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Review
The immobilization of high level radioactive wastes using ceramics and glasses

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An overview is given of the immobilization of high level radioactive waste (HLW) and surplus materials from a variety of commercial and defence sources employing glass and ceramic hosts. A number of specific host materials are reviewed, including borosilicate and phosphate glasses, glass-ceramics and crystalline ceramics. Topics covered include wasteform processing and manufacture, in addition to wasteform stability, durability and mechanical behaviour. Although, at the present time, borosilicate glass is the generally accepted first generation wasteform for the immobilization of HLW, the emergence of new sources of radioactive materials requiring immobilization has renewed interest in many of the alternative candidates. These include, in particular, titanate, zirconate and phosphate based ceramics, together with iron phosphate based glasses and basaltic glass-ceramics. The relative merits and limitations of each host material are compared and discussed, with particular reference to processing considerations and to current and likely future requirements.

1. Introduction

The immobilization of highly radioactive waste materials in glass or ceramic hosts has been under investigation for many years (e.g. [1–38]). Until recently, most of the available data have related to the development of materials for the long term storage or disposal of high level nuclear waste materials either from the reprocessing of spent commercial reactor fuels, or from a number of defence reprocessing operations. More recently, driven partly by public concern over the safety of nuclear power plants, particularly since the accidents at Three Mile Island in 1979 and Chernobyl in 1986, many governments have abandoned or restricted their plans for future nuclear plants. Consequently, materials that would have been employed in new power plants are now less likely to be required; therefore there is an increasing interest in immobilizing or disposing of excess commercial stocks of uranium and plutonium fuel [39, 40]. In addition, with the ending of the Cold War, interest has also recently been shown in the immobilization of surplus plutonium and related materials from dismantled nuclear weapons [41–45].

Although many different types of glass and ceramic materials have been investigated as possible candidates for the immobilization of HLW, at the present time borosilicate glass is the generally accepted first generation wasteform (e.g. [46]). As a result of this decision, many commercial vitrification plants are now in operation throughout the world using borosilicate glass as the first generation host for the immobilization of HLW. With the increasing demand for the immobilization of large quantities of HLW from many additional and diverse sources, there is, however, a strong incentive to reconsider many of the alternative types of wasteform and to identify new candidate materials, in particular, alternative glass compositions, glass-ceramic materials, and titanate and related ceramics.

The present contribution reviews and compares the more important glass and ceramic based materials and processes considered for the immobilization of HLW and surplus materials, and discusses the merits and limitations of each.

2. Types of waste

Radioactive waste is generated from a number of sources including the reprocessing of spent fuel, certain defence reprocessing operations, hospital, university and commercial research activities, industrial use of isotopes, and mining and refining of uranium ore [4, 31]. Unprocessed spent nuclear fuel may itself require immobilization if the U is not to be recovered. More recently, a requirement has arisen for the immobilization of certain surplus materials. Some of the more important high level waste and surplus nuclear materials are discussed below. Typical waste constituents are summarized in Tables I and II.

2.1. Nuclear reactor wastes

Following commissioning in the UK of the first commercial reactor for the generation of electricity in 1956

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TABLE I Composition of high level liquid wastes[a] ($g\,l^{-1}$)

Component	Savannah River (USA)	Hanford (USA)	West Valley (USA)	Idaho Falls (USA)	Tokai (Japan)	Lanchow (China)	Sallugia (Italy)	Sicral 1 (France)	La Hague (France)	Magnox (UK)	THORP (UK)	HEWC (Belgium)	HAWC-WAK (Germany)	WIP (India)
H^+	–	–	–	–	2.5 M	1.5 M	1.3 M	–	–	–	–	–	–	–
Al	7.7	1.5	3.9	4.2	–	4.5	20.4	32.5	–	26.0	–	44.0	0.2	–
Na	5.9	4.1	10.3	3.1	44.5	31.0	–	20.5	–	–	0.1	1.9	16.0	6.6
K	0.3	–	0.1	0.9	–	0.6	–	–	–	–	–	–	0.4	0.2
Mg	0.2	–	0.3	–	–	–	–	4.0	–	30.0	–	–	0.2	–
Fe	29.7	6.1	20.6	–	8.4	13.5	0.6	16.0	20.0	13.0	4.0	1.3	5.2	0.5
Ni	2.8	0.6	0.5	–	2.2	2.9	–	1.5	3.2	1.4	–	–	1.2	0.1
Cr	0.3	0.1	0.3	–	2.2	1.2	–	1.5	3.4	1.6	–	0.1	1.3	0.1
Mo	0.2	0.2	–	–	–	0.7	–	–	–	10.8	18.3	–	–	–
Zr	0.6	3.4	0.4	11.4	–	0.7	–	–	–	11.8	20.1	–	–	–
Hg	1.8	–	–	–	–	–	1.0	–	–	–	–	2.8	–	–
Cl	0.9	0.1	–	–	–	–	–	–	–	–	–	–	–	–
SO_4	0.8	0.2	1.1	2.6	–	4.8	0.6	–	–	–	–	3.2	–	0.5 M
NO_3	4.2	2.8	20.6	12.5	–	–	–	–	–	11.0 M	–	–	–	4.1 M
FPs[b]	<3.0	<2.5	<1.5	<1.0	49.0	2.7	–	24.5	87.0	–	–	0.5	40.5	1.1
TRUs[c]	<0.2	<0.1	<0.2	<0.1	12.6	17.9	–	3.0	5.1	2.0	4.5	0.1	6.9	7.6

[a] Data from [46].

[b] FPs, fission products.

[c] TRUs, transuranic elements.

M = Molar.

THORP = Thermal oxide reprocessing plant.

HEWC = Highly enriched waste concentrate.

HAWC = Highly active waste concentrate.

WIP = Waste immobilization plant.

TABLE II Composition of calcined Magnox fission products[a]

Oxide	Amount (wt %)
MoO_3	14.4
ZrO_2	13.9
Nd_2O_3	13.1
Cs_2O	9.4
CeO_2	8.5
RuO_2	7.8
BaO	4.6
La_2O_3	4.2
Pr_6O_{11}	4.0
Tc_2O_7	3.8
PdO	3.3
SrO	2.9
Sm_2O_3	2.6
Rh_2O_3	2.2
Y_2O_3	1.7
TeO_2	1.6
Rb_2O	1.1
Pm_2O_3	0.5
Eu_2O_3	0.3
Sb_2O_3	0.2
Ag_2O	0.1
In_2O_3	0.1
Gd_2O_3	0.1

[a] Data from [12].

a wide range of nuclear power reactor designs are now in use worldwide [46]. All the reactors currently in operation rely on the fissioning of the ^{235}U isotope, which constitutes $\approx 0.7\%$ of natural U, by neutrons that have passed through a moderator; for example, water, heavy water or graphite. The purpose of the moderator is to slow the neutrons down sufficiently to enable fission to take place. In most reactor designs uranium enriched in ^{235}U is employed [excluding Magnox or Canadian deuterium uranium (CANDU) reactors that both use natural U]. The heat produced by fission is used to produce steam that is subsequently used to drive a turbine, in much the same way as steam is employed to drive turbines in coal or gas fired power stations. The uranium is used in the form of fuel rods, of which there are several different types, depending on the design of the reactor [47]. In advanced gas cooled reactors (AGR), for example, the fuel is in the form of UO_2 pellets contained in stainless steel fuel cans. In the case of pressurized water and boiling water reactors (PWR and BWR, respectively) and CANDU reactors, the UO_2 fuel is enclosed in zirconium alloy fuel cans. In Magnox reactors, a uranium metal rod is encased in magnesium alloy fuel cans, while in old USSR designed reactors oxide pellets are contained in fuel cans manufactured from zirconium–niobium alloy.

The precise composition of the spent fuel will depend on the type of reactor and the operating conditions [46, 47], but differences in the radioactive fission products that are obtained will normally be small. Spent fuel elements may either be stored intact or may be reprocessed to retrieve the unused U fuel. Currently, a large proportion of spent fuel, particularly in Canada and the USA, is being stored temporarily awaiting a decision as to whether or not to dispose of this fuel without first retrieving the U (together with some Pu that is formed during the burn-up process.)

Reprocessing of spent fuel rods normally involves removal of the cladding material followed by dissolution in nitric acid. This stage is then followed by chemical solvent extraction of the U together with the Pu formed during the fuel burn-up process. The remaining solution contains the dissolved fission products (FP) together with impurities from the cladding materials, inactive process chemicals, transuranic (TRU) elements formed by neutron capture, and traces of unseparated Pu. This constitutes a high level liquid waste product, HLLW. This HLLW is normally concentrated by evaporation and stored as aqueous nitric acid solution in stainless steel tanks. Alternatively, the solution may be neutralized by addition of an alkali. These solutions therefore contain a host of products ranging from fission products with atomic weights distributed around 46 (half the atomic weight of U; e.g. Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Cs, Ba, La, Ce Pr, Nd and Sm with smaller concentrations of Ag, In, Sb, Eu and Gd); to fuel alloying elements including Fe, Al, Si and Mo; cladding elements including Zr, Mo, Nb and Mg; TRU elements including Np, Am, Cm and some residual Pu; and process chemicals including kerosene, tributyl phosphate and related organic materials [11, 12, 46, 47].

Although storage of this concentrated HLLW has been regarded as an acceptable solution in the short term, it has now become necessary to replace liquid storage by an alternative longer term storage system based on waste solidification and immobilization of the radionuclides, ultimately in a deep underground repository. Wastes that have been stored as concentrated HLLW over a long period of time may also contain corrosion products from the tanks in which the liquid waste has been kept, in particular iron, chromium and nickel impurities; and these too need to be incorporated into the solidified wasteform.

The disposal of these highly radioactive waste materials has been described as the Achilles' heel of nuclear power [48] because it is difficult to convince the public that such materials can be disposed of safely, particularly when considering geological timescales. The question of nuclear waste disposal is undoubtedly one of the factors responsible for the decline in nuclear power programmes worldwide over recent years.

2.2. Defence wastes

Defence wastes differ from commercial wastes, and have mainly arisen as by-products from the processing of Pu and tritium for use in nuclear weapons [4, 31]. In the USA these wastes are stored in underground stainless steel tanks at a number of sites, including the Hanford and Savannah River (SRP) plants. These acidic wastes are neutralized with NaOH and stored as an alkaline liquid sludge. Consequently, these wastes contain high concentrations of sodium. The wastes at Savannah River also contain high concentrations of Fe and Al, together with some Ni, Hg, chloride, sulphate and nitrate; while the wastes at Hanford contain Fe, Zr, Al and nitrate. Smaller quantities of waste from the reprocessing of fuel from naval reactors are stored as calcined products at the Idaho chemical processing plant (ICPP). These wastes contain high concentrations of nitrate, together with Zr, Na, Al and sulphate. With the exception of the naval reactor waste, the defence wastes do not in general contain high concentrations of fission products, and they may therefore be considerably less radioactive than their commercial equivalents.

2.3. Surplus materials

Interest in the immobilization of excess stocks of commercial and military materials, including uranium and plutonium, has grown considerably in recent years, particularly with the ending of the Cold War. Both the USA and former USSR currently have comprehensive programmes aimed at examining methods that may be suitable for the immobilization of these excess materials in a safe, proliferation-resistant form that will prevent their recovery for weapon use. In the USA a number of immobilization strategies have been addressed for this special category of material [49–57]. The most important include storing the material in its current form in safe guarded vaults, using the material as a mixed oxide (MOX) fuel in nuclear reactors, irradiation of material in a fission reactor to produce alternative less radioactive wasteforms, vitrifying the material in a borosilicate glass, and immobilization as an oxide ceramic wasteform.

3. Immobilization of radioactive waste

In general, UK commercial wastes contain high concentrations of Al, Mg, Zr, Mo and Fe, while materials from the USA, which mainly consist of defence wastes, contain high concentrations of nitrate, Fe, Na and Al. French waste products can also be high in Al, Na and Fe; while Chinese waste is high in Na, TRU elements, Fe and sulphate; and Indian waste is high in Na, nitrate, phosphate and TRU elements. Japanese materials are particularly high in Na and TRU elements. Details of waste compositions are summarized in Tables I and II.

The rationale behind the immobilization of radioactive waste materials in glass or ceramic hosts is to provide a solid, stable and durable material that can be more easily stored or disposed of than the current liquid wastes. Immobilization may be accomplished either by dissolution of the waste elements on an atomic scale within the host lattice, or by encapsulation of the waste within an inert matrix. Wasteforms can be temporarily stored at the solidification processing plant (during which time the heat generated by the decay of the fission products decreases), but the longer term strategy is to dispose of them permanently in an underground repository as part of a multibarrier approach. The immobilized waste would therefore form only one part of an engineered system designed to prevent contamination of the biosphere with radioactive elements.

Proposed repository or vault designs consist of a number of deep boreholes (at a depth of around 300–1000 m), possibly including interconnected galleries, in which the solidified waste contained in metal canisters would be buried [12, 18]. The canisters would be surrounded by an overpack material that in turn would most probably be surrounded by an inert overfill. Three types of geological formations have been suggested as suitable for the construction of a repository, namely salt, clay and hard rock (granite or basalt). The rationale behind the choice of salt is that there are salt deposits throughout the world that have remained stable for millions of years. Clay offers the advantage of being extremely impervious to water, while granite or basaltic rock formations are found in deep geologically stable environments. The overpack material would consist of a corrosion resistant metal, such as Ti, or a thicker layer of an iron alloy that would corrode at a slow, predictable rate. The backfill is likely to be composed of a clay with a low permeability to water or, alternatively, a cementitious material. Assuming the resulting vault remains undisturbed (i.e. there are no earthquakes or related phenomena), the only mechanism by which radionuclides could reach the biosphere would be by dissolution of the wasteform in groundwater, followed by migration of the radioactive solution to the surface. It follows that one of the major factors in selecting a wasteform material for ultimate disposal in an underground repository is its resistance to leaching by groundwater that may eventually penetrate the repository environment.

Many different types of glass and ceramic wasteforms have been studied over a long period of time, and a number of evaluation studies have been conducted around the world. Some of the wasteforms considered include borosilicate, aluminosilicate, high silica and phosphate glasses, silicate-based glass-

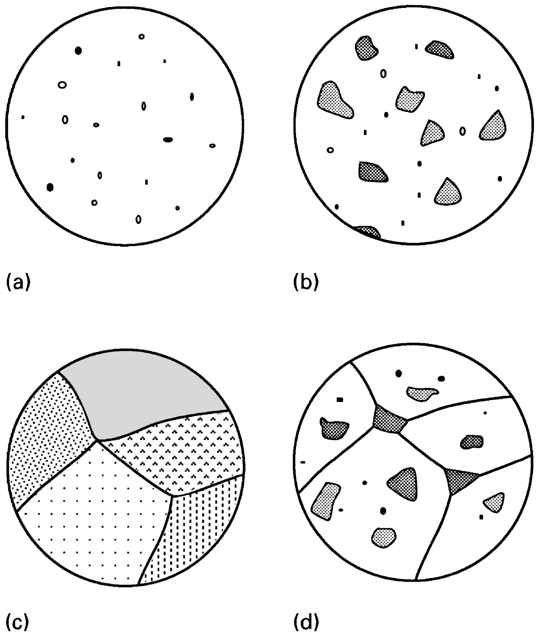

Figure 1 Schematic illustrations of different wasteforms: (a) homogeneous glass, with some bubbles and inclusions; (b) waste particles encapsulated in a glass matrix; (c) ceramic wasteform with waste phases in solution; and (d) ceramic with encapsulated waste phases.

ceramics, titanate-based crystalline ceramics, alumina-based ceramics, clay-based materials, and various forms of cement and concrete. Wasteforms have been examined in which the radionuclides and other waste elements are incorporated directly into the wasteform lattice on an atomic scale as solid solutions, in addition to forms in which the wastes are incorporated macroscopically into a separate matrix phase, which may be either metallic or non-metallic, to form a composite material. Some generic forms are shown schematically in Fig. 1.

4. Immobilization as a vitreous wasteform

4.1. Background

Immobilization of high level nuclear wastes by vitrification is a well established process that has been studied extensively over the last 40 years in the UK, Germany, Italy, Canada, USA, former USSR, India and Japan [10, 12, 18, 46]. A suitable glass host is used to dissolve the HLW to form a glassy (vitreous) homogeneous product that can be cast into suitable forms, including large glass blocks. Under suitable conditions, it is possible to incorporate up to 25–30 wt % HLW into a glass. The choice of glass composition is a compromise between high HLW solubility, manageable glass formation temperature, and low leachability in repository environments. Various glass systems have been shown to be suitable for producing waste glass forms that are thermally and mechanically stable and exhibit good chemical durability. The main advantages of the vitrification route include the fact that glass is a good solvent for HLW; glass can be processed at reasonably low temperatures; glass is very tolerant of variations in waste composition; glass exhibits reasonable chemical durability; and glass is radiation resistant and can accommodate changes occurring during radioactive decay of HLW constituents. The technology for preparing glass wasteforms, both in laboratory size samples and multitonne forms, is well established and vitrification plants are operational throughout the world. Many tonnes of HLW immobilized in glass are currently in interim storage at various vitrification plants awaiting the construction of suitable underground repositories for their permanent disposal.

The potential use of glass as a nuclear wasteform was initially investigated in the early 1950s in Canada using a natural silicate mineral, nepheline syenite, as the starting material [10]. This was mixed with an acidic solution of the waste material together with lime, and the mixture melted at 1250–1350 °C in a fireclay crucible. An active pilot plant was subsequently constructed at Chalk River in order to demonstrate the feasibility of the vitrification process on a larger scale. Radioactive blocks of glass were produced between 1958 and 1960. The development of glass wasteforms was terminated in 1960 because no fuel reprocessing was foreseen in Canada at that time; a new programme was not initiated until 1976.

