cycles during the purification of uranium and plutonium by reducing the flow rate and thereby increasing the extraction efficiency of fission products and minor actinides.

Reprocessing fuel involves separating out the uranium and the plutonium (some of the ^{238}U is transmuted even in thermal reactors) from the rest of the fuel. These 2 elements can consist of 97-99% of the spent fuel with the remaining being high level waste including fission products and some of the minor actinides, including neptunium, americium and californium. While the idea is simple, the mechanics of the process are far from simple and will not be discussed here; for a detailed description of the process see reference [15]. Once reprocessing is complete, the uranium and plutonium are stored waiting to reenter the fuel cycle at the enrichment or fuel fabrication step.

Future Role of Fast Reactors

Reprocessing fuel provides a source of plutonium and while some of this is currently being used in the form of MOX for PWRs and AGRs this material can be used as a fuel for fast reactors. If this is ever started, by using the depleted uranium formed in the enrichment process, this type of reactor can actually produce more new plutonium fuel than it consumes by breeding the ^{238}U to ^{239}Pu. This creates a situation where the cycle is virtually closed.

2.3 Nuclear Waste

2.3.1 Introduction

Any kind of industry develops waste materials along side the desired products and the nuclear industry is no different. The sources of waste in the nuclear industry mainly come from the following operations:

- Reprocessing spent fuel
- Final decommissioning when a plant reaches the end of its lifespan

- Military Waste
- Surplus Materials

Primary wastes from fuel reprocessing include the fission products, minor actinides and the remains of the cladding. Secondary wastes that are formed during reprocessing can include solvents that are no longer recoverable, worn out equipment or clothing and other domestic waste that may have been contaminated with radioactive material. The industry aims to minimise the amount of secondary waste generated and to convert as much of the radioactive material into a form that is both suited to long-term storage and final disposal whilst taking up as small a volume as possible. While doing this the environmental impact should be kept As Low As Reasonably Attainable (ALARA).

Waste Types

In the U.K. solid radioactive waste is normally classified by its radioactive content as high, intermediate, low or very low level wastes (HLW, ILW, LLW, VLLW). These are defined as:

- VLLW: Very Low level wastes can be disposed of with normal household waste. Each cubic metre must contain less than 400 kBq per tonne of beta or gamma activity and less than 40 kBq/t for any single item.

- LLW: Low level waste consist of materials with activities greater than that for VLLW but not more than 4 GBq/t of alpha or 12 Bq/t of beta/gamma activity.
- ILW: Intermediate level waste is classified and anything exceeding the activities for LLW but does not require the heating effect of radioactive decay to be taken into account in the design of storage or disposal facilities.
- HLW: High level waste is classified and any material sufficiently radioactive such that it produces sufficient heat to require special design factors for long term storing and eventual disposal.

HLW mainly consists of fission products after reprocessing. ILW is mainly cladding remnants or plutonium contaminated material that it is not economical to remove (including filters and processing residue). LLW consists of discarded equipment, tools and protective clothing. It also consists of material suspected of being contaminated such as waste paper from offices in controlled areas [15]. These definitions are rather arbitrary in that they only consider current activity without any regard for the half-lives of the material [15].

Liquid wastes are similarly divided into high, medium and low active streams. Current practice for the disposal of both liquid and solid waste in the U.K. will be summarised in the next section.

2.3.2 Current Practice in the U.K.

Liquid Wastes

Over the last 20 years huge improvements have been made to reduce the activity of liquid waste discarded into the sea from the Sellafield reprocessing plant in Cumbria. Figure 2.3 shows the current liquid waste handling process at Sellafield.

In order to reduce the contamination later on in the process, reprocessing is delayed slightly and the fuel is cooled. This allows isotopes with a very short half life, for example ^{131}iodine (8 days) and ^{95}niobium (35 days), to decay to very low levels. Delay periods are also used after reprocessing to reduce the activity of slightly longer lived radionuclides destined for discharge.

The highly active wastes from the first stage of fuel processing contain the majority of the fission products and minor actinides. This waste is concentrated up to 100 times by repeated evaporation. The concentrated residue is stored in cooled double wall stainless steel tanks until it is ready for vitrification, this process will be described in detail in section 2.3.4.

The medium active waste mainly consists of residues from the purification of uranium and plutonium. Some of these can be combined with the highly active stream but those which cannot, for chemical compatibility reasons or simply due to the fact that there is too much, are fed into a separate evaporator and stored.

Before 1980 the medium activity wastes were stored for at least three years

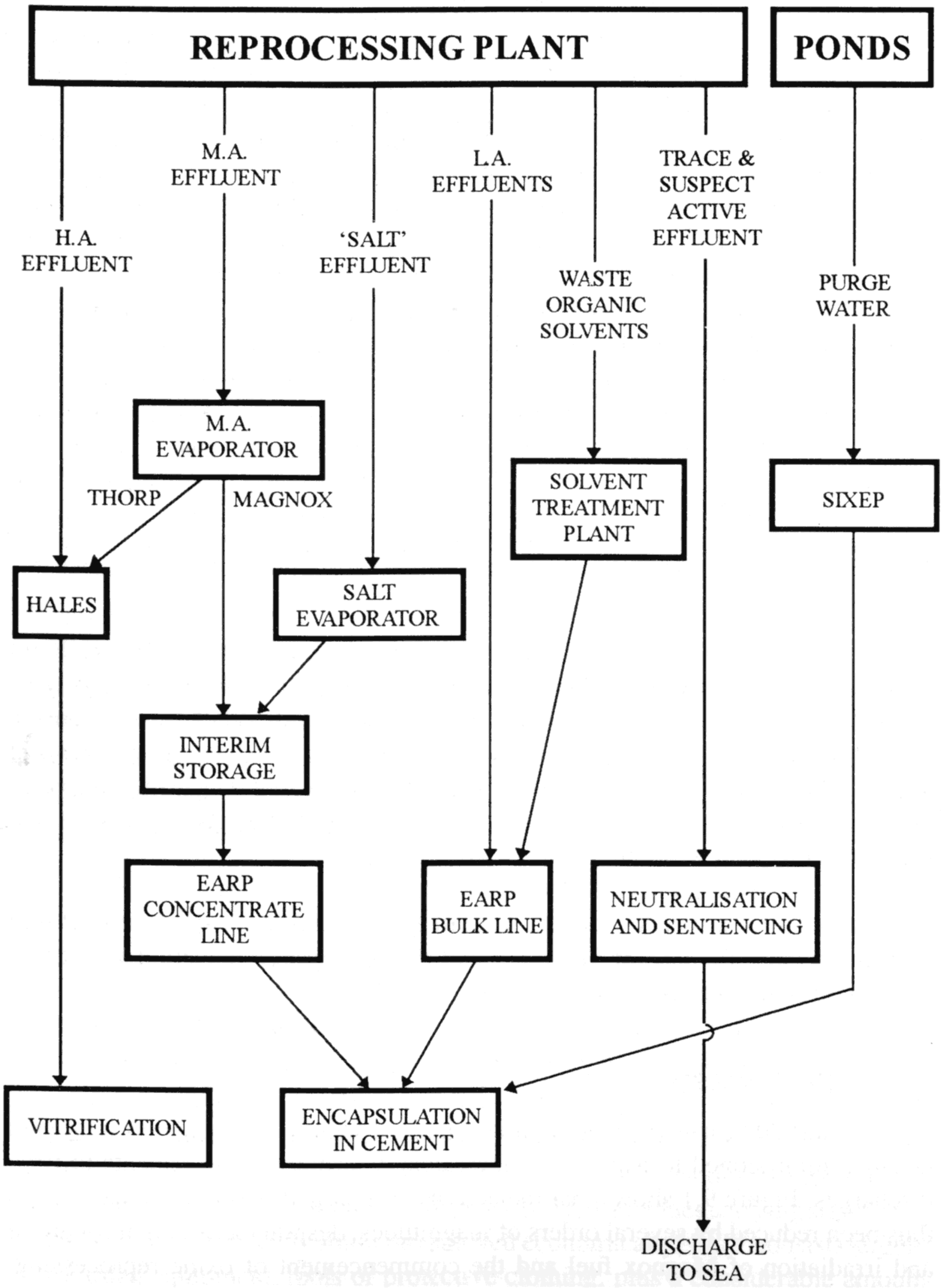

Figure 2.3: Liquid waste treatment at Sellafield [15].

and then discharged to sea. This allowed the almost complete decay of ruthenium, zirconium and niobium which constituted the majority of the activity. After 1980 the process was stopped as it was realised that the activity was now dominated by much the longer lived isotopes of some of the actinides and it was decided to store this material until these could be removed in the enhanced actinide removal plant (EARP).

Salt wastes have a high sodium content and are incompatible with the medium active waste evaporator and thus have their own dedicated device. Like the medium active wastes, these are now processed through EARP.

Strontium and caesium are the main source of contamination from the fuel storage ponds. There are also significant quantities of magnesium hydroxide from corrosion of Magnox fuel cladding. These wastes are too dilute to be processed via an evaporation route and an ion exchange method is used. The details of this process can be found in [15]. This process reduces the levels of strontium and caesium by factors of 500 and 2000 respectively and the remaining liquid waste is discharged into the sea. The solid residues from the ion exchange beds are used to replace fillers, such as sand, in the cement.

EARP takes concentrated residue from the medium active and salt waste evaporators and uses a precipitation and filtration method described in [15] to extract significant quantities of the actinides, cerium, ruthenium and strontium from the liquid before it is tested for activity and either put through the system again or discharged to sea.

2.3.3 Solid Wastes

Solid wastes include fragments of fuel cladding and any radioactive isotopes or toxic materials that have been precipitated or otherwise removed from the liquid waste streams. All types of waste need to be encapsulated for long term storage and other methods for this process will be discussed later in sections 2.3.4 and 2.3.5.

Solid HLW originates from the highly active liquid stream, it is currently solidified by a vitrification process described later in section 2.3.4. Once it has been vitrified and placed inside steel containers, the HLW is stacked up to 10 high in closed tubes in a store cooled by the natural convection of air. At the present time it is planned to store the vitrified waste for 50 years to allow the worst of the radioactivity to decay [14,15]. Currently the U.K. does not have a final strategy for the long term disposal of HLW [24, 25].

ILW has been stored at the Sellafield site in dry or water filled silos according to the content. This requires constant supervision and is not acceptable as a long term solution and so ILW is currently being encapsulated for future long term storage although, like HLW there is no final strategy for the process at the current time [15,24,25] (see section 2.3.8 for information on possible final disposal options.)

In the U.K., cement has been found to be the best encapsulation material for all types of ILW [15]. It has proved superior to other matrices including polymers and polymer modified cements, both during the encapsulation process and after. Ordinary Portland cement (OPC) is unsuitable as an encapsulant as the hydration reaction produces too much heat and leaves too much thermal stress in the material. In order to prevent this, the mixture must be diluted. Many diluting materials have been considered, including sand, pulverised fuel ash, ground blast furnace slag and contaminated clinoptilolite from the ion exchange plant.

The encapsulated waste must remain durable enough for handling for at least 100 years or at least until final disposal. This means the physical and mechanical properties, the chemical and radiation stability, and the leaching behaviour should not change significantly over this period [15].

There are two processes used for the encapsulation of ILW in the U.K., one for solid wastes and the other for slurries. Solid wastes are packed into 500 litre stainless steel drums and the voids are filled with cement. Slurries are mixed with grout forming materials and left to cure in the drums. For both types, the lid is then fitted and the outside is decontaminated with high pressure water jets. The drums are then stored above ground awaiting the construction of a suitable deep geological repository [15, 24, 25].

LLW is placed into drums which are then compacted and loaded into iso freight containers. These are then taken to the U.K. LLW disposal facility at Drigg, near Sellafield, where they are placed in concrete vaults. When these vaults are filled, they will be capped with clay. there is sufficient storage space at the Drigg site to accommodate al the LLW from nuclear power stations and hospitals for many years to come. [15, 24, 25].

2.3.4 Immobilisation in Glasses

Introduction

Immobilisation of highly active waste sludge and plutonium has been or is being achieved via a vitrification process in the U.K, U.S.A., Belgium, India, Japan and Russia [26]. Vitrification involves dissolving (or just encapsulating) the waste into a glassy (vitreous) host material. Once it has been vitrified, the wasteform can then be cast into any suitable structure [27], in the U.K. 400 kg containers are used [15]. It is possible to incorporate up to 25-30 wt % HLW into a glass wasteform [27].

The glass composition is chosen by taking into account factors such as HLW solubility, glass formation temperature and leaching performance under repository conditions. Many compositions have been shown to have the required properties including high thermal and mechanical stabilities. Other advantages that these glass compositions possess include the ability to be formed and processed at relatively low temperatures, they are sufficiently radiation resistant (see section 2.3.6), show high chemically durability, they can accommodate changes in composition due to radioactive decay, furthermore they are tolerant of changes in HLW composition [15, 26, 27]. Many tonnes of vitrified HLW is currently stored in interim storage facilities awaiting construction of geological repositories for permanent disposal [15, 27].

Vitrification Methods

Immobilising nuclear waste in glass was first developed in Canada early in the 1950s using nepheline syenite (a natural silicate mineral) as the host. [27]. The U.K. also started vitrification methods in the 1950s. The initial work considered using natural soils as the base material but these had to be melted at high temperatures (1500 °C) [27] and were later replaced with an alkali-borosilicate glass that melted at lower temperatures (850 °C) [15, 27].

The process involved calcining and then melting HLW and glass frit together in a stainless steel crucible or pot, which also served as the eventual container. Once this process was complete the pot was removed and another put in its place so the process could be repeated [27].