In the UK also, work started in the 1950s, initially using natural soils as the base material for glass formation [10]. These glasses had to be melted at very high temperatures (about 1500 °C) in order to produce homogeneous, bubble-free products. Subsequently, alkali borosilicate glass compositions were developed that could dissolve up to 30% waste oxides and that could be melted at lower temperatures. Between 1958 and 1962 a vitrification pot process was developed at the UK Atomic Energy Authority's Harwell laboratory called the fixation in glass of active liquors (FINGAL) process. This process involved calcining and then melting HLW together with glass frit in a stainless steel crucible or pot, with the pot subsequently serving as the storage container. After the glass and waste had been calcined, melted and homogenized, the pot was removed and replaced with another pot containing waste and frit ready to be calcined and melted. The FINGAL process was later modified and scaled up, becoming known as the highly active residue vitrification experimental studies (HARVEST) process.

Although these and other related glass wasteform pot manufacturing processes were successful in pilot plant trials, batch processing considerations led France to choose a continuous melting process for full scale development. The French process has the addition of a separate calcining stage [46]. Waste is first calcined employing a rotary kiln before being fed under gravity into a metallic pot heated inductively. This is a continuous process with new glass frit and waste material being supplied to the furnace and molten glass being fed from the furnace via a freeze–thaw valve directly into a separate storage canister. The major advantage of this process is that much higher throughputs can be achieved. Radioactive operation of an industrial pilot plant initially commenced in 1968 at Marcoule in France, and full scale operation started in 1978. This particular method is now known as the atelier de vitrification de Marcoule (AVM) process. Similar plants have since been built at La Hague in France. The advantages offered by the AVM process, coupled with its successful full scale operation in France, led the UK (British Nuclear Fuels Limited, BNFL) to choose this process, in preference to the HARVEST method, for its commercial waste vitrification plant at Sellafield [58].

An alternative continuous process has been developed using a Joule-heated ceramic melter [46]. In this process the glass is melted in a tank constructed from refractory ceramic blocks by passing an electric current through the molten glass using submerged electrodes. Calcined HLW mixed with glass frit may be fed into the furnace from a rotary calciner, similar to the AVM method, or, alternatively, a slurry of waste and frit may be added directly to the furnace, with evaporation and calcination occurring within the furnace environment, as in the pot process. A highly viscous glassy layer forms at the walls of the ceramic containment vessel so that, in effect, the glass itself acts as its own crucible. A major advantage of this method is that it does not produce a large number of contaminated crucibles or furnaces. In addition, because cold material covers the surface of the molten glass, evaporation losses, particularly from volatile fission elements, such as Ru and Cs, are minimized. The first large scale development of a ceramic melter for vitrification of HLW was carried out at Battelle Pacific Northwest Laboratories (PNL) in the USA where a pilot plant was commissioned for radioactive use in 1984. A ceramic melter was also commissioned for radioactive work in 1985 at Mol in Belgium. Further large scale ceramic melters are under construction at Savannah River and West Valley in the USA and Tokai in Japan. A related process employs a cold crucible induction melter. In this method the glass frit is melted in a water cooled metal crucible. As in the case of Joule heating, the melt does not come into direct contact with the crucible.

More recently, attention has been turned to the immobilization of excess uranium and plutonium from commercial operations and dismantled nuclear weapons using glass or ceramic hosts. Articles on the potential use of vitrification techniques for the immobilization of weapons plutonium have recently appeared in the popular press, including *New Scientist* [41, 42]. Immobilization of fissile materials introduces additional considerations, in particular the question of criticality, which are discussed later.

Many different families and compositions of glass have been studied since the 1950s, when the idea of using glass as a wasteform host was first considered. Some of the more important of these are discussed in the following sections.

4.2. Glass requirements

4.2.1. Glass-forming ability

It is now generally recognized from the kinetic theory of glass formation that most materials are glass forming, providing that the cooling rate is high enough to avoid crystallization, and the final ambient temperature on cooling is below the glass transition temperature, T_g, of the material (see e.g. [59]). There are, however, a number of categories of material that will form glasses readily without having to impose a rapid quench rate, including certain oxides, chalcogenides and salts. In fact, many of these materials will form glasses at very low cooling rates, often $<0.1\,\mathrm{K\,s^{-1}}$, and these materials can be produced in bulk form by conventional casting routes. An important parameter in glass technology is the critical cooling rate for glass formation, R_c, that for any given material is the minimum cooling rate required to avoid crystallization. This can be calculated from kinetic data, usually by constructing time–temperature–transformation (TTT) or continuous cooling transformation (CCT) curves. The value of R_c is given by the minimum cooling rate required in order just to by-pass the nose of the TTT or CCT curve. The smaller the value of R_c, the larger the cross-section of material that can be produced in a glassy form without crystallization occurring. Glasses for the immobilization of HLW must in general be capable of being cast into relatively large blanks without crystallizing, so that candidate glasses must possess low critical cooling rates for glass formation. These topics are considered more fully in Section 9.1.

4.2.2. Thermal stability

Glassy materials are, of course, metastable with respect to temperature and time (see e.g. [59]). The thermal stability of a glass is therefore of additional practical importance. The glass must be sufficiently stable to enable the glass to be annealed without crystallization occurring. In general, all glasses will crystallize if heated at a sufficiently high temperature for a sufficiently long period of time. Usually this crystallization proceeds in an uncontrolled manner by nucleation of large crystals from external surfaces, and this leads to the formation of undesirable stresses that may cause the glass to crack. Thermal stability is particularly important in the case of glasses to be used for the immobilization of HLW because poor stability may lead to the formation of crystals either during annealing of the glass, or during its time in storage. If serious cracking of the glass subsequently occurs, leaching rates may be significantly enhanced. This is also considered more fully in Section 9.1.

4.3. Types of glass

4.3.1. Borosilicate glasses

Silicate glasses have long been the preferred wasteform for the immobilization of HLW. This is because they readily dissolve a wide range of waste compositions and they can be easily modified in order to optimize their properties. In addition, they form the basis of the commercial glass industry, and have been studied extensively for many years. They are, therefore, well characterized and their properties are well known and understood.

Ideally, the most durable wasteform would be vitreous silica, but this material requires too high a processing temperature. Commercial glass compositions therefore reflect a compromise between glass durability, processing ability and economics. Boric oxide is most commonly employed to modify the behaviour of silica, this additive substantially lowering the processing temperatures required for glass formation and workability, while maintaining good durability within given composition ranges. As a result of a number of early studies, borosilicate glass has become the first choice of material worldwide for the immobilization of nuclear waste materials, and it is the only qualified "reference" HLW wasteform at the present time. This selection was based on the flexibility of borosilicate glass with regards to waste loading and the ability to incorporate many different kinds of waste elements, coupled with good glass-forming ability, chemical durability, mechanical integrity, and excellent thermal and radiation stability. Compositions studied have generally concentrated on the sodium borosilicate system with minor additions of other modifying oxides, including alumina, lithia, calcia and zinc oxide. A very large data base has now been established for borosilicate glasses for the immobilization of HLW, with extensive information available on the processing characteristics, durability and corrosion behaviour, mechanical performance, thermal stability including devitrification behaviour, and radiation stability (e.g. [10, 12, 60, 61]).

More recently, attention has been turned to the possible use of borosilicate glass as a host for high concentrations of actinides, in particular surplus plutonium and uranium from both civil and military operations. For example, Taylor *et al.* [40] have summarized the findings of a study aimed at identifying materials for the disposal of stocks of waste plutonium from civil operations. A number of different wasteforms were considered in this study. It was concluded that borosilicate glass offered the preferred wasteform option for applications involving the immobilization of plutonium. This was despite the fact that these glasses have been designed specifically as solvents to accommodate high concentrations of reactor fuel elements and fission products, and the solubility of actinide elements was relatively low, i.e. <3 wt %. Use of borosilicate glass has also been proposed for the immobilization of excess Pu from dismantled nuclear weapons [50].

Compositional data and selected properties for a number of borosilicate glasses that have been considered for the immobilization of HLW are summarized in Tables III, IV and V, respectively.

4.3.2. Phosphate glasses

Although the majority of glasses studied to date for the immobilization of HLW have been based on borosilicate compositions, some work has also been reported on phosphate systems [65–72]. The atomic bonding characteristics of phosphate glasses in many respects more closely resemble organic polymers than silicate networks, and this leads to many differences in properties between the two families of glasses [73]. In general, phosphate based glasses are less stable thermally than their silicate equivalents and they are considerably less durable, particularly in aqueous environments, although there are some notable exceptions. They also exhibit lower melting temperatures, lower melt viscosities and substantially different temperature–viscosity behaviour.

Interest in phosphate glasses was high during the early immobilization studies, due in part to the relatively low formation temperatures required, coupled with their high solubility for sulphates and metal oxides (sulphates cause phase separation of silicate glasses and lead to a decrease in durability due to the formation of a soluble phase). Interest in phosphate glasses quickly declined, however, due to a combination of factors. These included the very poor chemical durability of the early compositions, coupled with their low thermal stability. In addition, phosphate melts are normally highly corrosive in nature, significantly more so than their silicate equivalents, and this is a factor that would seriously limit melter lifetime. Improved reprocessing also led to HLLW low in sulphate, so that high sulphate solubility was no longer required. Some work did continue, however, mainly in Europe (and particularly in the former USSR). A number of sodium aluminophosphate, iron aluminophosphate and zinc phosphate compositions were subsequently developed that exhibited improved chemical durabilities, although their thermal stabilities were still relatively low and they remained highly corrosive.

More recently, a new family of lead iron phosphate glasses has been developed at Oak Ridge National Laboratory in the USA. These glasses have been shown to exhibit good glass-forming characteristics, together with reasonable thermal stabilities and excellent chemical durabilities. In addition, these newer melts are not as corrosive as the earlier phosphate compositions. Lead iron phosphate glasses can be prepared at temperatures in the range 800–1000 °C, which is some 100–250 °C lower than the borosilicate compositions currently employed for immobilization of HLW, although it has been reported that a temperature of at least 1000 °C is required in order to dissolve HLW fully. It has been noted that the thermal stabilities of these glasses, although improved, are still not as good as those of the borosilicates. It is therefore unlikely that canisters similar in size to those currently used for borosilicate immobilized HLW could be employed without crystallization of the phosphate glass occurring. Although leach rates have been reported to be 10–1000 times lower than for the borosilicate compositions, once some initial crystallization of these phosphate glasses has been allowed to occur durability decreases markedly. In addition, durability in aqueous solutions also decreases markedly at temperatures >100 °C, which may be important when considering repository environments where temperatures may significantly exceed this figure. There is some evidence to suggest that increasing the Fe_2O_3 content of the glass, while reducing PbO, increases the glass durability, particularly in saline solutions, but more work is required in this area before definitive conclusions may be drawn. It has also been noted that addition of CaO to iron phosphate glasses improved durability [74].

The solubilities of actinide oxides in phosphate glasses are significantly higher than the solubilities associated with borosilicate compositions. Phosphate glasses, particularly those based on lead iron phosphate, would therefore appear to offer considerable promise for the newer applications involving immobilization of plutonium both from dismantled nuclear weapons and from curtailed civil operations.

Compositional data and selected properties for a number of phosphate glasses considered for the immobilization of HLW are summarized in Tables III, IV and V, respectively.

4.3.3. Rare earth oxide glasses

Only limited work has been reported in the area of rare earth oxide glasses for immobilization applications, but one commercial lanthanide borosilicate composition has been considered. This glass, described as “Löffler” glass, was developed originally as an optical glass in the 1930s and contained 55 wt % of lanthanide oxides. It has recently been suggested as a potential host for the immobilization of U, Pu and Am [62], exhibiting a higher solubility for these elements than conventional borosilicate glass.

TABLE III Glass compositional data, silicate[a] (wt %)

	Li_2O	Na_2O	K_2O	MgO	CaO	BaO	TiO_2	ZrO_2	ZnO	B_2O_3	Al_2O_3	SiO_2	PbO	Others
SON/64/G3	–	15.8	–	–	–	–	–	–	–	23.7	–	60.5	–	–
M5(189)	4.9	10.3	–	–	–	–	–	–	–	29.3	–	55.5	–	–
M22(UK209)	5.4	11.2	–	–	–	–	–	–	–	14.8	–	68.6	–	–
C/31-3	1.3	1.4	–	1.8	4.8	18.4	3.6	–	6.2	5.2	13.1	44.2	–	–
SON/64-G3	–	15.8	–	–	–	–	–	–	–	23.7	–	60.5	–	–
SM/58	4.2	5.2	–	2.4	4.3	–	5.1	–	–	13.8	1.3	63.7	–	–
PNL76-68	–	11.2	–	–	3.0	–	4.5	–	7.5	14.2	–	59.7	–	–
72-68	–	5.4	5.4	2.0	2.0	2.0	–	–	28.9	15.1	–	37.0	–	2.0 SrO
R7T7	2.4	11.8	–	–	4.8	–	–	1.2	3.0	16.7	5.8	54.3	–	–
SM513-LW11	4.7	6.5	–	2.2	5.1	–	5.1	–	–	14.7	3.0	58.7	–	–
DWPF(min)	4.3	11.4	2.9	–	1.1	–	0.8	–	–	13.7	4.0	61.8	–	–
DWPF(max)	4.8	12.7	4.8	–	1.3	–	1.1	–	–	10.7	7.5	57.1	–	–
SRL131	5.7	17.7	–	2.0	–	–	1.0	0.5	–	14.7	–	57.9	–	0.5 La_2O_3
76-101	–	11.2	–	–	3.0	–	4.5	–	7.5	14.2	–	59.6	–	–
SRL165	7.0	13.0	–	1.0	–	–	–	1.0	–	10.0	–	68.0	–	–
SON68	2.4	11.9	–	–	4.9	–	–	–	3.0	16.9	5.9	54.9	–	–
GP98/12	–	17.5	–	3.3	4.5	–	3.6	–	–	11.0	1.6	58.5	–	–
PO422	4.3	1.4	2.8	–	2.8	–	–	–	2.8	19.9	5.0	61.0	–	–
PO631	4.4	1.2	2.8	–	2.8	–	–	–	3.1	20.3	4.9	60.5	–	–
SM539	4.5	10.5	–	–	6.5	–	–	–	–	33.0	–	45.5	–	–
AVM8	–	18.6	–	–	–	–	–	–	–	25.3	–	56.1	–	–
ABS-39	–	14.2	–	–	–	–	–	–	–	21.0	3.4	53.2	–	1.9 UO_2 + 6.3 Fe_2O_3
ABS-41	3.3	10.3	–	–	–	–	–	–	3.3	17.5	2.7	57.1	–	1.8 UO_2 + 4.0 Fe_2O_3
SG7	–	7.4	–	1.0	2.7	–	–	–	–	8.3	8.6	72.0	–	–
PFR116	6.9	–	–	–	–	–	10.0	–	–	13.3	10.0	59.7	–	–
Aluminosilicate	–	5.8	1.1	2.8	14.4	–	5.4	3.6	–	–	11.9	55.0	–	–
VG98/12	–	17.5	–	2.1	4.1	–	4.6	–	–	12.4	2.6	56.7	–	–
'Borosilicate'	3.7	7.4	3.7	3.0	12.1	–	2.4	4.6	–	18.6	–	39.8		4.6 CuO
MW	5.3	11.1	–	–	–	–	–	–	–	21.9	–	61.7	–	–
Modified SRL165	6.2	13.5	–	1.0	1.2	–	–	–	–	8.8	6.0	63.2	–	–
EMS11	0.8	–	0.7	1.6	0.8	–	–	–	17.7	–	27.2	51.3	–	–
Lan-14	–	–	–	–	–	2.6	–	–	–	7.8	16.9	51.7	5.8	9.9 La_2O_3 + 5.5 CeO_2
Lan-17	–	–	–	–	–	2.7	–	–	–	6.9	19.9	46.4	4.9	5.7 La_2O_3 + 6.0 CeO_2 + 7.6 Nd_2O_3

[a] Data from [5, 12, 17, 18, 62–64].

TABLE IV Glass compositional data, phosphate (wt %)[a]

	Na_2O	CaO	Fe_2O_3	MnO_2	Al_2O_3	P_2O_5	PbO	Others
Fe phosphate	10.0	–	35.0	–	–	55.0	–	–
PbFeP	–	–	10.8	–	–	40.8	48.4	–
PAMELA 78/7	–	–	22.2	–	7.1	70.7	–	–
PbFeP/1C	–	–	11.5	–	–	34.4	54.1	–
PbFeP/4C	–	–	14.1	–	–	41.9	44.0	–
PbFeP/9C	–	–	21.1	–	–	44.1	34.8	–
PbFeP/1D	–	–	8.1	2.2	1.6	34.3	53.8	–
PbFeP/5D	–	–	10.3	2.9	2.0	45.9	38.9	–
PbFeP/KfK	–	–	9.0	–	–	50.0	41.0	–
Rus1	25.0	–	–	–	19.6	55.4	–	–
Rus2	44.0	–	–	–	20.0	36.0	–	–
Rus3	44.0	–	–	–	20.0	24.0	–	12.0 SO_3
Rus4	44.0	5.0	5.0	–	10.0	29.0	–	7.0 SO_3

[a] Data from [65–70].

4.3.4. Alternative glasses

High silica glasses have better leaching resistances than the borosilicate compositions but require higher temperatures for melting. Consequently, work on high silica glasses has mainly been limited to materials prepared by sintering, as described in Section 4.3.5.