The French approach was similar in many regards but they preferred a continuous melting process over the batch system developed in the U.K. in order to achieve higher throughput. Waste is calcined in a rotary kiln at 850 °C under reduced pressure where it is progressively evaporated to leave as a dry finely divided powder. The calcine is then fused with the base glass in an inductively heated metallic furnace at a wall temperature of about 1100 °C. This furnace is designed to produce at least 25 kg of waste an hour with a waste content of approximately 25% waste loading. When the volume of material in the melter reaches a certain level the product is drained into a stainless steel product container, this generally takes 8 hours [15]. This process is now used in the U.K. at the commercial Sellafield reprocessing plant [15, 27]

Types of Glass Used for HLW Vitrification

Silicate glasses are currently the preferred wasteform for HLW [27]. This is because they readily dissolve a wide range of waste compositions and they are easily modified in well understood ways in order to optimise their properties. They have also been extensively studied as they have been used in the commercial glass industry for decades so they are the best understood glasses [27].

Recently, attention has returned to borosilicate glasses as a wasteform for the surplus uranium and plutonium from civil and military sources and it has been concluded that borosilicate glass is the preferred wasteform for plutonium [27, 28]. This is despite the fact that the solubility of plutonium in these glasses is low (less than 3 wt %) [27].

Phosphate Glasses: Interest in phosphate glasses was high during the early immobilisation studies because of their low glass formation temperatures and high solubilities for metal oxides. Interest soon waned for a number of reasons, including poor chemical durability, low thermal stability and that they are highly corrosive [27]. This highly corrosive nature would severely limit the lifetimes of the melting equipment.

Rare Earth Glasses: There has been limited work on rare earth oxide glasses and only one rare earth borosilicate glass has been commercially considered. This glass has the name “Löflers” glass and was originally developed int the 1930’s as an optical glass [27]. It contains about 55 wt % rare earth oxides and has recently been suggested for the immobilisation of uranium, plutonium and americium as it can accommodate higher concentrations of these elements than a standard borosilicate glass [27].

Durability of Glass Wasteforms

Many factors affect the durability of glass wasteforms, including composition, waste loading, pH, temperature crystallisation effects and effects of radiation damage [27]. Unlike more common glass compositions, which are reasonably resistant to corrosion in acidic solutions, HLW glasses show higher leach rates in acidic solutions which is probably due to the high loading of alkali oxides in the glass [27]. In a closed system these rates decrease with time but if there is transport of these leachates away from the repository, for example if there is flowing water, then these rates remain a constant. The solubility of the leachate can be affected by the pH, especially if it contains Zn, Al, Fe, Ti or Mg [27]. Transport of the leachate away from the glass can be inhibited, and thus the durability is increased, by the formation of solid layers at the surface of the wasteform. It was noted by Chick *et al.* [29] that the durability of the wasteform could be improved by increasing the silica or alumina concentration in a borosilicate glass or by decreasing the amount of alkali oxide.

Solubilities of various elements vary according to their charge state which can change due to reduction or oxidation reactions in the wasteform material. Examples of such materials include the actinides and technetium which show much reduced solubilities in glasses in their 4+ state than in their higher oxidation states. The solubility of iron is also affected by the ratio of Fe^{2+} to Fe^{3+} ions [27]. This means that it is essential to know the elements that are sensitive to this reaction and make sure conditions in the repository are favorable to maintaing the state of maximum solubility.

2.3.5 Ceramic Wasteforms

High level waste and surplus weapons material may also be immobilised in a ceramic wasteform. There are no current commercial operations using this technique although significant interest in the possibility has been shown in the literature [27, 30–60]. Immobilising radioactive elements in a ceramic is based around the idea of emulating naturally occurring minerals that are known to have stably contained radioactive elements for tens to hundreds of millions of years [60]. This can then be used as an argument that man made wasteforms based on these will also remain stable for similar periods of time. Other benefits of ceramic wasteforms include the fact that: they can contain higher loadings of certain waste elements than glasses, they can have higher thermal conductivities (which keeps temperatures at the centre of the wasteform lower and allows for larger containers), they can withstand higher temperatures (occurring due to the internal heating) and as part of a solid solution they can selectively accommodate specific chemical species [60]. The accommodation of HLW in ceramics is fundamentally different from that for glasses as instead of being dispersed randomly throughout the material, the radionuclides are accommodated at specific sites within the lattice forming a dilute solid solution [61]. This means that in order to accommodate the wide range of species that make up HLW, multi-phase systems of complex structures tend to be used [61].

Many different types of ceramic have been considered for the immobilisation of nuclear waste materials including spinel based ceramics, the titanate rich SYNROC family, silicate based ceramics, phosphates, fluorite and related ceramics. These will be discussed here:

SYNROC and Related Ceramics: SYNROC or SYNthetic ROCk is the most widely known ceramic wasteforms and was developed in Australia in the 1970's by Ringwood *et al.* [39,40]. SYNROC is a ceramic wasteform designed to immobilise HLW from reprocessing spent fuel and consists of four titanate phases, "hollandite" $BaAl_2Ti_6O_{16}$, zirconolite $CaZrTi_2O_7$, perovskite $CaTiO_3$ and rutile TiO_2. It also contains small amounts of a dispersed metal alloy [39,40,42] although almost all of the fission products, actinides and processing contaminants are incorporated in the ceramic phases [39, 40, 42]. Various types of SYNROC have been developed for different applications, including SYNROC-C for waste from the reprocessing of spent fuel, SYNROC-D for the disposal of HLW resulting from the U.S.A. defence programme, SYNROC-E is an improvement in SYNROC-C which is encased in rutile to improve its long term performance and SYNROC-F for unprocessed spent fuel [27,42,43].

The hollandite phase has a particularly accommodating structure and possesses a high solubility for ions with a wide range of radii. This is mainly due to the presence of large tunnels along the c-axis [60]. See Figure 2.4 for a representation of this (generated using structural data from [62]). Figure

2.4a shows a view straight down the c-axis and Figure 2.4b is a perspective view showing 2 unit cells along the c-axis. In this structure only half of the Cs-sites are occupied whereas all possible sites are shown here. These tunnels are capable of accommodating ”very large” cations including Ba, Cs, Sr, K and Rb which are fission products of uranium [60]. The smaller octahedral site normally occupied by Ti^{4+} and Al^{3+} can accommodate the medium sized cations including Mo^{4+}, Ru^{4+}, Fe^{3+}, Fe^{2+}, Ni^{2+} and Cr^{3+} [60]. Single phase hollandite ceramics containing Cs and Sr ($CsAl_2Ti_6O_{16}$ and $SrAl_2Ti_6O_{16}$) have been synthesized [60] showing that the hazardous forms of Cs and Sr can also be accommodated successfully. The presence of the large tunnels in the structure may suggest that it is prone to leaching but the large Ba ions present in the tunnels act as plugs to preventing easy transport of HLW ions through the structure.

Zirconolite is the phase responsible for the accommodation of uranium and the tetravalent actinides. It can also accommodate smaller concentrations of trivalent actinides and rare earth elements [42, 60]. It has a monoclinic structure and is related to both the pyrochlore and fluorite structures [60]. Figure 2.5 shows a graphical representation of the structure, generated using structural data from Rossell [63]. Figure 2.5a shows a view of the structure up the c-axis with the a axis going across the page and Figure 2.5b shows a perspective view of the structure. It should be noted that this is an idealised version of the structure since the structural data indicates a degree of cation disorder on all cation sublattices and one of the titanium sites is only half occupied whereas this diagram shows the majority ion on each site and shows all sites as fully occupied. Kesson *et al.* [42] found that U^{4+} is

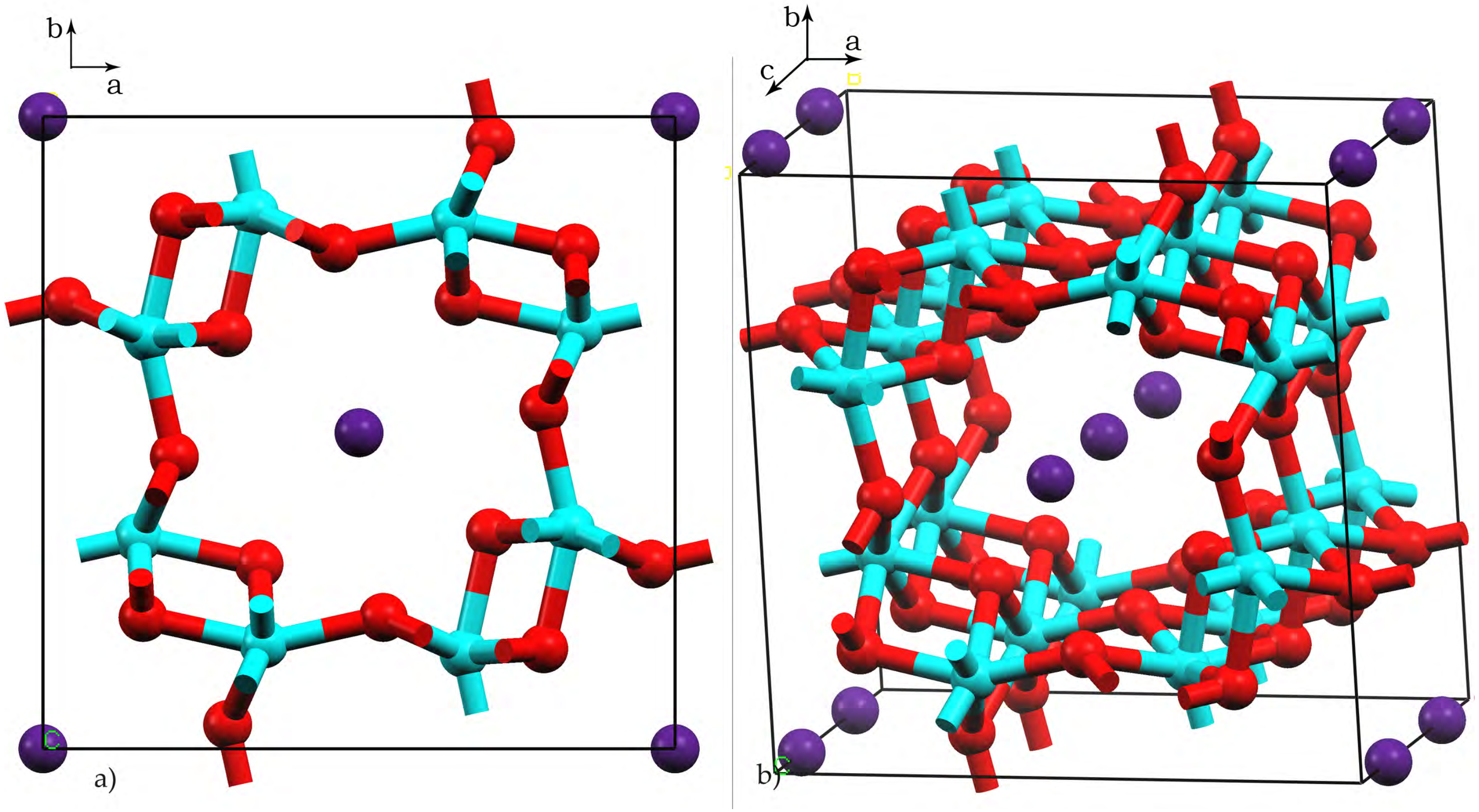

Figure 2.4: The Hollandite Structure. a) View directly down the c-axis b) perspective view. Cs^{4+} ions - Purple, Ti^{4+} Ions - Light Blue, O^{2-} ions - Red.

accommodated at both the Ca and Zr sites when a smaller lower valence cation (for example Mg^{2+}) is allowed to simultaneously be accommodated at the Zr site. This allows the loading of UO_2 to be increased from the 13 wt % that is apparent at just the Zr site to 26 wt % with coupled substitution onto both sites [42]. Thorium, like uranium seems to substitute onto both Ca and Zr sites but it substitutes preferentially onto the Ca site with charge compensation by small 2+ cations on the Zr site. This way 20 wt % ThO_2 has been accommodated into the zirconolite phase [42]. The high loadings of actinides (compared with borosilicate glasses) that are possible in zirconolites has meant that significant work has been undertaken by research groups throughout the world with the aim of using these phases for the immobilisation of actinides and weapons grade material with and without using the other SYNROC phases [41–53, 56].

The final major phase in the SYNROC system is perovskite $CaTiO_3$ (see figure 2.6 generated using structural data from Chakhmouradian *et al.* [64]). Figure 2.6a shows a view from the front of the structure with the a-axis across the page and c axis vertical, Figure 2.6b shows a top down view of the structure with tha a-axis across the page and b-axis vertical and 2.6c shows a perspective view. This phase is also known to accommodate many elements in solid solution. The primary reason for its inclusion into SYNROC is for the accommodation of Sr^{2+} onto the Ca site and U^{4+} onto the Zr site. Substitution of Mo^{4+}, Zr^{4+}, Nb^{5+}, Pu^{4+}, Ru^{4+}, Fe^{3+}, Cr^{3+} and Al^{3+} onto the titanium site and Ba^{2+}, Na^{+}, Cd^{3+}, Cm^{3+}, Am^{3+}, Pu^{3+} and rare earth $(RE)^{3+}$ onto the Ca site have been reported [60].