Aluminosilicate glasses were investigated in the early days of waste vitrification (e.g. [27]), but these too normally required higher melting temperatures than the borosilicate compositions. Aluminosilicate glass blocks containing active waste were buried below the water table at Chalk River in Canada in 1960 and monitored until 1978 when they were finally removed. This represents the only publicized example of immobilized active vitreous waste being monitored in this fashion. It was calculated from the data obtained in this experiment that it would have taken 20 million years for the glass to have been totally dissolved under these environmental conditions.

Aluminosilicate glasses have been examined more recently by Vance *et al.* [63] as a host for U-rich HLW. It was reported that up to 20 wt % UO_2 could be retained if the melt was cooled rapidly, while $\leqslant 10$ wt % was retained if a cooling rate of 5 °C min^{-1} from 1400 °C was employed. High melting temperatures (≈ 1600 °C) were required for these glasses due to their high silica contents. Durability was reported to be good, with superior resistance compared with borosilicate glasses. A low alkali aluminosilicate glass has also recently been evaluated as a potential second generation wasteform with improved durability [75].

4.3.5. Sintered glass

Due to problems associated with the manufacture of high silica glasses by melting, some work has been aimed at producing these materials by a sintering route. By using sintering a reduction in the processing temperature of several hundred degrees can be accomplished. These lower temperatures minimize or eliminate evaporation losses from volatile fission elements, particularly Cs, Ru, Mo and Tc.

The sintering of calcined HLW mixed with glass frit was first reported by Ross in 1975 [76]. Later work by Terai *et al.* [77] examined hot pressing of simulated waste with a number of different glasses, including pyrex borosilicate. It was subsequently confirmed by work at Kernforschungszentrum Karlsruhe (KfK) in Germany that hot pressing was essential in order to produce wasteforms of sufficiently high density, particularly for samples of size above ≈ 20 cm in diameter [64]. In the work at KfK, simulated waste loadings of up to 35 wt % were demonstrated for sintered glass prepared by hot pressing; compact densities $>95\%$ of theoretical were achieved. These wasteforms were prepared by uniaxially hot pressing mixtures of simulated HLW calcine and glass powder in a He atmosphere using graphite dyes. Relatively low pressures were employed, in the range 0.2–2.0 MPa, high pressures not being required to densify glassy inorganic materials. Sodium borosilicate based glass compositions were used in these studies, and the resultant wasteforms were shown to exhibit good chemical durability and mechanical integrity. From microscopic examination it was established that much of the waste was incorporated into the glass not by dissolution, but rather mainly by encapsulation, although diffusion into the glass of some species did occur, notably Cs and Ba, and some chemical reaction occurred with other constituents, for example, Ce, Nd and Zr.

In an alternative approach, a candidate high silica porous glass wasteform was developed at the Catholic University in the USA [78]. In this process, a homogeneous glass is first phase separated to give an interconnected structure consisting of a silica-rich phase and a phase low in silica. The phase low in silica is subsequently dissolved in acid to yield a porous glass consisting of interconnected pores 10–50 nm in size distributed in a high silica matrix. Rods of this material may be soaked in liquid waste, the waste being taken up into the pores by capillary action. The rods are then heated at 900 °C to seal the waste into the structure. The main advantage of this process is the high chemical durability of the wasteform. In terms of scaling up the process it has been proposed that porous silica rods could be made in an inactive facility prior to waste loading and processing. Treated rods could subsequently be stored in their treated condition, or could be used as part of a multibarrier

TABLE V Selected properties of glass wasteforms

Code	Waste loading (wt %)	Density ($g\,cm^{-3}$)	T_g (°C)	T_m (°C)	MOR (MPa)	Young's modulus (GPa)	Poisson's ratio	Vickers hardness (10^4 Pa)	Fracture toughness ($MPa\,m^{1/2}$)	Thermal expansion ($10^{-6}\,K^{-1}$)	Thermal conductivity ($W\,m^{-1}\,K^{-1}$)	Specific heat ($J\,g^{-1}\,K^{-1}$)
Borosilicate	$\leqslant 33$	2.60	–	–	–	82	0.22	720	0.97	8.1	1.1	0.90
Sintered	$\leqslant 33$	2.56	–	–	32	73	0.22	–	–	6.8	1.3	0.81
Pb-Fe-phosphate	16	4.7	477	518	–	–	–	–	–	11.0	0.6	0.40
Pb-Fe-phosphate	6	5.0	502	544	–	–	–	–	–	10.3	0.6	0.40
PNL 76–78	–	–	–	–	–	81	–	620	0.65	9.0	–	–
SON68	–	–	–	–	–	84	–	910	0.95	8.3	1.09	0.84
UK209	–	–	–	–	–	90	–	–	0.69	8.4	1.29	–
SM513	–	–	–	–	–	89	–	720	0.98	9.1	1.01	0.9
GP98/12	–	–	–	–	–	82	–	610	0.84	8.1	1.33	0.9
72–68	–	–	–	–	–	–	–	–	–	–	–	0.18
M5	–	–	–	–	–	–	–	–	–	–	1.2	–
MW	–	2.7	–	–	–	–	–	–	–	–	–	–
VG98/12	0	2.55	537	–	–	–	–	–	–	–	–	–
VG98/12	15	2.75	–	–	36	73	0.24	–	–	10.4	1.05	0.84
SG7	0	2.38	567	–	–	–	–	–	–	–	–	–
SG7	15	2.56	–	–	32	73	0.22	–	–	6.8	1.30	0.81
Rus2	–	2.58	397	–	–	–	–	230	–	16.0	–	–
Rus4	–	2.60	429	–	–	–	–	190	–	18.0	–	–

[a] Data from [66–70].

T_m = end of melting temperature.

approach by encapsulation in a suitable matrix material.

4.4. Processing of vitreous wasteforms

There have been programmes in many countries throughout the world concerned with the development of suitable industrial-scale vitrification plants. A simplified flow chart is given in Fig. 2 that summarizes the main stages required in a HLW vitrification process. All processes follow the same basic procedure whereby HLLW first undergoes evaporation. This is then followed by calcination and subsequently vitrification to produce a solid, homogeneous wasteform. Melting temperatures are usually limited to around 1100–1200 °C to minimize volatilization of fission products.

In pot vitrification processes calcination and vitrification generally take place in the same reaction vessel. Glass frit together with HLW (either as a partially evaporated liquid or as a solid produced by complete evaporation of HLLW) is fed into a crucible or pot heated electrically or inductively. The pot may subsequently serve as the container or may serve as a crucible from which molten glass can be fed off into a separate container or canister.

In a modification to the pot process, calcination of the HLW is carried out prior to the vitrification stage, either in a rotary calciner or a spray calciner. The calcined HLW is subsequently fed, together with glass frit, into the melting vessel.

In a further modification to the process, a ceramic melter is employed, the mixture of glass frit and HLW (either precalcined or as a slurry) being melted in a ceramic tank by Joule heating. As glass only conducts ionically at moderately high temperatures, $> T_g$, a separate preheating stage is required in which the first batch of glass is melted in the tank electrically or radiantly. Once at a suitable temperature, submerged electrodes are employed to pass an electric current through the glass. Further additions to the tank of glass frit and HLW are then melted directly by Joule heating. The electrodes may be manufactured from Mo, Ni-based alloy (e.g. Inconel 690) or tin oxide. Molten glass is fed from the bottom of the tank into containment vessels; for example by means of a freeze – thaw valve.

Simple pot vitrification processes that do not employ a separate calcination stage have been used in the UK (FINGAL and HARVEST processes), in France (Pilote Verre – PIVER), and in Italy and the People's Republic of China. Such a process is currently used commercially in India (WIP) for the immobilization of HLW generated during the reprocessing of spent fuel. Pot vitrification employing a separate calcination stage has been studied extensively. Commercial plants are currently in operation in France and the UK (AVM process).

The newer Joule-heated ceramic melter technology has also been widely studied, and ceramic melters are currently employed or about to be employed in commercial plants in the USA, Belgium, Japan, the former USSR and the People's Republic of China.

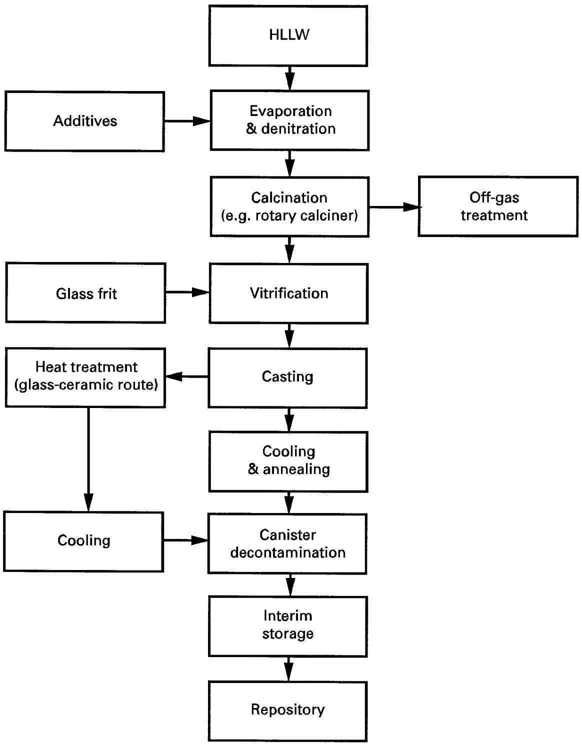

Figure 2 Flow chart for glass wasteform manufacture (with heat-treatment schedule shown for production of glass-ceramics).

German activities in ceramic melter technology were concentrated in the Pilot Anlage Mol zur Erzeugung Lagerfähiger Abfälle (PAMELA) project situated at Mol in Belgium. PAMELA is a continuous vitrification process in which waste in the form of a HLLW slurry together with glass frit is fed into a Joule-heated ceramic melter equipped with two drainage systems. One drain is employed to produce glass blocks, while the second drain is used to feed a glass bead production unit. This produces glass beads with a diameter of 50 mm. The beads are subsequently dispersed in a lead alloy matrix to produce a product called "vitromet". The PAMELA melter is provided with four Inconel 690 electrodes and can operate at power levels up to $\approx$100 kW. Molybdenum disilicide electrical resistance heating elements are provided for startup. The defence waste processing facility (DWPF) at Savannah River, the West Valley demonstration project (WVDP) and the Hanford waste vitrification plant (HWVP), all in the USA, also employ continuous ceramic melters fed with a slurry of waste and glass frit.

Experience gained at PAMELA has shown that noble metals (e.g. Pd, Rh and Ru) gradually accumulate at the bottom of the furnace and lead to increased power consumption due to the higher electrical conductivity of this layer. It is now recognized that a sloped furnace bottom is desirable, thus enabling the viscous noble metal rich layer to be purged more easily from the furnace. The Tokai reprocessing plant in Japan employs a ceramic melter with a steeply sloped floor. Use of a three electrode assembly also allows more effective heating and stirring of the melt, presumably resulting in a more homogeneous product.

A very large ceramic melter facility was constructed in the former USSR in the 1980s for vitrification of phosphate and borosilicate wasteforms. Molybdenum electrodes were used and the maximum power requirement of the melter was around 1.5 MW. It was reported that over an 18 month period this facility incorporated almost 1 km^3 of radioactive solutions into phosphate glass.

A high temperature melter has been proposed [79] aimed at increasing the solubility of HLW in borosilicate glass from around 30 to 45% simply by increasing the melting temperature. This would offer the advantage that it would lead to a reduction in the overall volume of the wasteform and consequently lead to lower disposal costs. The higher temperatures involved would, however, require the use of a more complex melter design due to the increased volatilization of a number of waste species, in particular Cs; and this would add to the capital costs of the melter in addition to increasing the overall running costs. Other studies have suggested that HLW concentrations as high as 45 wt % can be incorporated into borosilicate wasteforms at temperatures as low as 1100–1150 °C (e.g. [80]).

5. Immobilization as a ceramic wasteform

5.1. Background

Immobilization of HLW may also be achieved by direct incorporation into a crystalline ceramic wasteform. Unlike vitrification, however, there are currently no commercial plants in operation for the immobilization of HLW employing crystalline ceramic materials. Compositional data and selected properties of a number of candidate ceramic wasteforms are given in Tables VI and VII, respectively.

5.2. Titanate ceramics

Titanate-based ceramics have been the most widely studied ceramic wasteform. There have been a number of investigations aimed at assessing the suitability of these materials for the immobilization of HLW and transuranic wastes, of which the most widely known is the synthetic rock (SYNROC) family. SYNROC was developed by Ringwood and coworkers in Australia in the 1970s [85–87]. This family of materials is used to immobilize radionuclides by incorporating them and the other waste constituents as solid solutions in the crystal lattices of the various ceramic phases. The rationale behind the choice of these materials as a wasteform is that SYNROC is a titanate ceramic based on naturally occurring minerals, which incorporate actinide elements in nature. SYNROC is usually a combination of hollandite ($BaAl_2Ti_2O_6$), perovskite ($CaTiO_3$), zirconolite ($CaZrTi_2O_7$) and rutile (TiO_2). A wide range of cations of different charges can be incorporated into these crystalline phases, and the mineralogy tends to adjust spontaneously to any fluctuations in waste composition (at least within certain limits). A number of different kinds of SYNROC have been reported [81, 88–103], the specific composition depending on the proposed application; for example, SYNROC-C developed for immobilization of commercial waste from the reprocessing of spent power reactor fuel, SYNROC-D for defence waste, SYNROC-E with improved long-term stability, and SYNROC-F for unprocessed spent fuel containing significant amounts of U and Pu. Typically, 10–20 wt % of HLW oxides can be incorporated into the first three SYNROC phases, with any metallic elements still remaining, e.g. Pd, Ru, Rh, Mo, Re and Tc, being microencapsulated within these phases and within the rutile phase. Zirconolite is the phase that tends to host the actinide elements. Trivalent elements substitute in the Ca site of zirconolite, while tetravalent elements substitute in the Zr site.

There have been a number of studies aimed at assessing the suitability of SYNROC for immobilizing alternative wastes and surplus materials, particularly actinide phases [87–90, 104–112]. For example, Vance and coworkers [88–91] and Kesson and Ringwood [110] have studied modified SYNROC formulations (SYNROC-F) that are rich in zirconolite, while Solomah *et al.* [95] have incorporated uranium-rich waste into a modified SYNROC formulation designated SYNROC-FA. Blackford *et al.* [111] have prepared SYNROC formulations containing a combination of simulated waste and actinides, including Np, Pu and Am.

Single phase zirconolite, with Pu directly substituted for Zr, has been prepared by Clinard *et al.* [105], while Vance *et al.* [112] have incorporated U, Np and Pu into zirconolite. Weber and coworkers [104, 106] have reported the influence of actinide

TABLE VI Ceramic compositional data (wt %)[a]

	Na_2O	K_2O	MgO	CaO	BaO	TiO_2	ZrO_2	Al_2O_3	SiO_2	P_2O_5	Others
SYNROC-B	–	–	–	15.9	7.2	59.5	11.4	6.0	–	–	–
SYNROC-C	–	–	–	11.1	5.5	71.2	6.8	5.4	–	–	–
SYNROC-D	–	–	–	10.3	–	31.8	8.5	33.6	15.8	–	–
DR-FBR[b]	0.4	0.4	0.45	0.45	–	0.45	–	78.6	18.7	–	0.45 Fe_2O_3
DR-LWR[b]	0.65	0.65	1.95	1.95	–	0.3	–	71.8	22.3	–	0.3 Fe_2O_3
NTP 10–21[c]	7.3	–	–	–	–	38.4	–	–	–	54.3	–
NTP 60–28[c]	1.7	–	–	–	–	20.1	–	–	–	78.2	–
Titanate	–	–	–	11.7	–	59.1	27.3	1.9	–	–	–

[a] Data from [6, 81, 82].
[b] Aluminosilicate.
[c] Titanium phosphate.

TABLE VII Selected properties of ceramic wasteforms[a]

Code	Waste loading (wt %)	Density ($g\,cm^{-3}$)	Compressive strength (MPa)	MOR (MPa)	Young's modulus (GPa)	Poisson's ratio	Vickers hardness (10^4 Pa)	Fracture toughness ($MPa\,m^{1/2}$)	Thermal expansion ($10^{-6}\,K^{-1}$)	Thermal conductivity ($W\,m^{-1}\,K^{-1}$)	Specific heat ($J\,g^{-1}\,K^{-1}$)
Titanate	$\leqslant 12$	4.29	–	163	–	–	–	–	8.8	5.8	–
SYNROC	$\leqslant 20$	4.35	–	134	–	0.30	840	1.83	10.5	2.1	0.55
FUETAP	–	–	80	–	–	–	–	–	4.7	1.0	–
Titania	0	4.22	–	170	261	–	–	–	8.66	12.8	0.68
Titania	6	4.29	–	163	207	–	–	–	8.84	5.8	–
SYNROC-B	0	4.23	690	295	190	0.29	970	1.9	10.2	2.4	0.6
SYNROC-C	10	4.35	800	110	134	0.30	840	1.83	10.5	2.6	0.55
SYNROC-D	69	4.00	279	65	158	0.28	868	–	–	–	–
Zirconolite	–	–	–	–	–	–	–	–	12.5	–	–

[a] Data from [6, 83, 84].

phases on the properties of a number of titanate compositions with the pyrochlore structure, including $Gd_2Ti_2O_7$ and zirconolite. Shoup *et al.* [113] have reported the synthesis of $SrPu_2Ti_4O_{12}$ and $Pu_2Ti_2O_7$ together with solid solutions of $Pu_2Ti_2O_7$ and $Ln_2Ti_2O_7$ (where Ln is Gd, Er or Lu).