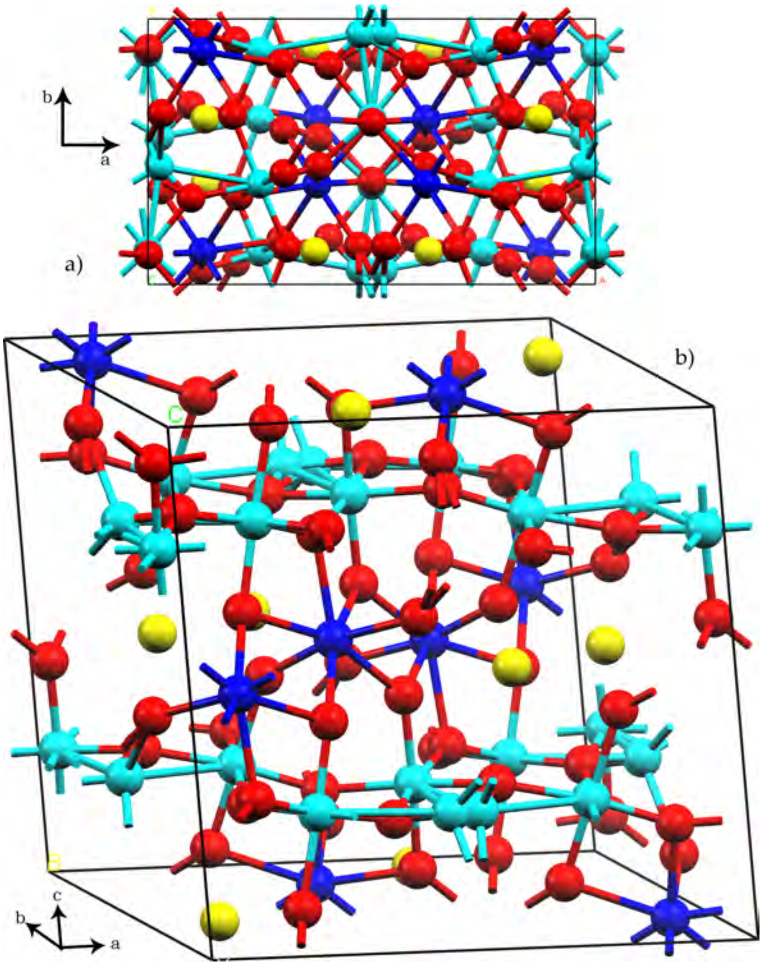

Figure 2.5: The Zirconolite Structure. a) view along c-axis, b) perspective view. Ca^{2+} ions - Yellow, Ti^{4+} ions - light blue, Zr^{4+} ions - dark blue, O^{2-} ions - red

The rutile phase (TiO_2) is normally a relatively minor constituent but in SYNROC-E it is the dominant phase as all the other phases are encapsulated inside it [42]. It is used as an extra barrier to impede the flow of contaminated material into the environment. In other SYNROC variants rutile is formed when processing and tailoring additions are not adequately controlled [60].

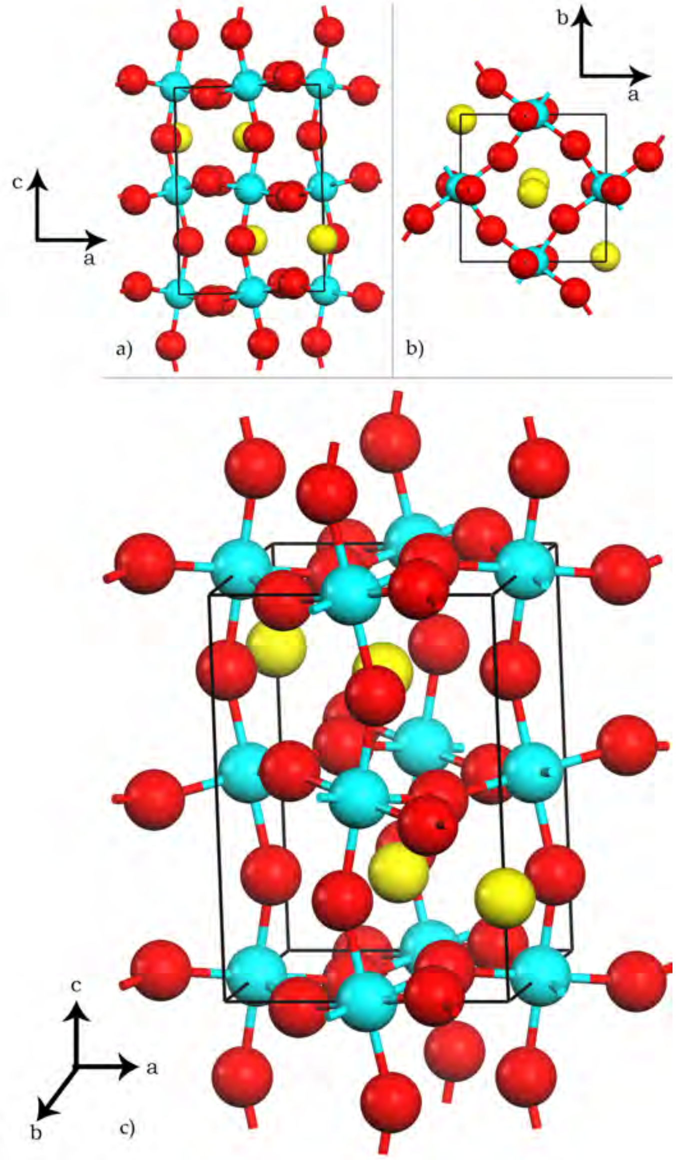

Figure 2.6: The Orthorhombic Perovskite Structure ($CaTiO_3$). a) View from front with the c-axis up the page; b) view from top, a-axis across the page; c) perspective view. Ca^{2+} ions - yellow, Ti^{4+} ions - light blue, O^{2-} ions - red.

Smith *et al.* performed a study on the durability of SYNROC containing 10% simulated waste [43]. They placed a sample in doubly deionised water held it at 150 °C for up to 532 days. After this time period they performed scanning electron microscopy on the sample and the leachate was analysed for its composition. They concluded that SYNROC is highly durable even under these conditions and that most of the material leached from the material originates in the minor phases which make up less than 5% of the material. Analysis of the leachate showed that leach rates of Al, Ba, Ca, Ce Cs,Mo, Nd and Sr range from 0.017% to 0.093% after 337 days. The analysis of the relative corrosion resistance of the major phases showed zirconolite to be the most resistant since it showed no alteration even after 532 days. The hollandite phase was the next most stable, showing only small crystals of anatase forming on the surface and lastly, the perovskite phase was least corrosion resistant major phase and showed corrosion to a depth of $< 0.2\ \mu$ m (less than half the grain size) after 532 days [43].

The study described above does not consider the effects of radiation damage on the ceramic. Furthermore, due to the types of material immobilised in the different components, different types of damage will be incurred. The hollandite will be subjected to α-particle and β/γ irradiation whereas the perovskite and the zirconolite phases will be subject to α-decay processes and α recoil events as well [61]. It has been assumed that β/γ irradiation has virtually no lasting effect on any of these species [61] and work has been carried out using various techniques to simulate α-particle and α-recoil events in these phases (including computer simulations described in chapter 6). This will be discussed in greater detail in section 2.3.6 but, in summary, the zirconolite [65–67] and perovskite [61] phases undergo α-decay induced amorphisation with a volume change between 6 and 8% and the hollandite changes structure with an associated volume change of up to 2.5% [61]. Volume changes are detrimental to ceramic wasteforms as these materials are brittle and can cause the material to fracture and become more prone to leaching.

Phosphate Ceramics: There are some naturally occurring phosphate minerals based on monazite that are known to contain actinide elements. Lanthanide phosphate materials based on this have been prepared by various techniques on a laboratory scale and a wide range of HLW materials can be incorporated into these materials. Leach resistance and radiation tolerance of wasteforms based on this system are reported to be good [27].

Samples of monazite in nature have been found with significant concentrations of actinides. Samples from Italy have been found to contain about 15 wt % UO_2 and 11 wt % ThO_2 and this suggests that these materials could be good candidate hosts for the more massive actinides, like plutonium, not normally found in the environment. The long term stability of these compounds is good as samples of monazite found in Brazil have been dated at over 2 billion years old [27]. They also posses a negative temperature coefficient of solubility meaning that as the material cools more HLW can be dissolved into it. This is a useful property to have as the wasteform will be subject to the internal heating effect of radioactive decay to start with and this will slowly decrease with time and for conventional ceramics this means a decrease in solubility with temperature which could lead to leaching problems thousands of years in the future.

Lanthanide phosphates exist in a several different structures including tetragonal, hexagonal and monoclinic and have high transition temperatures [27]. This is good as it means as the wasteform cools with time it is unlikely to go through structural changes. Unfortunately, they also possess high melting points, in excess of 2150 °C. This makes them expensive to produce and special processing techniques have been developed to reduce the formation temperature. Wet chemistry techniques have been used to form highly reactive precursor powders and these can then be hot pressed or sintered at 1300 °C to achieve theoretical densities of up to 97% [27] with up to 50% of HLW simulant loading.

Silicate Based Ceramics: The first demonstration that ceramics could be used to immobilised nuclear waste were the "supercalcine" ceramics developed at Pennsylvania State University by McCarthy *et al.* [60]. Their approach was to add Si , Al, Ca and Sr oxides to the waste before it was calcined so that each radionuclide is immobilised in one or more phase of the resulting ceramic. These ceramics were complicated polyphase materials, containing up to 9 separate phases [60]. The key phases in the material are pollucite ($CsAlSi_2O_6$), scheelite ($CaMoO_4$), fluorite ($[U,Zr,Ce]O_2$), apatite ($Ca_5(PO_4)_3OH$) and monazite.

There has been some more recent work on apatite minerals for the immobilisation of radionuclides to identify diffusion rates of immobilised species [55, 68, 69]. Meis *et al.* [55] state that the fluorapatite phase should be a good material for the immobilisation of plutonium whereas Martin *et al.* [68] find that there is preferential diffusion of rare earth elements to surfaces in hydroxyapatite and suggests that these materials are more suitable as backfilling materials (see section 2.3.8 for an explanation of backfilling).

Another silicate ceramic that has been receiving attention is zircon [69–76]. Zircon ($ZrSiO_4$) is a stable mineral that contains radioactive U and Th in nature [71]. Natural zircons have been found with uranium and thorium concentrations of up to 10 wt % can be very durable [71]. It has been studied extensively as it is used for the dating of minerals by analysing the U:Pb ratio [27,71]. Furthermore Pu can completely substitute for Zr to form $PuSiO_4$ which makes it a very good prospective material for the long term disposal of weapons plutonium [27, 71]. In dissolution tests, even once it has undergone α-induced amorphisation, the dissolution rate of zircon is 2 orders of magnitude slower than that of borosilicate glass [71]. One drawback is the very large volume change on amorphisation of 18 - 20% [71, 73]. It is suggested that annealing of the damage by self heating (in a wasteform doped with 10 wt % ^{239}Pu) can maintain the crystallinity if the temperature remains above 225 °C [71]. Several processing operations have been developed at the laboratory scale for the production of zircon and Pu containing zircon and these include a sol gel route and hot pressing [27].

Fluorite Related Ceramics Other ceramics are being considered for use as materials for the immobilisation of HLW and these are generally variants of the fluorite structure (including pyrochlore). These will be discussed in depth later on in chapter 5.

2.3.6 Radiation Effects In Wasteform Materials

Introduction

The dominant source of radiation in an immobilised HLW form will vary with time but consists mainly of α-decay of actinide elements (mostly U, Np, Pu Am and Cm on commercial wastes) and β-decay of fission products (including ^{137}Cs and ^{90}Sr) [77]. Minor contributions are made by spontaneous fission of the actinides and although α-neutron reactions are yet another source of fission fragments and neutrons, compared with α and β-decay events, these are rare.

During the first 500 years, the accumulated damage is mostly due to the β-decay of the shorter-lived fission products (28.1 years for ^{90}Sr and 30.2 years ^{137}Cs). After about 1000 years the damage processes become dominated by α-decay (the half life of ^{239}Pu is 2.411×10^4 years) [77].

Decay events can cause damage in one of three ways:

1. Elastic collisions between the particle (the β-particle/α-particle/α-recoil nucleus) and the atoms in the host matrix. This can cause atomic displacements creating isolated Frenkel defect pairs (a vacancy and interstitial of the same species) or intense collision cascades.
2. Ionization effects associated with the α-particles, β particles and γ rays.
3. The transmutation of radioactive nuclei into different elements.

Out of these three effects, it is displacement processes that cause most damage as these cause rearrangements of the crystal structure and impact the physical and chemical processes of the material the most [77]. A very comprehensive study of α–decay damage in actinide bearing minerals was performed by Lumpkin [78]. Each α-decay event results in an average of 1500 ion displacements while a β-decay even only causes around 0.15 [77]. One of the differences between glass wasteforms and oxide ceramic based wasteforms is that oxide ceramic wasteforms seem to suffer little from ionisation events [77] whereas complex borosilicate glasses have been show to decompose by a ionisation driven process that produces baubles containing molecular oxygen [79].

The cumulative radiation dose that a wasteform will receive can be very high. Table 2.3 shows the anticipated cumulative doses for α and β radiations for waste glasses produced at the Savannah River Plant in South Carolina [80]. This shows that a glass wasteform containing 25% HLW (Defense Waste) will experience in excess of 0.0025 displacements per atom (dpa) or about 7×10^{10} rads in just 1000 years [77]. Cumulative doses for wasteforms containing commercial waste are several orders of magnitude higher than this due to the high concentration of fission products. After about 10,000 years, a SYNROC wasteform containing a 20 % loading of commercial waste will have absorbed a dose corresponding to 4×10^{18} α-decay events per gram or 0.32 dpa. A wasteform containing zircon will become metamict (or amorphous) at doses as low as 0.3dpa [77].

Table 2.3: Cumulative decay events and dose for a nuclear waste glass [80]

Time (years)	α-Decays per gram	β-Decays per gram	α-Dose (rad)	β-Dose (rad)
1	2×10^{14}	5×10^{16}	2×10^{7}	6×10^{8}
10	2×10^{15}	5×10^{17}	2×10^{8}	6×10^{9}
100	2×10^{16}	2×10^{18}	2×10^{9}	3×10^{10}
1,000	1×10^{17}	5×10^{18}	9×10^{9}	6×10^{10}
10,000	3×10^{17}	5×10^{18}	3×10^{10}	8×10^{10}
100,000	5×10^{17}	5×10^{18}	4×10^{10}	1×10^{11}
1,000,000	1×10^{18}	5×10^{18}	8×10^{10}	1×10^{11}

Radiation Damage Processes

When any solid is irradiated three basic responses are possible. It can be subject to heating, experience localised displacement of ions or become globally disordered. This section covers how the different kind of radiation affect the nuclear waste and how different kinds of wasteform perform.