In the report by Taylor *et al.* [40] on the immobilization of plutonium from civil operations, SYNROC was considered to be second choice only to borosilicate glass. It is possible, therefore, that SYNROC-based materials may become the second generation wasteform for advanced applications.

Work has also been reported on the use of titanate ion-exchange materials for the absorption of waste elements. Materials may subsequently be hot-pressed to form a rutile-based ceramic wasteform [107]. Various types of inorganic ion-exchange materials, including titanates, zeolites and sodalites, have also been suggested for the immobilization of radioactive materials, (e.g. [19, 108]).

5.3. Phosphate ceramics

There have been a number of studies to assess the suitability of alternative ceramics to SYNROC for the immobilization of HLW and related materials [82, 114–119]. For example, analogues of monazite, a lanthanide phosphate mineral that hosts actinides in naturally occurring mineral deposits, have been prepared by urea coprecipitation, calcining and sintering on a laboratory scale with HLW simulants. A wide range of HLW materials can be incorporated into this material and the leach resistances and irradiation behaviours of the resultant wasteforms are good.

Typical monazite materials found in nature contain significant amounts of Th and U, with monazite from Piona in Italy containing ≈ 15 wt % UO_2 and 11 wt % ThO_2. This suggests that these lanthanide orthophosphates could act as useful hosts for the heavier actinides not normally found in nature, in particular Pu. Monazite deposits found in Brazil have been dated as over two billion years old, thereby confirming their excellent stability. In addition, monazites are known to possess negative temperature coefficients of solubility, in contrast to other candidate nuclear wasteforms, including borosilicate glass, for which solubility in aqueous media increases with temperature.

Lanthanide phosphates exist in several crystalline forms, including hexagonal, monoclinic and tetragonal varieties, with transition temperatures ranging from ≈ 400 to 600 °C. They also exhibit very high melting temperatures, typically $\geqslant 2150$ °C. In order to facilitate hot pressing or sintering of these materials at realistic temperatures special processing conditions are required. This can be accomplished using wet chemistry techniques in order to produce highly reactive precursor powders of small particle size; for example, urea coprecipitation methods. Using reactive powders, Abraham *et al.* [117] prepared $CePO_4$ samples up to 97% theoretical density by hot pressing at 1300 °C, while Floran *et al.* [118] reported the preparation of $LaPO_4$ in excess of 90% theoretical density by hot pressing or sintering at 1100 °C. Dense samples of lanthanide phosphates loaded with up to 50% simulated wastes have also been prepared successfully by cold pressing and sintering at temperatures as low as 900 °C [117].

Other phosphates investigated (e.g. [8, 115, 116, 120]) have included a single phase sodium zirconium phosphate (NZP) with the composition $NaZr_2(PO_4)_3$. The structure of NZP contains three types of crystallographic sites and exhibits great compositional flexibility. Waste loadings up to 20 wt % have been incorporated into this structure using sol–gel and sintering techniques while maintaining a single phase material. For loadings $>20\%$ it has been observed that a two-phase material is formed, with monazite as the second phase. Work has also been reported on substitution of Ti for Zr to yield a sodium titanium phosphate (NTP), which under suitable conditions can accommodate up to 60% waste loadings [82].

Work has also been reported on the direct synthesis of Th and U phosphates employing a wet chemistry and sintering route [119, 120]. It was noted that $Th_3(PO_4)_4$ was produced as expected, but that the analogous U compound was not formed; instead a mixed valence compound was formed that was identified as $U(UO_2)(PO_4)_2$.

5.4. Alternative ceramics

Some of the earliest work on the immobilization of HLW in ceramics, which predated the SYNROC concept, produced materials described as "supercalcine", which were generally based on calcium silicate [121]. Early work also assessed the feasibility of utilizing natural clays for the immobilization of HLW [122]. A number of alternative mineral phases, including perovskite, pyrochlore, monazite and nepheline have since been examined for specific HLW compositions, and high HLW loadings and densities achieved using hot isostatic pressing techniques [9].

Recently crichtonite, $SrM_{21}O_{38}(M = \text{Ti, Fe, Mg, Mn, Zn, Cr, Al, Zr, Hf, U, V, Nb, Sn, Cu, Ni})$, has been proposed as a host for both actinide and fission product phases [123]. A wasteform consisting of cubic zirconia, Fe_3O_4 and $BaZrO_3$ crystalline phases has also recently been proposed [124] for immobilizing purex wastes containing high concentrations of Fe and Zr. The material can be made by a wet chemistry route to produce precursor powders. After calcination these powders may be cold pressed and sintered. Lanthanum zirconate, $La_2Zr_2O_7$, together with a number of alternative pyrochlore phases have been suggested as prospective hosts both for actinide and lanthanide rich phases [125, 126]. Mixed $La_2Zr_2O_7$–$2CeO_2 . 2ZrO_2$ phases have also been prepared [125] by cold pressing and sintering at 1400 °C in air or reducing atmosphere. It was noted that actinide elements could be accommodated in either 3^+ or 4^+ lattice sites depending on the reducing conditions employed.

There are few details at present on alternatives to SYNROC as crystalline ceramic hosts for the immobilization of uranium or plutonium from dismantled nuclear weapons or from civil operations. In one study, however, Ewing *et al.* have proposed the use of zircon [127]. Zircon, $ZrSiO_4$, is a stable, naturally occurring mineral that contains radioactive U and Th in nature. Zircon is commonly employed in the dating of mineral samples (from the U/Pb ratio present) and consequently its mineralogy has been studied intensively. It has been noted that Pu can substitute directly for Zr and the pure end-compound $PuSiO_4$ has been successfully synthesized. Several processing operations have been demonstrated on a laboratory scale for the preparation of zircon and Pu substituted zircon, including sol–gel and hot pressing. Other complex rare earth silicates have also been investigated as actinide host phases [106], including $Ca_2Nd_8(SiO_4)_6O_2$.

5.5. Processing of ceramic wasteforms

The most widely studied ceramic material has been SYNROC [6], and there have been many studies aimed at the development of processing routes for the manufacture of SYNROC and related wasteforms.

Early work on SYNROC processing relied on preparing precursor materials by conventional or traditional powder methods; for example, mechanical grinding and mixing. Later work has concentrated on the use of wet chemistry processes; for example, use of hydroxide and alkoxide precursors, and by sol–gel methods. These wet chemistry routes have been shown to be superior and more reliable and efficient than the conventional methods in achieving well reacted and homogeneous end products. In addition, use of highly reactive precursor powders allows lower sintering or hot pressing temperatures to be used.

For example, a method developed at Sandia National Laboratory (SNL) in the USA [101], employs reactive precursors with high specific surface areas. This technology was subsequently transferred and used as the reference process for precursor materials employed in the Australian SYNROC demonstration plant. In the later hydroxide process, methanol was added to a mixture of titanium isopropoxide, zirconium *n*-butoxide and aluminium sec-butoxide in the appropriate proportions [6]. This alkoxide feedstock was then hydrolysed and the resultant precursor was mixed with HLW in the form of a slurry. At the Atomic Energy Authority (AEA), Harwell, UK, a sol–gel process has also been used in which nitrate-stabilized titania and zirconia sols have been mixed with dispersible alumina together with barium and caesium nitrate solutions [96]. The resultant mixture was subsequently spray dried to produce a free-flowing powder.

Manufacture of SYNROC samples has been carried out using a variety of methods, including hot uniaxial pressing in graphite dies, hot isostatic pressing, and cold pressing and sintering of precursor powders (e.g. [6]). More recently, samples have also been prepared by melting oxide and nitrate mixtures at temperatures up to 1550 °C [128].

In the programme at the Australian Nuclear Science and Technology Organization (ANSTO), hot uniaxial pressing of precursor powders in stainless stell collapsible bellows has been employed to demon-

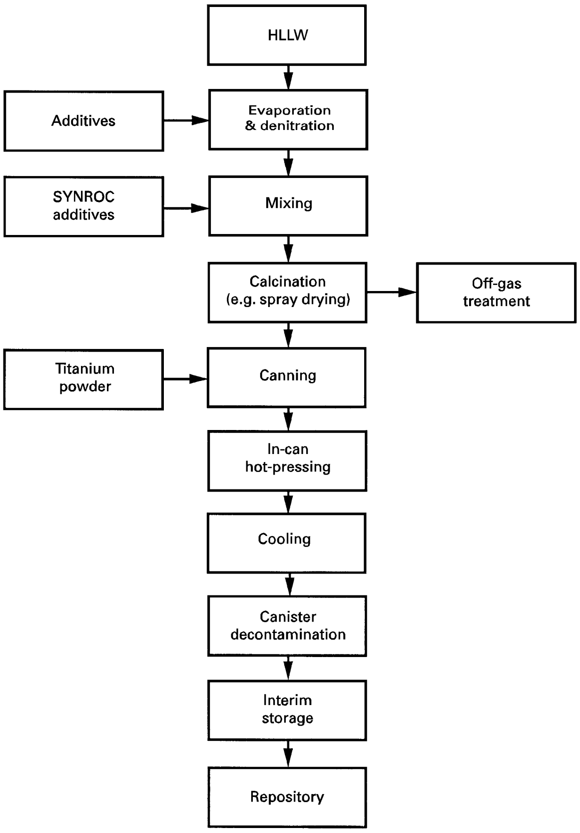

Figure 3 Flow chart for SYNROC manufacture.

strate the fabrication of SYNROC on a commercial scale. A simplified flow chart showing the general stages in hot pressing of SYNROC is shown in Fig. 3 (it should be noted, however, that SYNROC has not, to date, been employed for the commercial immobilization of active HLW). In this operation the precursor is mixed with simulated HLLW to form a slurry that is subsequently fed to a rotary calciner where it is dried and calcined in a reducing atmosphere. The calcined product is then mixed with 2 wt % titanium metal powder to act as an oxygen getter before being fed into the bellows. After filling, a plug is welded over the feed hole and the bellows evacuated. The closed bellows is then cold pressed to approximately two-thirds its original height before loading into a hot press and pressing at $\approx 1150\,^{\circ}\mathrm{C}$ and 14–21 MPa pressure. The process has gradually been scaled up to produce samples 436 mm in diameter. In an active commercial operation it is likely that a number of compressed bellows would be loaded into suitable canisters for disposal.

A comparison has been made of SYNROC prepared both by hot pressing and cold pressing and sintering routes [129]. It was concluded that, as long as an appropriate binder burn-out stage was incorporated, the sintering route gave good results comparable to those achieved by hot pressing.

6. Immobilization as a glass-ceramic wasteform

6.1. Background

Many ceramic phases are known to possess superior chemical durabilities to borosilicate glasses under typical repository conditions. Ceramics, however, are generally multiphase systems containing many minor phases in addition to the major crystalline phases, and it can be difficult to predict long term behaviour in repository environments. In addition, the technology associated with the manufacture of crystalline ceramics is, in general, more complex than that associated with the production of glasses (particularly with the requirement for remote handling facilities in a nuclear environment). It has, therefore, been proposed that glass-ceramics may offer a useful compromise between glasses and ceramics, being easier and less expensive to prepare than conventional ceramics, but offering higher durability than glasses.

Glass-ceramics are defined as polycrystalline ceramic materials prepared by the controlled bulk crystallization of suitable glasses [130]. Crystallization of conventional glasses normally occurs by the nucleation of crystals at external surfaces. This crystallization behaviour generally gives rise to a coarse microstructure with large anisotropic crystals that grow inwards from the surfaces of the glass. Such materials are usually weak mechanically. The success of the glass-ceramic process in producing mechanically strong, fine-grained polycrystalline ceramic materials depends on inducing a high crystal nuleation density within the bulk of the glass by providing a very large number of internal heterogeneities from which the major crystalline phases can form and grow. This can be achieved in practice by the use of specific nucleating agents that are added to the glass batch. Nucleating agents act either by inducing the glass to phase separate on a very fine scale, or by forming small crystallites (of the nucleating phase itself or of some compound formed by reaction with the constituents in the glass). In either case, many small heterogeneities are produced, onto which the major crystalline phases can nucleate and grow [130, 131].

Proposed modifications of the vitrification process for the immobilization of HLW include use of a glass-ceramic as the host for the waste materials. Vitreous blanks may be produced employing standard vitrification procedures. The glass blank can then be subjected to an additional heat treatment schedule in order to crystallize the glass into the glass-ceramic form.

In addition to offering ease of manufacture relative to conventional ceramics, coupled with higher durability than glasses, a number of further potential advantages have been associated with the use of glass-ceramics as HLW wasteforms. These include higher thermal stabilities than borosilicate glass, superior mechanical properties, and an ability to tailor many of their properties to meet the challenges of specific applications. In addition, glass-ceramics are more tolerant of variations in waste composition than are corresponding crystalline ceramics prepared by conventional routes. Glass-ceramics do, however, require an additional heat treatment relative to conventional glasses, thus leading to greater processing complexity, as discussed more fully later.

A number of different glass-ceramic families have been proposed for the immobilization of HLW

[132–157]. Much of the work is based on pioneering studies at the Hahn-Meitner Institute (HMI) in Berlin, the Whiteshell Nuclear Research Establishment (WNRE) in Canada, the Battelle Pacific Northwest Laboratory (PNL) in the USA, and the Power Reactor and Nuclear Fuel Development Corporation (PNC) in conjunction with the Nippon Electric Glass Co. in Japan. Compositional data and selected properties of the glass-ceramics considered for the immobilization of HLW are summarized in Tables VIII and IX, respectively. Work in this area is summarized below.

6.2. Barium aluminosilicate glass-ceramics

A number of modified borosilicate based waste glass compositions containing simulated waste were crystallized in the pioneering HMI studies to yield a selection of specific crystalline phases, including glass-ceramics with celsian ($BaAl_2Si_2O_8$) as the major phase [154]. Other phases present in these celsian glass-ceramics included pyrochlore ($RE_2Ti_2O_7$; RE = rare earth), scheelite ($BaMoO_4$), pollucite ($CsAlSi_2O_6$) and molybdenum-nosean [$Na_8Al_6MoO_4$ $(SiO_4)_6$]. It was noted that the pyrochlore phase acted as a host for actinides and Sr, while the host for Cs and Rb was pollucite. Noble metal fission products were observed to precipitate out as small metallic droplets. Melting temperatures in the range 1175–1250 °C were employed to produce the precursor glasses. The glasses were subsequently nucleated and crystallized at $\approx 620\,^\circ$ and 800 °C, respectively.

Radiation damage of celsian glass-ceramics has been measured directly by doping with Pu or Cm [8, 11]. Mechanical properties have also been studied. The leaching characteristics of the celsian glass-ceramics have been measured in a number of comprehensive studies (see [8, 11]) and have been noted to be comparable to the borosilicate glasses. The leach rates are in fact higher than many other glass-ceramics due to the relatively high boron content. As there is no significant advantage in the durability of celsian glass-ceramics over borosilicate glasses, additional work in this area has subsequently been limited.

6.3. Barium titanium silicate glass-ceramics

Studies at HMI have also included the production of fresnoite ($BaTiSi_2O_8$) glass-ceramics [154]. The aim of this work was to produce a glass-ceramic wasteform lower in boron than the celsian materials and consequently of greater durability. Additional phases in these glass-ceramics included Ba-priderite ($BaFe_2Ti_6O_{16}$), pyrochlore and scheelite. It was noted that the scheelite phase acted as host to Ba and Sr, while Cs remained in the residual glassy phase. A melting temperature of 1200 °C was employed to produce the precursor glasses. The glasses were subsequently nucleated at temperatures of the order of 700 °C and crystallized in the range 900–960 °C. Although these materials were found to exhibit improved mechanical properties relative to borosilicate glasses, unfortunately their durabilities were not enhanced. Consequently, additional work on these materials has also been limited.

6.4. Calcium magnesium silicate glass-ceramics

Glass-ceramics containing diopside ($CaMgSi_2O_6$) as the major crystalline phase have been produced at HMI [154]. Glass-ceramics based on the calcium magnesium silicate system containing diopside, powellite ($CaMoO_4$) and perovskite have also been reported by workers in Japan at the Nippon Electric Glass Co. [148]. Simulated waste loadings of up to 30 wt % could be achieved using these materials. The glasses were melted at 1300 °C. Crystallization was carried out at temperatures in the range 800–1100 °C, usually during controlled cooling of the melt, without the inclusion of a separate nucleation stage. This method of processing eliminated the requirement for a separate additional heat treatment schedule, thereby simplifying the manufacturing process. A bulk diopside glass-ceramic sample has been prepared with a diameter of 30 cm and weighing 65 kg.

Relatively low leach rates have been noted for some of these glass-ceramics, making them useful potential candidates for the immobilization of HLW.

6.5. Calcium titanium silicate glass-ceramics

Work at HMI has also included the preparation of perovskite ($CaTiO_3$) based glass-ceramics; again this work was later abandoned due to durability considerations.

On the other hand, glass-ceramics from the calcuim titanium silicate system with sphene ($CaTiSiO_5$) as the major crystalline phase have been extensively studied by Hayward and coworkers at WNRE as a candidate for the immobilization of potential CANDU wastes [8, 11, 135, 137, 138, 141]. The rationale behind the choice of these materials lies in the fact that sphene is a common constituent of many types of rocks, and calculations have shown that sphene is stable in the saline environment likely to be found within the Canadian Shield.