Heating: When any kind of radiation is absorbed by a solid the temperature of the solid will increase. The size of this increase depends of several factors: The rate at which the energy is absorbed, the physical properties of the material (e.g. the specific heat or the thermal conductivity)and the rate that the material can conduct the heat away to the surroundings. With commercial HLW loadings significant heating is possible and when placed in repository conditions could reach temperatures at high at 600 °C [77]. Even after 100 years temperatures are likely to remain as high as 300 °C and this can have significant effects on the radiation response of the material. Figure

2.7 shows 2 plutonium hemispheres from the core of a nuclear weapon that have been placed on top of each other. The heating effect causing it to glow red-orange is entirely down to radiation self heating.

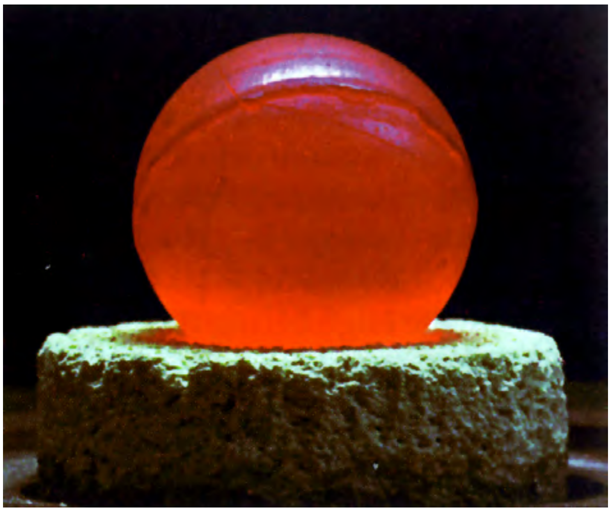

Figure 2.7: Radiation induced self heating 2 joined hemispheres of plutonium for use in a nuclear weapon [81].

Irradiation by α-particles and α-recoils: This is the most important form of radiation damage as it has the largest effect on the structure of the material. Typical energies of an α-particle are in the range of 4.5-5.5 MeV and the recoil atom has an energy in the range of 10-100 keV. Even though the α particle carries 98% of the energy of the decay event it has been calculated that this only accounts for accounts for a small fraction of the displacement energy imparted to the ions in the solid (between 6 and 11%) [77]. The reason for this counter-intuitive effect is due to the two primary ways in which moving particles can deposit their energy. These are: displacive (elastic collisions) or ionisation (inelastic) processes. Which of these that dominates depends on the relative velocity of the moving particle and that of the electrons orbiting the target ion. If the velocity of the particles is higher than the speed of the electrons then the dominating process will be electronic excitation but if it is moving slower, the probability of electronic excitation is small and most of the kinetic energy will be transferred to the nucleus. A rough rule for determining the dominating process is given by Ewing [77]: inelastic processes are important if the energy, expressed in keV, is greater then its atomic mass. Thus an α-particle with a mass 4 and energy 5,000 keV is predominantly slowed due to electronic excitation and an alpha recoil ion with mass 234 and an energy of 100 keV is stopped mainly via ballistic collisions. This means that an α-particle has lost most of its kinetic energy through electronic stopping before it can displace an ion in the solid. Therefore very few atoms are displaced by an α-particle and and furthermore this particle can travel a considerable distance of between 10 and 20 μm before it is stopped.

Irradiation by α-particles (and other light, high energy species) tends to result in the scattering of small numbers of ions along the entire path. This results in small clusters of Frenkel defects forming a damage track. This makes recombination of these defects relatively easy as they are surrounded by a large region of undamaged material [77].

In ceramic wasteforms (and most other solids) the only structural consequence of the electronic excitation is heating but in those affected by radiolysis (notably some borosilicate glasses), bond breaking and atomic displacements can occur. This effect allows crystalline silica (SiO_2) to undergo amorphisation by electrons which have an energy less than the displacement energy of the ions [82]. A similar effect has been observed in borosilicate waste glasses which can decompose by absorbing this ionizing energy and produce bubbles of molecular oxygen [79].

The heavier but lower energy α-recoil particle accounts for about 89% of the displacement energy in SYNROC [77] and unlike the α-particle these travel only very small distances, on the order of tens of nanometres (a factor of 1000 less than the range of the α-particle). This results in a large number of displaced ions in a small volume of the solid which can cause localised disordering. This is harder to anneal out than the small number of displaced atoms scattered widely as much of the surrounding order has been removed from the structure.

When an α-particle stops it becomes a helium atom and if the temperature of the wasteform is high enough to allow these to move through the material, they can collect and form helium bubbles in the material. The presence of these bubbles can have significant effects on the mechanical properties of the material, especially if they are located at grain boundaries [77].

Irradiation by β-particles: As mentioned earlier, in nuclear wasteforms β-particles are high-energy electrons formed mainly by the decay of fission products. Because of their very low mass β-particles tend to only create single displacement evens resulting in a Frenkel pair while the rest of their energy is dissipated via electronic excitation [77]. This means that β-particles have a very small damaging effect on most ceramic wasteforms but they could have a large effect on materials which are significantly affected by radiolysis.

β-decay is the principal cause of heating during the first 500 years and plays an important role in the recovery processes that occur in the wasteform.

Irradiation by γ-rays: Irradiation by γ-rays can only directly induce atomic displacements in materials susceptible to radiolysis. They can produce energetic electrons via interactions with solids but as mentioned in the discussion of β-particles, these are very inefficient in producing displacement events and combined with the low rate of production of these electrons, γ-rays are not a significant source of radiation induced structural changes in wasteform materials.

2.3.7 Other Options

It is impossible to eliminate all radioactive waste but there are technologies being proposed that, if implemented, could significantly reduce the quantity of waste ending up in geological repositories. Part of this has already been discussed in the reprocessing section (2.2.4) where recycling of uranium and plutonium (from both civil and defence sources) was discussed. While this redirects the majority of the volume of material from spent fuel away from encapsulation and burial, it still leaves the minor actinides and fission products to be stored. As shown in Figure 2.8 the radiotoxicity of the fission and activation products falls off to virtually zero after about 500 years whereas the radiotoxicity of the actinides and daughter products remains on the order of the original ore even after 1,000,000 years. If the actinides could be removed from the wasteform than the complexity of the disposal process would be significantly reduced. There is only one way that this process can be accelerated and this is by transmutation of these elements in pressurised water reactors, fast breeder reactors and possibly accelerator driven systems [83–87].

2.3.8 Final Disposal

Introduction

No matter how hard we try to reduce the volume of nuclear waste that has to be disposed of, either by reprocessing fuel or by the proposed transmutation of radioactive elements mentioned in section 2.3.7, there will always be some waste remaining that requires disposal. There are two seemingly incompatible approaches to the final disposal of nuclear waste. One is to concentrate and contain and the other involves dilution and dispersal. Both of these options are being used in the U.K. at the Sellafield reprocessing facility. The low level liquid wastes (after as much radioactive material is removed as possible) is pumped out to sea where it is diluted and eventually dispersed by the tides and ocean currents whereas the HLW is concentrated and then encapsulated into a glass wasteform awaiting later disposal.

Geological Repositories

It is almost certain now that the final resting place for high and intermediate level nuclear wastes will be in deep geological repositories [14, 15, 25, 77, 88–94]. The idea behind a repository is to store all the material in one place in such a way that the material does not re-enter the biosphere until the radioactivity has reduced to a level close to the natural background. Current policy for the Yucca Mountain repository in Nevada, U.S.A. is that it is necessary to demonstrate that no material will escape from the site for 10,000 years [93]. This may seem to be a long time but the radiotoxicity of the actinides in the wasteform remain higher than that for the natural uranium ore from which it was extracted for approximately 1,000,000 years see figure 2.8. The functions of a repository, according to the International Atomic Energy Agency (IAEA), change with time and are discussed in detail in the 2003 technical report [94] and summarised here:

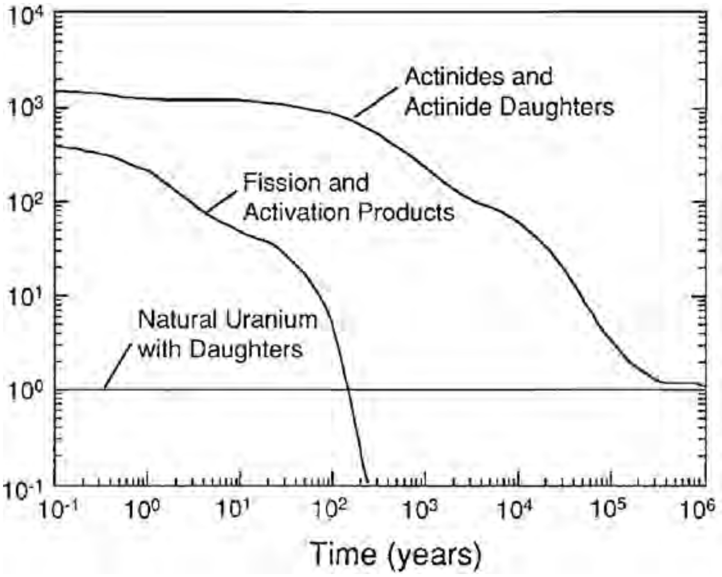

Figure 2.8: Relative radiotoxicity on inhalation of spent nuclear fuel with a burnup of 38 megawatt days/kg U. The radiotoxicity values are relative to the radiotoxicity (horizontal line) of the quantity of uranium ore that was originally mined to produce the fuel (eight tons of natural uranium yields one ton of enriched uranium, 3.5% ^{235}U) [95]

For the first few hundred years of its life, the repository should isolate the material from the fluctuation conditions on the surface and protect the biosphere from any contaminations i.e. while the radioactivity is at its peak. This should also be done in such a way as to isolate it from human activities so that it will be difficult and unlikely that it is disturbed either deliberately or accidentally. After the level of radioactivity has substantially decayed (after a few thousand years) the focus of the repository starts to shift from the complete containment philosophy to the acceptance that leaching of waste outside of the repository barriers is no longer serious. Processes should be in place that delay this point for as long as technically possible and keep this rate as low as possible. One way of ensuring this is the multi-barrier approach which will be discussed next. The final stage of the repository is to enable dispersion of the long lived radionuclides through the rocks that make up the repository. This can take many forms but one idea is for the dispersed material to encounter large bodies of water such that on return to the biosphere in tens or hundreds of thousands of years the concentrations are sufficiently dilute as to pose no threat.

In order to contain the waste for such long periods of time and eventually limit the rate of escape, repositories are designed around a multi-barrier approach similar to a set of Russian dolls [94, 96]. This idea is based on the fact that it cannot be guaranteed that any single barrier is capable of stopping the waste from escaping for a long time. The first barrier consists of the wasteform itself which is designed to be as durable as possible. This is then placed and welded inside a metal canister (e.g. stainless steel or copper [15, 94]). This container is then surrounded in a metallic overpack. Overpack and canisters are designed to protect the wasteform from corrosion more than act as a barrier against the release of the radioactive material.

They can be made from either corrosion resistant materials or a corrodible metal. If corrodible metals are used they should be of sufficient thickness to last until the short lived fission products have decayed. Once corrosion is complete the expected corrosion products (iron oxyhydroxides) can help further trap any radionuclides that have leached from the waste [94]. Corrosion resistant overpack materials (such as copper or titanium) have the potential to keep the wasteform isolated from water for much longer periods (100,000 years), maybe to the point where most mobile radionuclides have decayed to activities similar to natural uranium ore [94].

Once the waste packages have been loaded into the repository, backfill materials are packed around them. These vary depending on position in the repository and can include compacted bentonite clays to be packed around the HLW packages, crushed rock from the excavation process and concrete for use in regions for ILW [94]. The purpose of the bentonite clay around the HLW is threefold: The first is to limit the flow of water to and from the waste packages, bentonite clay has very low hydraulic conductivity. The second is, through its plastic nature, to isolate the package from damage due to small rock shifts caused by the heating effect of the waste or from minor earth tremors [94]. The final reason is that the clay has a sorption capacity that slows the migration of radionuclides. The crushed rock filling the rest of the repository (once sealed) is there to reduce the flow of water through the tunnels and provide structural support. In areas around the compacted bentonite, a mixture of bentonite powder and rock should be used as the clay expands upon contact with water and the backfill material must be dense enough to stop this material escaping.

The repository itself should be located in a geologically stable region. In this case stable means that there is a low probability of the site being damaged by earthquakes, volcanic activity, meteorite impact and flooding. Ideally due to the time periods involved it should also be in a region unlikely to be affected by the glaciation that may occur in another ice age. The repository should be made of impermeable rock so that, in the unlikely event of the container leaking, no waste will escape the region into the biosphere. This is also important as the atmospheric conditions in the repository should be kept constant as a change from reducing conditions to oxidising conditions, or vice versa, would change the behaviour of many of the material currently being researched [97]. Table 2.4 Shows the locations of major geological radioactive waste disposal research projects worldwide.

Table 2.4: Locations of major geological radioactive waste disposal research and operational projects [98]

Country	Location	Facility	Lithography	Age	Depth(m)
Belgium	Mol	URL	Clay	Paleocene	220
Canada	Lac du Bonnet	URL	Granite	Archean	420
Germany	Asse	URL	Salt	Permian	925
Germany	Gorleben	RCF	Salt	Permian	840-1200
Germany	Konrad	RCF	Sedimentary	Jurassic	1000
Germany	Morsleben (ERAM)	RCF	Salt	Permian	500
Japan	Tont	URL	Granite Margin	Cretaceous	150
Siberia	Tomsk	Aquifer	Sandstone	Cretaceous	300-400
Sweden	Stripa	URL	Granite Basement	Proterzoic	-
Sweden	Aspo	URL	Crystalline Basement	Proterzoic	450
Switzerland	Grimsel	URL	Granodiorite	Miocene	450
Switzerland	Mont Terri	URL	Clay	Jurassic	-
USA	Carlsbad (WIPP)	Repository	Salt	Permian	655
USA	Yucca Mountain	RCF	Tuff	Miocene	300

URL: Underground Research Laboratory

RCF: Rock Characterisation Facility