In the work reported by Hayward, compositions within the Na_2O–Al_2O_3–CaO–TiO_2–SiO_2 system were chosen for detailed study because these glasses were thermally stable and were therefore more receptive to controlled bulk crystallization. In addition, the residual aluminosilicate glassy phases were likely to be chemically durable. Numerous compositions were examined in this work. Glasses were melted in the temperature range 1250–1450 °C, and nucleated at 650–1050 °C and crystallized at 950–1050 °C for varying periods of time. It was noted that sphene was the major, or in fact the only, crystalline phase formed, together with a residual aluminosilicate glass matrix phase. It was observed, however, that crystallization occurred in an uncontrolled manner by nucleation at external surfaces and internal heterogeneities, and this resulted in a coarse microstructure. Glass-ceramics were subsequently prepared containing up to

TABLE VIII Glass-ceramic compositional data (wt %)[a]

	Li_2O	Na_2O	K_2O	MgO	CaO	BaO	TiO_2	ZrO_2	ZnO	B_2O_3	Al_2O_3	SiO_2	P_2O_5	Others
Celsian B1/3	3.0	2.0	–	1.5	5.0	18.4	5.7	1.0	4.5	7.9	15.9	34.6	–	0.5 As_2O_3
Celsian C31/3	1.3	1.4	–	1.8	4.8	18.1	3.5	1.0	6.1	5.1	12.9	43.4	–	0.6 As_2O_3
Celsian	1.3	1.4	–	1.8	4.8	18.2	3.5	1.0	6.2	5.2	13.0	43.8	–	–
Fresnoite BT04	–	–	–	1.5	4.0	38.0	22.5	–	–	–	–	34.0	–	–
Sphene	–	6.3	–	–	14.3	–	18.3	–	–	–	8.1	53.0	–	–
Basalt	–	2.4	2.0	2.7	10.0	–	13.0	3.7	–	–	8.0	40.0	–	15.0 Fe_2O_3 + 0.7 CeO_2 + 0.7 Gd_2O_3 + 1.8 UO_2
PNC/D62	–	–	–	8.5	8.5	–	3.4	–	–	–	8.5	59.2	–	11.9 Fe_2O_3
PNC/C27	–	–	–	–	5.0	16.7	6.3	–	3.4	6.3	18.8	43.5	–	–
PNC/P50	–	–	–	–	31.3	–	12.5	–	–	6.3	12.5	37.4	–	–
PNC/E63	9.4	–	–	–	–	–	7.5	–	5.0	–	15.6	62.5	–	–
PNC/P71	–	–	–	–	14.3	–	14.3	–	–	5.0	9.3	57.1	–	–
PNC/D62A	–	1.2	–	9.3	9.3	–	3.3	–	–	–	9.6	61.7	–	5.6 Fe_2O_3
PNL Basalt	–	2.7	–	6.8	10.3	–	1.6	–	–	–	14.1	52.4	–	11.9 Fe_2O_3 + 0.2 MnO
INEL 1EB	–	7.1	1.6	4.6	10.8	–	–	–	–	0.7	5.9	47.8	3.0	17.6 Fe_2O_3 + 0.2 Cr_2O_3 + 0.1 SrO + 0.5 SO_3
PNC D718	–	1.9	–	7.9	7.9	–	3.4	–	–	4.4	9.8	59.1	–	5.6 Fe_2O_3
MAS1	–	–	–	24.5	–	–	–	–	–	0.4	20.8	53.5	0.8	–
MAS2	–	–	–	23.3	–	–	–	–	–	0.5	20.3	50.9	5.0	–

[a] Data from [8, 11, 140, 157].

TABLE IX Selected properties of glass-ceramic wasteforms[a]

Code	Waste loading (wt%)	Density ($g\,cm^{-3}$)	T_m (°C)	MOR (MPa)	Young's modulus (GPa)	Vickers hardness (10^4 Pa)	Fracture toughness ($MPa\,m^{1/2}$)	Thermal expansion ($10^{-6}\,K^{-1}$)	Thermal conductivity ($W\,m^{-1}\,K^{-1}$)	Specific heat ($J\,g^{-1}\,K^{-1}$)
Celsian	–	3.1	–	–	–	–	0.95	7.9–10.8	1.3	–
Fresnoite	–	3.7	–	–	–	–	–	8.0–10.0	1.3	–
Sphene	–	2.78	–	–	–	–	–	6.4	–	0.71
Sphene	10	2.95	–	110	103	650	1.4	6.5	2.2	0.71
Diopside PNC 62	–	3.01	1185	630	–	–	–	8.6	1.77	–
Diopside PNC 718	–	2.94	1120	600	–	–	–	8.4	1.58	–

[a] Data from [8, 11, 140].

$\approx$25 wt % simulated waste oxides and it was noted that some of the waste elements contributed significantly to the crystallization behaviour. For example, U and rare earth ions were found to catalyse bulk crystallization to yield pyrochlore [$Ca(RE, U)Ti_2O_{7\pm x}$], a mixed rare-earth/U oxide phase with the fluorite structure, and wollastonite at 800–900 °C. These crystalline phases were then noted to react with excess silica at higher temperatures to form sphene. It was found that crystallization of cast blocks weighing 20 kg could be controlled relatively easily. A number of properties were monitored for sphene glass-ceramics containing various waste loadings. In general, chemical durabilities, mechanical properties and radiation stabilities were noted to be good, and were significantly improved over borosilicate glass wasteforms, potentially making sphene glass-ceramics useful candidates for the immobilization of HLW.

Sphene glass-ceramics have also been prepared by a sol–gel route, as reported by Vance [142]. Sol–gel prepared materials were calcined and then sintered at a temperature of $\leqslant$900 °C to yield glass-ceramic materials of near theoretical density. Simulated wastes at loadings of up to 5 wt % were also incorporated successfully. It was noted that the lower processing temperatures required to produce these glass-ceramics by sintering could reduce losses of volatile fission products.

Vance *et al.* [63] have prepared calcium titanium silicate glass-ceramics containing up to 50 wt % UO_2. The glass-ceramics contained $CaUTi_2O_7$ and UTi_2O_6 crystalline phases and were reported to be very leach resistant.

6.6. Basaltic glass-ceramics

Glass-ceramics prepared by the controlled crystallization of remelted natural basaltic rocks (a complex natural oxide based on Si, Ca, Mg, Fe, Al and Ti) have been reported [141, 146]. Based on earlier work at Corning glass works, Lokken *et al.* of PNL [146] have prepared basaltic glass-ceramics containing different waste loadings from a number of sources, including purex and TRU wastes. Glasses were melted in the range 1300–1400 °C. Nucleation and crystallization were carried out in the temperature ranges 670–700 and 900–950 °C, respectively. It was noted that glass-ceramics containing purex waste were composed primarily of augite [$(Ca, Mg, Fe)_2Si_2O_6$], powellite [$(Ca, Sr) MoO_4$] and nickel-iron spinel ($NiFe_2O_4$). The chemical durabilities of these glass-ceramic materials were superior to that of the borosilicate glasses.

Work on iron-enriched basaltic glass-ceramics has also been reported for the immobilization of both commercial and defence wastes, including TRU waste, ICPP and SRP simulated wastes, and zeolites used for decontamination of Three Mile Island containment water together with core debris [8, 11]. Glass-ceramics were prepared by melting batch materials and calcined waste at 1400–1500 °C. Crystallization of these materials occurred during controlled cooling after casting the glass into containers. The phases formed included iron spinel, plagioclase (a solid solution of $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$), augite, fluoroapatite [$Ca_5(PO_4)_3F$], zircon ($ZrSiO_4$), fluorite (CaF_2), cristobalite, hematite (Fe_2O_3) and mullite ($Al_6Si_2O_{13}$), together with residial aluminosilicate glass. Samples up to 75 kg in weight have been cast successfully. Additions of titania and zirconia have also been added to this family of glass-ceramics in order to promote the formation of zirconolite, which is an effective host for actinide phases [143]. In this case, the cast glasses were crystallized by holding at 1200 °C for 16 h. In addition to zirconolite, the crystallized phases included pseudobrookite (Fe_2TiO_5), augite and chevkinite ($Ce_4Fe_2Ti_3Si_4O_{22}$).

Glass-ceramics containing basalt-like crystalline phases have also been prepared from blast furnace slags. In the former USSR extensive work has been carried out on the manufacture of these calcium aluminosilicate based glass-ceramics, known as slag sitalls, for applications in the construction, architectural, chemical and petrochemical industries [155, 156]. The major crystalline phases present in these materials included wollastonite ($CaSiO_3$) and anorthite ($CaAl_2Si_2O_8$). The resulting materials possessed high mechanical strengths and good chemical durabilities. This work has been extended to include related glass-ceramic compositions for the immobilization of HLW [8, 11]. Waste loadings of up to 50 wt % have been reported, and the main crystalline phases have included diopside, montecellite ($CaMgSiO_4$) and fayalite (Fe_2SiO_4). One disadvantage in using slag sitalls for HLW immobilization is the long times that are required in order to crystallize these materials (typically 50–100 h), this adding to the processing costs.

Conley *et al.* [144] have crystallized zirconolite from iron-enriched basaltic melts containing titania and zirconia by controlled cooling. The resultant product consisted of zirconolite, pseudobrookite and augite crystals dispersed in a glassy matrix. The total crystalline content of these materials was relatively low, however, so that they could not be regarded as true glass-ceramics.

6.7. Alternative silicate based glass-ceramics

Alkali titanium silicate glass-ceramics have been prepared as candidate wasteforms for the immobilization of defence wastes from ICPP [8, 11]. These glass-ceramics were prepared by hot isostatic pressing, rather than by the normal glass-ceramic route involving fusion. Very high simulated waste loadings of up to 75 wt % were reported. Glass-ceramic compositions based on eucryptite ($LiAlSi_2O_6$) have also been studied at HMI and in Japan [8, 11].

6.8. Phosphate glass-ceramics

The great majority of the work reported on glass-ceramic materials has concentrated on silicate systems. Limited data are available on phosphate glass-ceramics, but most of the information relates to materials based on calcium phosphate and related

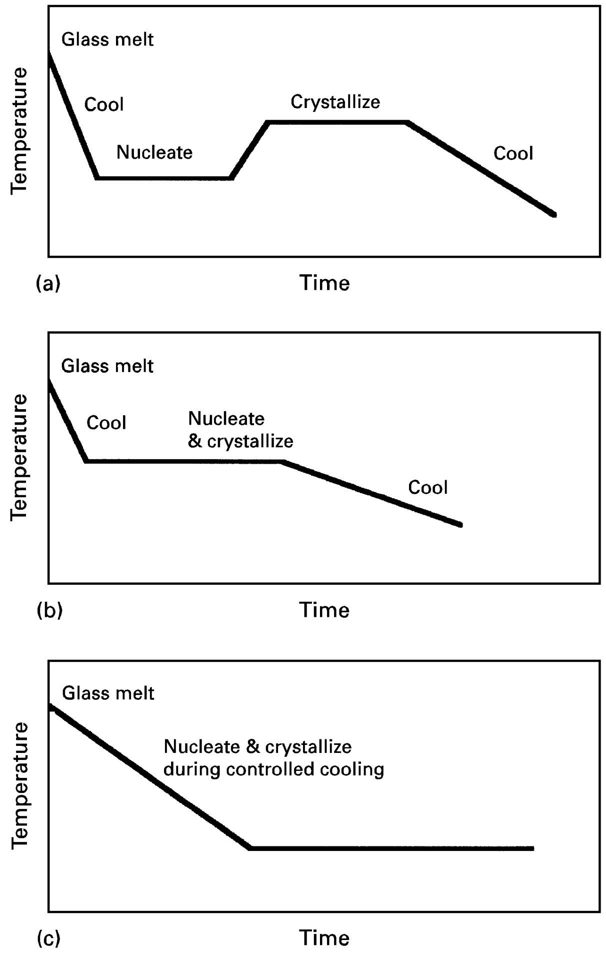

Figure 4 Glass-ceramic heat-treatment schedules: (a) separate nucleation and crystallization stages, (b) simultaneous nucleation and crystallization at a single temperature, and (c) nucleation and crystallization during a controlled cooling cycle.

phases with potential biomedical applications; for example, bone replacement and dental implants [73, 158, 159]. Some additional work has been reported on alternative phosphate-based glass-ceramics (e.g. [160]), but little has been reported on phosphate glass-ceramics for the immobilization of HLW.

6.9. Processing of glass-ceramic wasteforms

Programmes aimed at the development of glass-ceramic wasteform processing routes have in general been less extensive relative to borosilicate glass and SYNROC development. In any glass-ceramic process the starting glass composition and the heat-treatment schedule must be chosen carefully in order to provide a system that will undergo controlled bulk crystallization (rather than surface crystallization) to yield a material possessing desirable properties, e.g. fine grain size, high mechanical strength, good leach resistance, etc. Glass-ceramic wasteforms offer the advantage that they may be produced using conventional glass melting routes, but usually with the addition of a separate heat-treatment schedule after the casting stage, as summarized in Fig. 2. Depending on the composition of the glass, this extra heat treatment stage may consist of separate nucleation and crystallization stages, or it may consist of a simple heat treatment at a single temperature, or may even be by controlled cooling, as depicted in Fig. 4.

7. Immobilization by encapsulation

7.1. Background

Encapsulation relies on immobilizing radionuclides by isolating them from the environment within an insoluble matrix, rather than by dissolving them directly into a glass or ceramic host. The waste is therefore usually dispersed within the matrix as discrete particles, the matrix merely binding the particles together and providing mechanical integrity and a leach resistant coating. A major advantage associated with encapsulation is that it avoids problems that may be encountered when waste constituents are incorporated directly into specific ceramic host phases; for example, compositional inhomogeneities. A number of different materials have been suggested as possible encapsulants, including glasses, ceramics, cement and concrete, and metals. These are described below.

7.2. Glasses and glass-ceramics

Storage by direct encapsulation in a glass or glass-ceramic matrix is not well documented. Examples include the encapsulation of waste that has first been processed into vitreous beads by an inert borosilicate or lead silicate glass matrix. Encapsulation may be carried out by mixing matrix powder with these beads and then hot pressing or sintering. For example, McCarthy and Lovette [161] prepared a glass encapsulated wasteform by mixing calcined waste powders with glass powder followed by hot pressing to form cylindrical products, while Ross [162] employed sintering to produce similar wasteforms. Other work has included the encapsulation of calcined waste in both borosilicate and lead borosilicate glasses [155].

More recently, magnesium aluminosilicate (MAS), glass-ceramics have been investigated as an encapsulant for zirconia based wastes originating from Zr alloy cladding [157]. For this application a MAS glass-ceramic composed of enstatite, indialite and cordierite crystalline phases was developed exhibiting thermal expansion characteristics similar to zirconia. Simulant wasteforms were produced by cold pressing and sintering mixtures of zirconia and glass powder. It was noted that 20 wt % zirconia could be accommodated easily within the MAS matrix, whereas 40 wt % produced a highly porous product.

7.3. Ceramics

More work has been reported on the encapsulation of waste in crystalline ceramic matrices [83, 162–168]. Ceramics, in general, are mechanically hard, durable and corrosion and oxidation resistant materials. They are, therefore, ideal candidates for use in encapsulation and shielding of HLW from the environment in a non-radioactive matrix.

Titanium oxide in particular is an inexpensive, chemically durable ceramic, and it is this material that is largely responsible for the excellent leach resistance

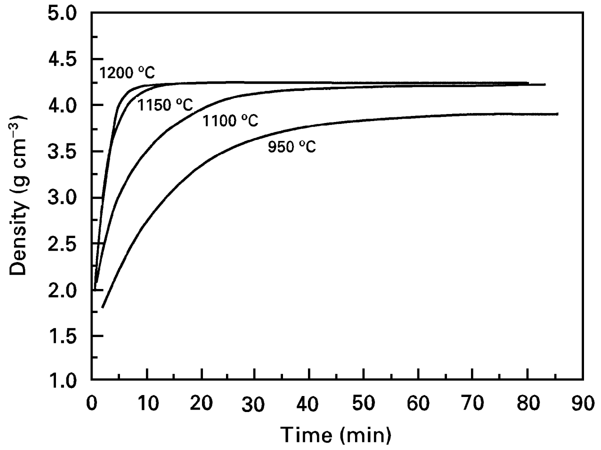

Figure 5 Densification characteristics of titania (anatase powder) at different temperatures (after [83]).

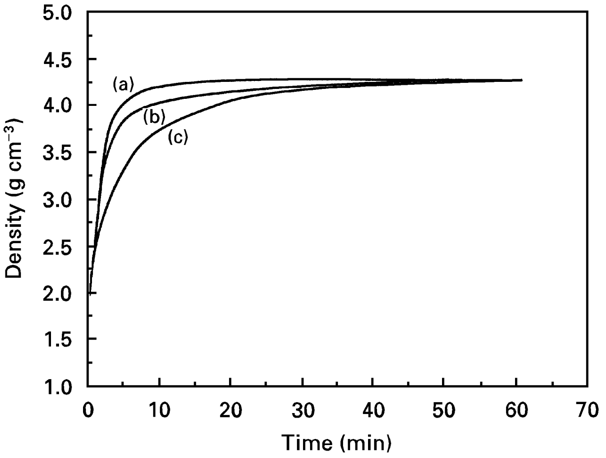

Figure 6 Densification characteristics of titania-based materials. (a) titania at 1150 °C, (b) titania with 6% simulated HLW at 1150 °C, and (c) titania with 1% boron sintering aid and 6% simulated HLW at 950 °C (after [83]).

of SYNROC. The waste composition to be encapsulated is relatively unimportant (unless undesirable reactions occur) because the HLW particles are simply embedded in the ceramic matrix during hot pressing or sintering. It has been noted that certain titania wasteforms can be prepared by hot pressing at temperatures in the range 950–1150 °C [83]. Simulated waste loadings up to 12 wt % have been reported, with the waste particles embedded heterogeneously. In general, hot pressing of rutile powder requires temperatures too high for HLW immobilization, i.e. >1325 °C. It has been noted, however, that anatase can be hot pressed to $>99\%$ of theoretical density at temperatures as low as 1100 °C, as illustrated in Fig. 5. The anatase transforms to rutile during hot pressing, with the accompanying phase change aiding the densification process. The effect of sintering aids has also been investigated, in particular boron and boron oxide. It was noted that 1 wt % boron aids sintering at lower temperatures, down to 950 °C, as illustrated in Fig. 6. In leach tests it was found that hot pressed titania exhibited excellent durability and this was not significantly affected by addition of boron. More work is, however, required in this area.

Alumina and aluminosilicate ceramics have also been employed to encapsulate HLW [83, 163–167] with much of the work involving sol–gel methods. In the sol–gel method HLW is coprecipitated with aluminium hydroxide after seeding with submicrometre size alumina particles; the material may then be sintered at relatively low temperatures. Some elements are incorporated into host phases that are, in turn, encapsulated by the bulk material. Processing of these wasteforms has also included mixing a pH-adjusted slurry of material, followed by hot extrusion to yield cylindrical pellets. High TRU waste loadings are reported by this method. It has also been noted that the aluminosilicate compositions are superior to pure alumina for immobilization of Cs and Rb.

Nepheline ($NaAlSiO_4$), has been used to encapsulate high sodium content wastes [21]. In one process the waste was mixed with kaolinite [$Si_2Al_2O_5(OH)_4$] as a slurry, followed by drying, calcining and hot isostatically pressing to give a dense material consisting almost entirely as nepheline with the radionuclides dispersed within this phase. Durability was noted to be comparable to that of the borosilicate glasses.

7.4. Cements and concretes

In general, cements have been used only for the immobilization of low or intermediate level radioactive wastes, due in part to the high concentration of water that these materials contain (e.g. [169]). Higher levels of radioactivity are likely to lead to radiolysis of the cement during which hydrogen gas is produced as a consequence of the breakdown of water or hydroxyl groups. In addition, many of the inactive constituents of waste streams can prevent the cement from hardening adequately. Further problems arise due to the microporous nature of cement, coupled with its alkaline character, which can lead to the precipitation of alkaline-insoluble waste species. These species are subsequently likely to be leached out of the cement by leachants of different pH. Nevertheless, various cements, concretes and cement-based composites have been proposed as candidates for the immobilization of intermediate waste, HLW and TRU (e.g. [84, 170–179]).

The use of a simple cement to encapsulate HLW does offer some advantages. The material is relatively inexpensive and is readily available. In addition, processing does not require the use of high temperatures. It was reported, for example, that a highly acidic waste has been encapsulated in a cement mix with sodium hydroxide added to retard the curing time and to allow the material to set in the final canister, rather than during mixing with the HLW.

In order to minimize the problem of radiohydrolysis, the use of concrete formed under elevated temperature and pressure (FUETAP) has been proposed as a method for reducing the amount of entrapped water to $\approx 2\%$ [84]. Work by Roy and Goulda [177] in the early 1970s examined the feasibility of hot pressing concrete at temperatures in the range 150–400 °C while applying pressure in the range ≈ 180–345MPa.

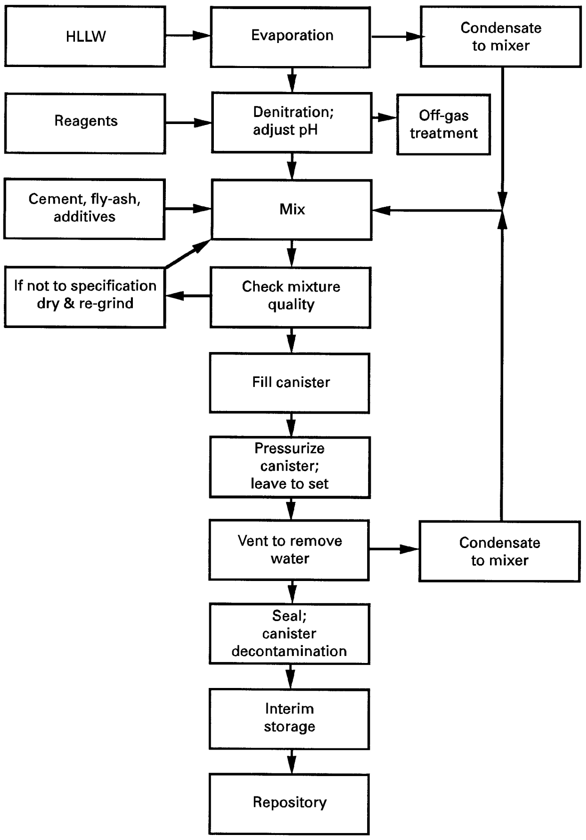

Figure 7 Flow chart for the manufacture of FUETAP (formed under elevated temperature and pressure) concrete.

A number of simulated radioactive waste compositions were employed in these studies. Subsequent work at the Oak Ridge National Laboratory in the USA used lower temperatures and pressures to consolidate materials with very low residual porosity successfully. This work led Moore [176] to consider FUETAP concrete for the immobilization of HLW. When HLW was used, the thermal power of the waste helped to cure the concrete, which in these studies was kept under a pressure of only 0.1–4.0 MPa at 100–250 °C. In principle the concrete mix can be tailored to a certain degree for specific waste streams, and to promote different properties, e.g. good mechanical strength, high density and high thermal conductivity. The processing of FUETAP concrete is unfortunately a relatively complex procedure (particularly when considering remote handling facilities), as illustrated by the flow chart shown in Fig. 7. Most of the research into FUETAP was curtailed in the early 1980s following the decision to use borosilicate glass as the preferred wasteform at the Savannah River Plant.

7.5. Multibarrier approach

The principle behind the use of multibarriers is the "Russian doll" approach, with specific materials serving specific purposes in the containment of the HLW. This approach is therefore related to that of encapsulation, but in general relies on the provision of additional barriers [180–184]. For example, Treat [185] reported the encapsulation of waste immobilized in calcium silicate pellets in a lead matrix. The aim of this approach was to improve the leach resistance and impact strength of the resulting wasteform. In related studies immobilized waste pellets have been coated with pyrolytic graphite, before encapsulating in a metal matrix, in order to improve the leach resistance further [186, 188]. Application of other coatings has also been reported, including alumina, titania, silica, silicon carbide, chromium silicide and chromium oxide, together with a variety of metals including Ni, Fe and Mo. Dual coatings of pyrolytic graphite and alumina have also been reported [189]. Metal matrices have included Pb-based alloys (e.g. Pb–Sb, Al, Sn), Al-based alloys (e.g. Al–Si, Cu, Ti), and Cu.

In one variation of the commercial PAMELA process glass beads containing HLW are produced by passing molten glass through nozzles. The beads are subsequently fed into a container and infiltrated with molten lead alloy to produce a composite wasteform ("vitromet"). The beads, with a diameter of ≈ 50 mm, occupy up to 66% of the total volume. Increased thermal conductivity of the wasteform leading to lower waste temperatures is one of the most important advantages of this product.

Cermets are related composite wasteforms in which radionuclides in the form of small oxide or silicate particles ≈ 1 μm in size are dispersed in a metal matrix. Waste loadings of up to around 30% have been reported [9].

The multibarrier approach can also refer to the use of canisters and containers for storing nuclear materials. Each canister will normally be composed of a number of materials, usually metallic alloys, each with a specific purpose; for example, to impart corrosion resistance, radiation shielding, mechanical strength, etc. The use of ceramic canisters has also been proposed [190].

8. Stabilities and durabilities of wasteforms

8.1. Thermal and mechanical stabilities

The mechanical properties of some candidate nuclear wasteform materials have been reasonably well characterized. Data are available for flexural strength (both uniaxial and biaxial), compressive strength, elastic moduli, mechanical hardness and fracture toughness [191–200]. Thermal data include thermal expansion, thermal conductivity and specific heat. Related properties have also been monitored, including thermal shock resistance (e.g. [191]).

Data have also been collected for a number of waste glasses that have enabled TTT or CCT curves to be constructed [5, 12, 201, 202]. Use of these curves makes it possible to determine whether or not glass stability is likely to present a problem for specific materials, cooling regimes or the storage conditions likely to be encountered in a repository. Fig. 8 shows a schematic TTT curve for a glass. This shows that if the cooling rate of the glass is too low, the cooling curve will intersect the TTT curve and crystals will be formed. The greater the area intersected, the greater the proportion of crystalline phases in the final

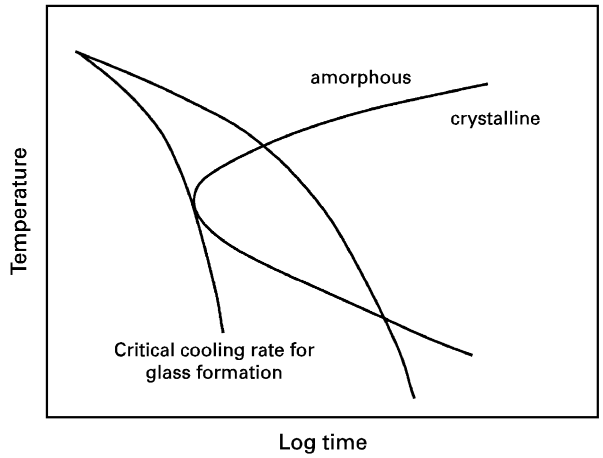

Figure 8 Schematic TTT diagram for a glass showing superimposed cooling curves. The critical cooling rate for glass formation is defined as the minimum cooling rate required to avoid detectable crystallization. It is given by the cooling curve that just coincides with the nose of the TTT curve.

product. A number of TTT curves derived for specific glasses are shown in Fig. 9. Cooling curves for a PAMELA derived glass are given in Fig. 10.

8.2. Chemical durability

8.2.1. General background

There have been numerous studies aimed at determining the chemical durabilities of glass and ceramic wasteforms in different environments [203–252]. In general, vitreous wasteforms exhibit reasonable overall durabilities, although certain crystalline ceramics wasteforms can be produced with superior chemical durabilities relative to that of the vitreous forms. These studies have concentrated both on the durabilities in distilled water at various temperatures and, more recently, on the durabilities of materials in simulated repository environments containing salt and other dissolved mineral phases of various pH.

Many different test methods have been employed for determining the chemical durabilities of wasteforms, and it is now generally agreed that great care must be taken when interpreting the data from such experiments, with many misleading results being obtained in the past due to inadequacies in experimental design. Methods include static tests in which samples are exposed to a fixed volume of water or other leachant, together with various dynamic tests in which circulation or regular replacement of leachant is used.

One of the most widely employed methods is the high-flow-rate Soxhlet test in which a material is normally exposed to large volumes of distilled water. In this method water is boiled in a flask fitted with a reflux condenser. The sample to be tested is held in the neck of the flask so that the condensed water flows over it. The temperature of the water is normally close to 100 °C, but water at a lower temperature can be used by reducing the pressure in the flask. The water may be changed frequently in order to expose the sample to a large overall volume of liquid. This scenario is unrepresentative of a repository environment, but can be used as a rapid test to screen candidate wasteform materials. Various alternative methods have been employed for assessing durability, including tests using powdered rather than solid specimens.

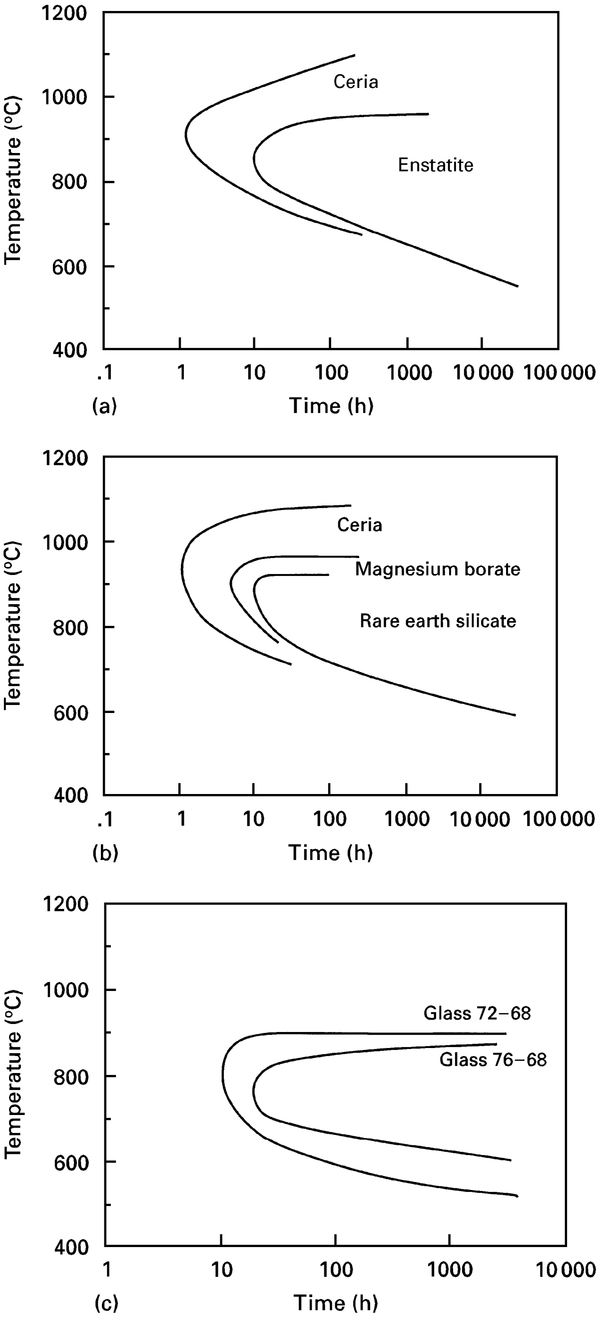

Figure 9 Experimentally derived TTT curves for a number of waste glasses (after [12, 18]) : (a) M22 borosilicate glass showing stability ranges for ceria and enstatite crystalline phases; (b) M5 borosilicate glass showing ranges for ceria, magnesium borate and rare earth silicate crystalline phases; and (c) start of detectable crystallization for 72–68 and 76–68 commercial borosilicate glasses.

More recently, in an attempt to standardize test methods, a series of tests has been proposed by the International Standards Organization's Materials Characterization Centre (MCC) situated at the Battelle PNL, USA. These tests simulate static (MCC-1), high temperature (MCC-2), solubility limited (MCC-3), low-flow-rate (MCC-4) and Soxhlet (MCC-5) conditions.

The MCC-1 test is now the most widely used, this method measuring the leachability of a sample in a relatively small volume of water (or other leachant)

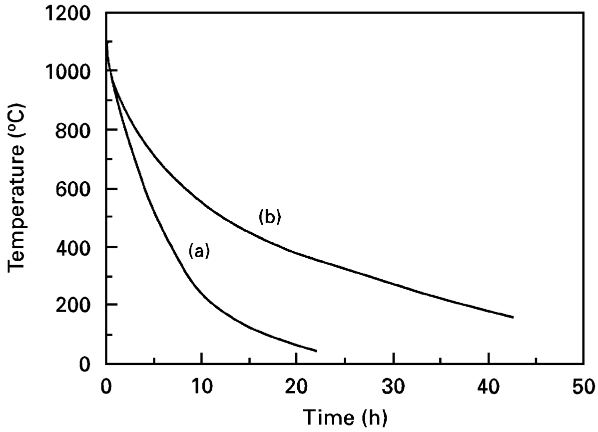

Figure 10 Experimental cooling curves for PAMELA borosilicate glass (showing centre-line temperatures for glass in a cylindrical steel container 30 cm in diameter by 74 cm long). (a) cylinder not insulated, and (b) cylinder insulated with 5 cm of kaowool (after [5]).

over a finite period of time. Samples of known surface area are immersed in the leachant for defined periods of time without agitation at temperatures 40, 70 or 90°C. Under these conditions, the leachant may become saturated with specific constituents from the wasteform and apparent leach rates may be reduced relative to tests carried out employing large volumes of leachant. This test is more relevant to behaviour in a repository than is the Soxhlet method. The MCC-2 test is a static, high temperature test, similar to MCC-1 except that temperatures of 110, 150 and 190 °C are employed. The test is carried out in a Teflon-lined steel capsule. Powdered samples are used in the MCC-3 solubility test, which uses a fixed ratio of leachant volume to sample mass at temperatures in the range 40–190 °C. The MCC-4 test is low-flow-rate method in which samples are immersed in leachant under single-pass flowing conditions, while Soxhlet conditions are employed in the MCC-5 test. Standardization of test methods and conditions has meant that the chemical durabilities of widely different materials can now be compared more directly.

Leach rate, *LR*, may be measured by weight loss according to the relationship

$$LR = (m_\mathrm{i} - m_\mathrm{f})/(SA \times t) \qquad (1)$$

where m_i and m_f are the initial and final sample weights, respectively; SA is the surface area of the sample; and t is the time exposed to the leachant. Typical units would be g $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$.

Alternatively, the leach rate may be monitored by chemical or radiochemical analysis of the leachate, this allowing the release rates of individual elements to be calculated

$$LR = m_j/(SA \times t) \qquad (2)$$

where m_j is the amount of component j leached during the time interval, t.

The leach rate may also be expressed as a normalized rate, $(NLR)_j$, using the expression

$$(NLR)_j = m_j/SA \times t \times m_{j_0} \qquad (3)$$

where m_{j_0} is the amount of component j in the unleached sample.

Many leach tests are carried out in distilled water and useful information on leaching mechanisms can be derived using data from such tests. In general it is more realistic to employ leachants with characteristics more closely matched to those of natural groundwaters. Depending on the geological location, these groundwaters may contain a range of ions, including Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO^{3-}, CO_3^{2-} and SO_4^{3-}, and may range from acidic (low pH) through neutral to alkaline in nature. Neutral to slightly alkaline groundwaters are typical of granite or basaltic rock formations, whereas neutral to acidic conditions are found in many salt environments. In addition to the composition of the leachant, other factors can be important in determining the overall leaching behaviour of a given wasteform; in particular, the temperature and the flow characteristics of the leachant. In static or low-flow-rate conditions leaching may lead to an increase in the concentration of dissolved species in the leachant. Ultimately, the solubility limit of these species may be reached, with the leaching rate of those species reducing to zero with time. Radiation effects may also affect the durability of a wasteform.

8.2.2. Glass durability

There are many factors that may affect the durability of a given glass wasteform. These include wasteform composition together with waste loading, leachant composition, pH and flow rate, redox potential, temperature, formation of surface layers, crystallization of the glass and the effects of radiolysis. In a repository multibarrier system the influence of the additional materials making up the multibarrier on the corrosion behaviour of the glass also needs to be taken into account as synergistic effects may occur.

Many common glasses are reasonably resistant to acidic solutions (with the exception of hydrofluoric or phosphoric acids), but are attacked more readily by alkaline solutions; however, HLW glasses usually show enhanced leach rates for acidic solutions, probably due to the high alkali oxide content of such glasses, as illustrated in Fig. 11. As a general rule, it is noted that glass corrosion rates decrease with time in closed systems but become constant with time in a flowing system if there are no transport barriers. The solubility products of a variety of components, for example, compounds containing Zn, Al, Fe, Ti and Mg, depend strongly on pH. Durability may also be affected by the formation of solid reaction layers that may impede the transport of specific species from the glass surface to the leachant, in particular boron. It has been noted that glasses with improved durabilities can be formulated according to known rules. For example, Chick *et al.* [61] systematically varied the composition of a borosilicate glass and monitored the resultant glass durability. It was found that durability could be improved by increasing the silica or alumina content or by decreasing the amount of alkali oxide present. A comprehensive summary of the effect of

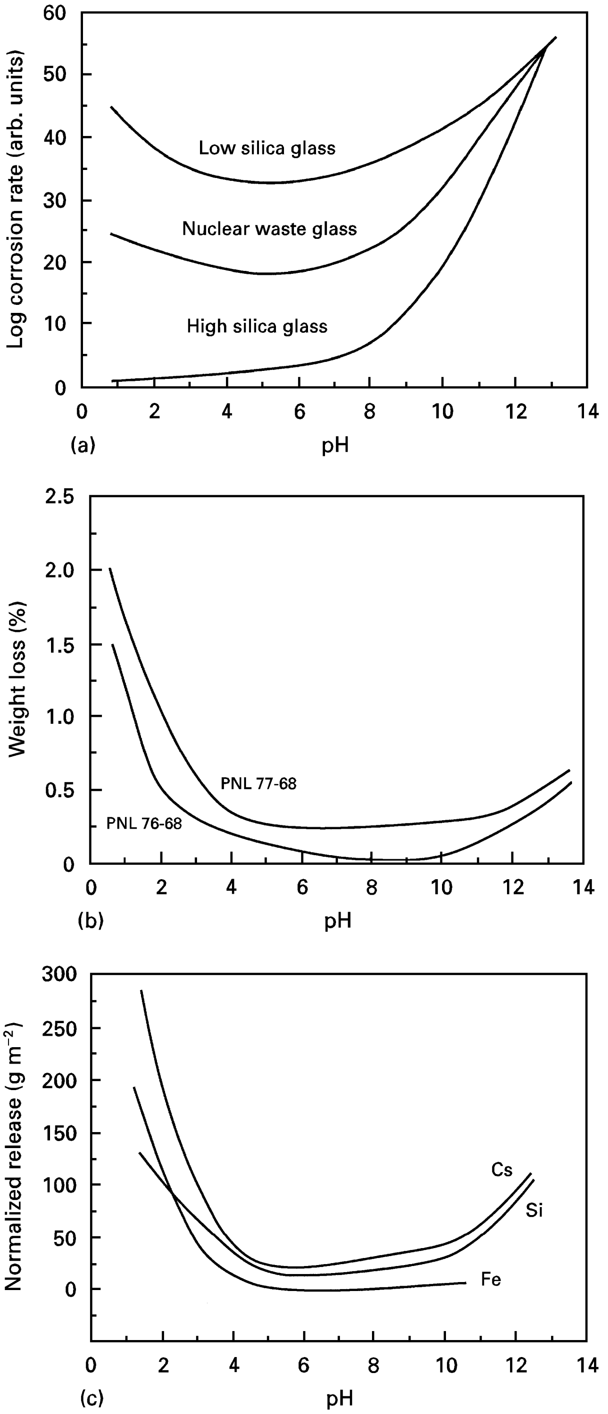

Figure 11 Leach rates for a number of silicate glasses as a function of pH (after [5,12,18]) : (a) comparison of overall leach rates for low and high silica glasses and nuclear waste glass; (b) overall leach rates for 77–68 and 76–68 borosilicate waste glasses; and (c) leach rates for elemental Si, Cs and Fe from borosilicate waste glass.

a wide variety of oxides and other additions to silicate based glasses has been published [253].

Many elements can exist in different valence states and are susceptible to redox reactions. The solubilities of certain species are therefore dependent on their ionic state. For example, the solubilities of a number of actinide elements and Tc are greatly reduced when in the 4^+ state, relative to higher oxidation states. Similarly, the solubility of Fe is influenced by the $Fe^{2+}:Fe^{3+}$ ratio. A knowledge of the behaviour of redox sensitive elements is therefore highly desirable when selecting candidate wasteform systems that will be durable under specific environmental conditions.

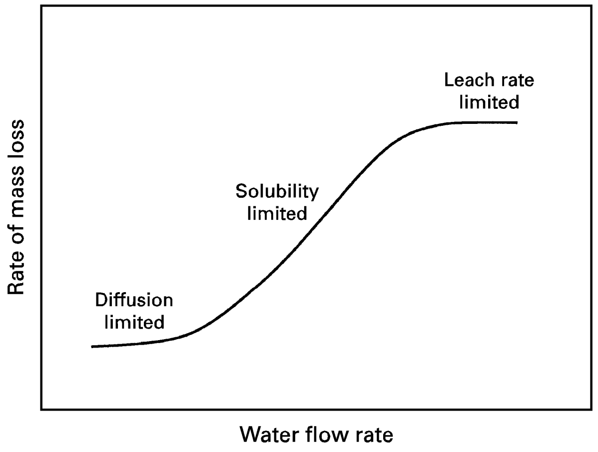

Figure 12 Schematic corrosion curve for a silicate glass in water showing the rate of mass loss as a function of flow rate.

In general, the corrosion rate of a given glass wasteform is proportional to the flow rate, within certain limited ranges. As the flow rate increases the corrosion rate reaches a maximum value and then becomes independent of the flow rate, while at low flow rates in an open system corrosion will proceed at a constant rate. If the system is closed, saturation effects may also lead to a reduction in the corrosion rate, as shown schematically in Fig. 12. In the case of the borosilicate glasses, the formation of silicic acid (H_4SiO_4), will be the rate-controlling species. Surface reaction layers are normally formed during the corrosion process due to the formation of insoluble compounds, but unless these layers form a diffusion barrier to silicic acid the corrosion rate will not be disturbed. The innermost layer of corroded glass adjacent to the pristine glass is termed the reaction zone and is usually of the order of 1 μm or less in thickness. Covering the reaction zone is a layer of altered glass with a lower density than that of the bulk glass. This layer will generally be porous enough to allow reaction products and water to migrate through it. In the outermost layer precipitates may form. The leachate beyond the outermost layer contains dissolved species from the glass. The overall corrosion kinetics of the glass may be affected by the surface layer in a number of ways. For example, the layer may or may not act as a diffusion barrier to the transport of additional species to or from the glass. In the former case, the thickness of the layer should be proportional to $t^{1/2}$.

Waste package components may have an influence on the corrosion processes. For example, corrosion may be enhanced in the presence of iron and steel corrosion products due to the formation of iron silicide colloids that can lower the chemical activity of dissolved silica and keep the reaction rate high.

Temperature can also have a strong influence on glass corrosion, with leach rates typically increasing by two orders of magnitude between 25 and 100 °C. Fig. 13 illustrates the effect of temperature on leach rate for different values of pH for a borosilicate waste glass. Activation energies for leaching have been

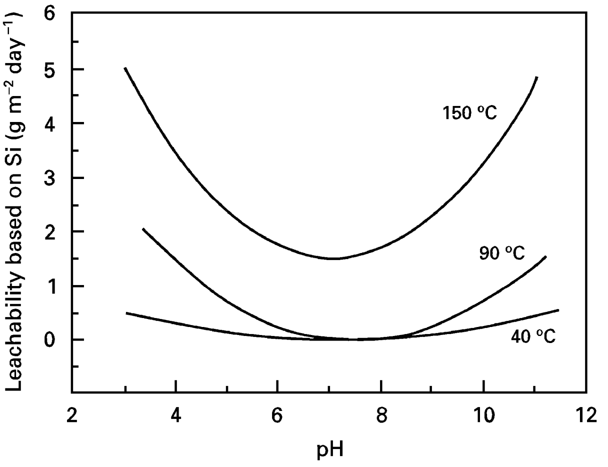

Figure 13 Effect of temperature on leach rate for different values of pH for a borosilicate waste glass (after [18]).

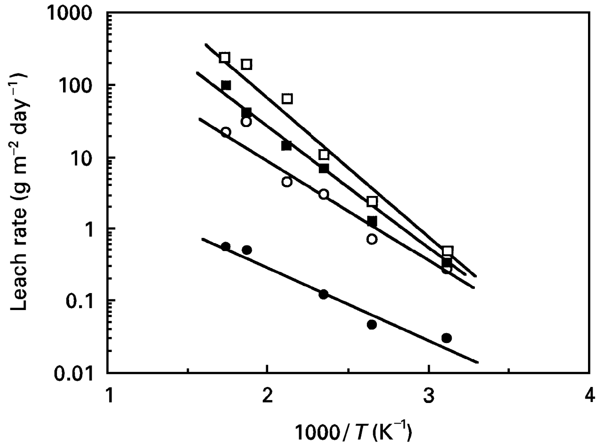

Figure 14 Activation energy plots for leach rates of glass and SYNROC (after [6] and [228]) : (□) Cs From glass, (■) glass, (○) Cs from SYNROC, (●) SYNROC.

derived for a number of glass and leachant compositions, and typically are of the order of $\approx$30–145 kJ mol^{-1}. Activation energy plots for leach rates of SYNROC and borosilicate glass are given in Fig. 14, illustrating that the leach rate of SYNROC increases less with temperature than that of borosilicate glass.

In general, phosphate based glasses exhibit very poor chemical durabilities in aqueous environments; however, a particular exception is found with iron phosphate based materials. For example, lead iron phosphate glasses have been shown to exhibit excellent durabilities in certain environments, and may even be superior to silicate glasses, as noted in Fig. 15. There is evidence, however, that their excellent durabilities do not extend to salt brines [67]. It has also been noted that certain sodium aluminophosphate based glasses can exhibit reasonable durabilities (e.g. [65, 203]).

Some glass-ceramic materials have been shown to exhibit superior chemical durabilities relative to borosilicate glasses in a range of environments. The release of waste ions from a glass-ceramic will depend on a number of factors, including their relative partioning between crystalline and glassy phases and on the dissolution behaviour of these phases. In general, however, the overall corrosion rate of a glass-ceramic will be limited by the durability of the glassy matrix.

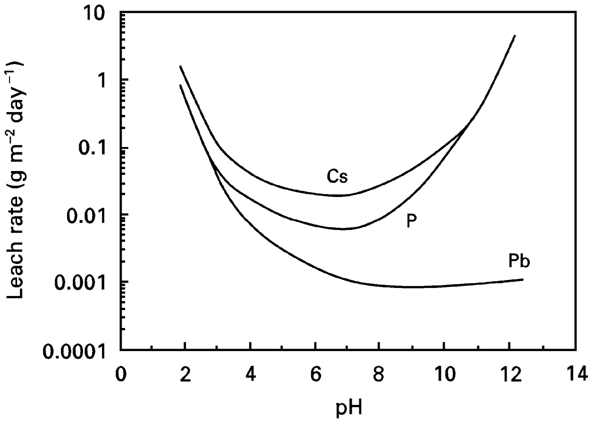

Figure 15 Leach rates for a lead iron phosphate glass containing simulated waste (after [67]).

8.2.3. Ceramic durability

The majority of chemical durability studies on ceramics have concentrated on titanate-based materials of the SYNROC variety. In general, the matrix elements, Ti, Zr and Al have extremely low solubilities in proposed repository environments, far lower than the main borosilicate glass forming elements, Si and B. The overall durability of SYNROC is controlled by the most leachable waste elements, which include alkali and alkaline earth species, together with Mo and Tc. The leach rate of SYNROC containing waste elements is driven initially by the dissolution of some of the waste elements, in particular Cs, which tend to concentrate at grain boundaries due to incomplete equilibration during hot pressing. Leach rates then decrease markedly with time, because the leachable elements must subsequently migrate through a surface layer that is enriched in the matrix elements and that increases in thickness with time. The short term leaching of SYNROC is therefore dominated by release of elements from non-equilibrium phases and from exposed grain boundaries, while the long term behaviour is dependent on the migration of leachable species through the matrix or along grain boundaries, or is governed by the solubility of the titanate matrix itself. Matrix solubility is difficult to measure accurately, but long term data suggest a release rate of the order of 10^{-4} to 2×10^{-3} g m^{-2} for MCC-1 test conditions. This is equivalent to a solubility limit in the range 10^{-3} to 2×10^{-2} g m^{-3} (1 to 20 p.p.b. total dissolved solids).

Unlike borosilicate glasses, the pH of the leachant has only a relatively small effect on the durability of SYNROC. Durability plots as a function of pH are summarized in Fig. 16.

The durability of SYNROC is less affected by flow rate than is the case for the borosilicate glasses. In order to determine whether leach rates are governed by solubility limits or kinetics, Reeve *et al.* [90] studied the durability of SYNROC using both static

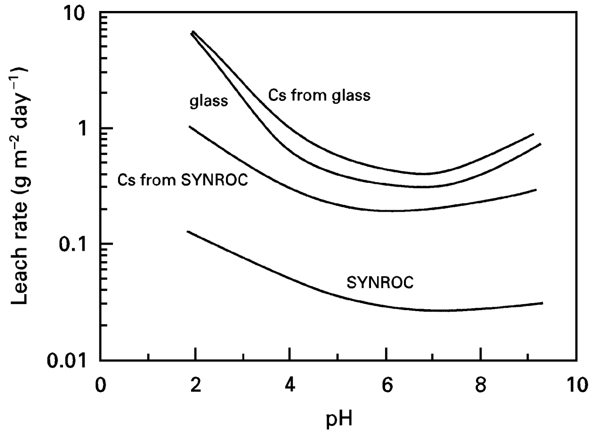

Figure 16 Leach rates for SYNROC compared with borosilicate glass as a function of pH (after [6]).

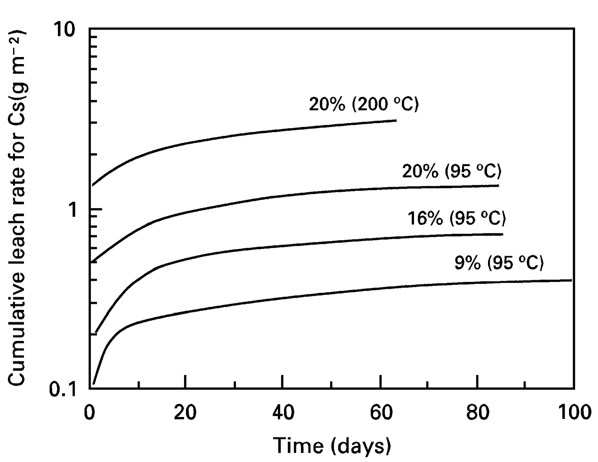

Figure 17 Leach rates of SYNROC as a function of waste loading (after [6]).

and flow test conditions. They noted that elemental losses were similar and concluded that release rates were therefore controlled by kinetics. Additional proof of kinetic control has been provided by other tests.

Waste loading has a desirable effect on SYNROC processing, with an increase in loading leading to a reduction in the hot pressing temperature required for densification. If the waste loading is too high, however, this may have an undesirable and disproportionate effect on durability due to the formation of additional less durable phases. Durability plots as a function of waste loading are given in Fig. 17.

The durability of SYNROC has also been shown to be dependent on the process conditions employed for making precursor powders. For example, SYNROC synthesized using precursors prepared by the hydroxide route exhibit lower leach rates for Cs, Ca and Mo than corresponding material fabricated using the oxides. In addition, durability depends strongly on the density of the wasteform, increasing by around two orders of magnitude as the density decreases from $\approx$100% of theoretical density to $\approx$90%. This is expected due to the greater mobility of soluble species that can be transported via open or interconnected porosities. It is also important that processing of SYNROC is carried out under reducing conditions, otherwise formation of soluble molybdates and technetates may occur.

8.3. Radiation stability

8.3.1. General background

The effects of radiation damage due to self irradiation of wasteforms have been extensively studied [254–267]. The internal radiation source will be more intense initially, with β- and γ-decay of fission products prevailing. The major radiation effect in the longer term will be from the α-decay of actinides, each decay involving the ejection of a high energy α-particle (He nucleus) and an accompanying recoil of the actinide nucleus. These effects produce displacement damage in the atomic structure of the wasteform. A small fraction of some heavy radionuclides will also undergo spontaneous fission; for example nuclear transmutation of Cs and Sr, following the sequences [5, 12]

$$^{137}\text{Cs}^{+}(30\text{y}) \rightarrow {}^{137\text{m}}\text{Ba}^{2+}(2.6\text{m}) + \beta^{-} \rightarrow {}^{137}\text{Ba}^{2+} + \gamma \qquad (4)$$

$$^{90}\text{Sr}^{2+}(28.5\text{y}) \rightarrow {}^{90}\text{Y}^{3+}(64\text{h}) + \beta^{-} \rightarrow {}^{90}\text{Zr}^{4+} + \beta^{-} \qquad (5)$$

The overall decay behaviour of a highly radioactive waste is shown in Fig. 18. In the first few hundred years the behaviour is dominated by the β- and γ-emitting radionuclide fission products, while at longer times the transuranic actinides are dominant. Table X lists the activities of some of the most important radionuclides that may be found in HLW.

Various techniques have been employed in order to simulate the effects of radiation damage in wasteform materials, including actinide doping of wasteforms or doping with alternative α-emitters with short half-lives (e.g. ^{238}Pu, ^{241}Am or ^{244}Cm with half-lives of 86, 433 and 18 years, respectively, or ^{242}Cm with a half-life of only 163 days), and irradiation with fast neutrons or charged particles. Doping with actinides is the most

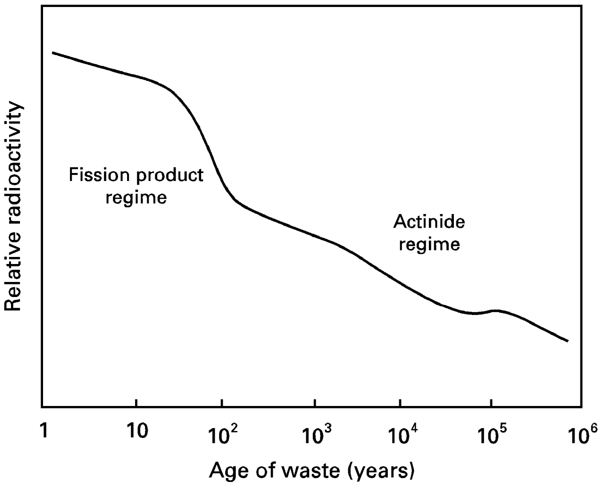

Figure 18 Schematic overall decay behaviour of HLW as a function of time. The influence of the fission products is dominant for the first few hundred years.

TABLE X Activities of principal fission products and actinides in HLW as a function of storage time[a]

Species	Activity (GBq g^{-1})		
	(4 years)	(50 years)	(500 years)
Fission products			
^{134}Cs	5.9	0.000 001 3	–
^{137}Cs	19.0	6.6	0.000 21
^{90}Sr	14.0	4.6	0.000 07
^{144}Ce	2.2	–	–
^{147}Pm	3.3	0.000 016	–
^{151}Sm	0.12	0.085	0.0024
^{152}Eu	0.001	0.000 071	–
^{154}Eu	0.61	0.083	0.0003
^{155}Eu	0.14	0.0029	–
^{93}Zr	0.000 19	0.000 19	0.000 19
^{99}Tc	0.0016	0.0016	0.0016
^{106}Ru	5.2	–	–
^{107}Pd	0.000 012	0.000 012	0.000 012
^{126}Sn	0.000 12	0.00012	0.000 12
Actinides			
Np	0.000 03	0.000 03	0.000 03
Pu	0.0014	0.0016	0.0008
Am	0.07	0.06	0.03
Cm	0.004	0.001	0.000 06

[a] From [12].

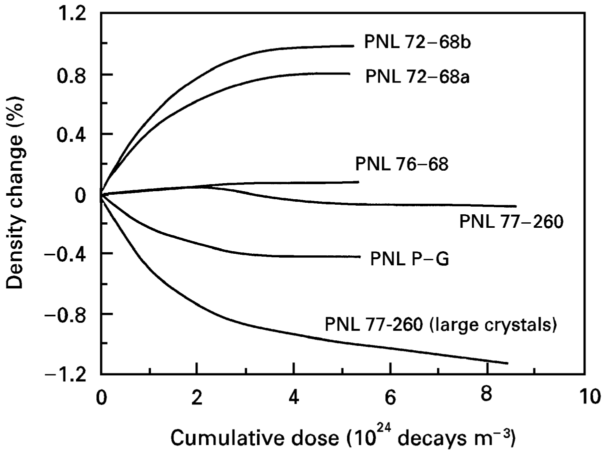

Figure 19 Density change of a number of waste glasses doped with ^{244}Cm as a function of dose (after [5]).

realistic method, it being possible to accumulate damage in a few years or less that is equivalent to several hundreds or thousands of years for real waste. Radiation damage can also be simulated to a greater or lesser extent by irradiation with charged particles, e.g. electrons, α-particles, heavy ions, etc. Although not as realistic as the actinide doping method, this technique does offer the advantage that the irradiated simultants do not become radioactive and therefore can be handled directly.

8.3.2. Glass stability

In the case of glasses, radiation induced density variations, $\Delta\rho$, may be observed, the overall effect being dependent on the radiation dose received and the composition of the glass. Values for $\Delta\rho$ generally do not exceed $\pm 1\%$ and density changes tend to saturate after a dose of $\approx 10^{25}\,\alpha\,m^{-3}$ has been received, as noted in Fig. 19. Stored energy also increases with increasing radiation dose reaching saturation at similar doses to density. Stored energy has been studied extensively to determine whether a sudden release of energy might occur that would lead to a rise in temperature sufficient to result in crystallization and cracking of a wasteform. Structural changes of crystalline phases that form within HLW glasses can occur; for example, crystalline phases such as $Ca_3Gd_7(SiO_4)_5(PO_4)_2$ and gadolinium titanate have been observed. Radiation induced density changes in glass are not yet fully understood, but experimental evidence suggests that the sign of the density change is dependent on the chemical composition of the glass. It is known that the density changes can be annealed out of glass, with some recovery taking place even at room temperature.

Each α-decay reaction generates one He atom when the highly energetic α-particle comes to rest in the glass and captures two electrons. The accumulation of He is proportional to the α-dose and may lead to swelling or cracking of the glass. In addition, the formation of He bubbles provides nucleation centres within the glass and may lead to uncontrolled crystallization if the repository temperature is high enough. This would subsequently introduce undesirable internal stresses that could promote cracking of the wasteform and lead to higher leach rates. In general, experimental data suggest that the He generated in a glass remains in solid solution, rather than forming discrete bubbles or diffusing out of the glass. It is likely that only a very small fraction of generated He will be released during storage, unless the temperature is abnormally high. The solubility of He in a HLW borosilicate glass (PNL 72–68), for example, has been found to be 1.5×10^{22} atoms m^{-3}.

It may be concluded that, in practice, radiation effects in glass do not seem to be particularly detrimental to the longer term integrity or chemical durabilities of glasses, at least over the time scales so far examined.

8.3.3. Ceramic stability

Similar effects are observed in crystalline ceramic wasteforms, but in this case the crystalline structure of the material is gradually destroyed, with the formation of amorphous (metamict) phases. This can lead to larger volume changes than associated with glasses, and may lead to some cracking with time.

The α-decay damage of SYNROC is confined almost exclusively to the perovskite and zirconolite phases that host the actinides. It has been noted that natural zirconolite retains a monoclinic crystal structure up to doses of the order of $4.4 \times 10^{24}\,\alpha\,m^{-3}$. At increased doses, up to $3 \times 10^{25}\,\alpha\,m^{-3}$, the structure forms a mixture of crystalline and amorphous domains, while at higher doses, $> 10^{26}\,\alpha\,m^{-3}$, the structure becomes both X-ray and electron amorphous. It appears that the chemical durability of natural zirconolite is not adversely affected by radiation damage.

8.4. Use of natural analogues

One of the most critical aspects of the evaluation of nuclear wasteforms is extrapolation of data determined in short term testing to longer time scales. Unlike standard life assessment studies where a component or product may need to be reliable for a period of a few tens of years at most, nuclear wasteforms must be stable, or at least their properties accurately predicted, for thousands if not millions of years. In particular, wasteforms that are designed for storage in underground repositories must be shown to be chemically durable within the repository environment over very long time spans. As it is not possible to extrapolate short term behaviour over such long time spans with any degree of certainty natural analogues have been studied in some detail [268–270].

Natural analogues are naturally occurring materials of great age that can be employed in order to gain an understanding of the long term behaviour of synthetic wasteforms. By use of such analogues it should be possible to confirm whether or not the thermodynamic and kinetic models used to extrapolate the short term behaviour of nuclear wasteforms are valid within the given time scales involved.

Glassy analogues include volcanic tektites, rhyolites and basaltic glasses. These can range in age from recent to many millions of years. Tektites are commonly found in sediments recovered from deep sea cores and occur as glassy fragments ranging up to several centimetres in size. Hydration and devitrification effects are noted in such materials but their overall durabilities are very high and are attributable to their high silica contents (70–75%). Both tektites and rhyolites, which are similar in composition, can be considered as analogues for high silica wasteforms, including porous glass. Basaltic glasses are lower in silica and have been considered as analogues for borosilicate glass [5, 269]. In comparing the corrosion behaviour of natural glasses and nuclear waste glasses analogous behaviour has indeed been confirmed. In particular, the relative thermodynamic stabilities of glasses predict the observed similarity in behaviour of basalt and borosilicate glasses, and the rates of corrosion observed are consistent with the models used to describe the corrosion behaviour.

In the case of crystalline ceramics a number of naturally occurring minerals have been suggested as analogues; for example, monazite and zircon. The mineral monozite is a mixed lanthanide orthophosphate that contains significant amounts of radioactive U and Th. Monazite is found as individual large crystals and is also distributed in granite formations and alluvial deposits. Natural monazite that has been subjected to radiation damage over very long time spans has been employed in laboratory experiments in order to obtain comparative data on leach rates for undamaged material and material that has been exposed to radiation. In general, there is little evidence for alteration. Monazite is therefore a good candidate for the immobilization of actinide containing wastes. Zircon is also a well characterized naturally occurring mineral containing small amounts of U and Th, which has been shown to be extremely durable.

The reference form of SYNROC consists of the four main titanate minerals, zirconolite, hollandite, perovskite and rutile. Evidence shows that similar minerals have survived for millions of years in a wide range of natural geochemical environments. There is therefore strong supporting evidence from these natural analogues of the excellent durability and radiation resistance expected of SYNROC.

Natural analogues have therefore been shown to provide strong supporting evidence confirming the long term stabilities of synthetic nuclear wasteforms.

9. Discussion

9.1. Current wasteforms

Borosilicate glass is currently the only accepted wasteform for the immobilization of HLW. Borosilicate glass was chosen as the preferred first generation wasteform due to a combination of many factors. In the first instance, because of its already established importance as a commercial material, an extensive technological base exists on the manufacture and properties of this type of glass. Many of the alternative wasteforms are not as well established, and comprehensive data on their preparation and properties do not exist. As outlined in Section 4 it has been established that borosilicate glass exhibits many useful attributes specific to immobilization applications. It is, for example, an excellent solvent for HLW; it is tolerant of variations in waste stream composition; it is relatively easy to manufacture; and it possesses acceptable thermal, mechanical, physical, chemical and radiological characteristics. The chemical durability of borosilicate glass has been exhaustively examined under a diverse range of conditions, including exposure to salt solutions of different composition, concentration, pH, temperature and flow rate. The effects of radiation damage on chemical durability are also well established. In addition, a comprehensive data base exists on the properties of borosilicate glass containing not only simulants, but also active HLW. Based on these results, computer models have been employed for predicting the long term behaviour of borosilicate glasses in repository environments. It is now widely accepted that the performance of a borosilicate wasteform will meet all the current safety and environmental criteria. This has led to the large scale commercial manufacture of borosilicate glass wasteforms and the manufacturing processes have been demonstrated successfully for a number of years in many different countries.

It is generally recognized that SYNROC is the second choice wasteform. It has been almost as widely characterized as borosilicate glass; however, it has not yet been employed for the commercial immobilization of active HLW, although this may be due more to the early commitment by many countries to follow a glass route, rather than to economic considerations or a lack of technical data. In general, SYNROC exhibits superior mechanical behaviour when compared to borosilicate glass. It is also more durable, more stable thermally, and can accommodate higher concentrations of certain types of HLW, particularly those wastes rich in actinides. One disadvantage is its greater processing complexity, which involves hot pressing.

9.2. Alternative wasteforms

Many different types of wasteform have been studied over the last 30 years, as summarized in Table XI. These range from hydrated ceramics, including cement-based materials, to inorganic glasses, glass-ceramics and ceramics, and cover a diverse range of compositions. The majority of this work has concentrated on the development of materials for the immobilization of HLW from the reprocessing of spent nuclear fuel and certain defence operations. Although many different types of materials were initially considered for these applications the choice of borosilicate glass as the first generation wasteform for the immobilization of French, UK, USA and Indian wastes led to a severe curtailment of work in other areas, with the notable exception of SYNROC. It is only recently, with the advent of a whole new range of potential additional waste and surplus materials, that significant renewed interest is being shown in many of the older alternative wasteforms and in the development of alternative new materials. These include in particular the iron phosphate based glasses, together with zirconolite, zircon, phosphate and pyrochlore ceramics for immobilizing actinides, e.g. U and Pu.

9.3. Comparison of wasteforms

A comparison of wasteforms can be made based on their applications, properties and manufacturing processes. A qualitative comparison is given in Table XI, which summarizes some of the more important properties of a variety of generic and actual materials. Specific properties of a number of materials are summarized in Tables V, VII and IX.

Many factors need to be addressed when comparing HLW wasteforms for a particular application. Maximum waste loading for a given wasteform volume is particularly important as this will dictate the overall size of both the intermediate storage facility and the long term repository required for a given quantity of HLW. This, in turn, will have an influence on the economics of the overall immobilization process. The thermal properties of the wasteform may also be important. For example, thermal conductivity and thermal expansion will dictate the magnitude of residual internal stresses due to radiation induced heating of the wasteform. The higher the conductivity and the lower the expansion the lower these stresses will be. If these residual stresses are high enough, internal cracking of the wasteform will occur, and this will lead to a higher surface area and consequently a higher rate of corrosion.

In general, when considering conventional HLW, crystalline SYNROC-type ceramics can usually accommodate higher waste loadings than borosilicate glass; in particular, these ceramics can immobilize much higher concentrations of actinide phases. SYNROC ceramics, which are usually composed of hollandite, perovskite, zirconolite and rutile phases, have been shown to be extremely versatile in incorporating a diverse range of waste elements into the crystalline structure of their component phases. For example, in hollandite with the general formula $A_xB_yC_{8-y}O_{16}$, the large A cations are mono- or divalent, while the B and C sites can be occupied by a variety of di-, tri-, tetra- and pentavalent cations. A large number of different waste ions can therefore be readily incorporated into the hollandite structure. These include Na^+, K^+, Rb^+, Ti^+, Sr^+, Ba^+, Mg^{2+}, Fe^{2+}, Ni^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Ti^{4+} and Si^{4+}. Perovskite, of general formula $AB\text{O}_3$, is the main host for Sr^+, Na^+, intermediate rare earths and trivalent actinides. Zirconolite, $CaZrTi_2O_7$, belongs to the pyrochlore structure, $A_2B_2\text{O}_7$, and is the main host for actinide phases, with U, Np, Pu and Am readily substituting for Ca and Zr. One possible disadvantage associated with SYNROC ceramics is the greater processing complexity, which involves hot pressing, although recent work has shown that good results can be achieved by sintering [129]. It may also be feasible to produce SYNROC by a melting route [128]. Both the sintering and melting processing routes are intrinsically less expensive than hot pressing, particularly on an active scale, and may therefore warrant further investigation.

Immobilization of HLW through the use of glass-ceramics is reasonably well documented, but most of the work has only been on a relatively small scale. In principle glass-ceramics should provide a wasteform offering many of the advantages of glass, i.e. ease of manufacture, but with improved properties, in particular superior mechanical behaviour, thermal stability and chemical durability. One of the major disadvantages associated with glass-ceramics is the additional heat-treatment schedule that is normally employed for their manufacture, although it is possible for some compositions to undergo nucleation and crystallization satisfactorily during the cooling cycle, as has been shown for calcium magnesium silicate glass-ceramics containing diopside as the major crystalline phase. Calcium titanium silicate glass-ceramics containing sphene as the major phase have been shown to be particularly versatile, and have been proposed for immobilizing waste materials from CANDU reactors. These glass-ceramics can also be crystallized during controlled cooling if they contain U or rare earth elements that act as efficient bulk crystallization aids. Iron-enriched basaltic glass-ceramics have also been shown to exhibit useful properties, including an affinity for immobilizing TRU wastes; and they too can be crystallized successfully during controlled cooling.

Conventional borosilicate glasses are not efficient solvents for actinide phases, and therefore are not ideally suited for immobilization of some of the more recent wastes and surplus materials that may contain high concentrations of actinide phases. Although some of the more recent alternative candidates show considerable promise for actinide immobilization,

TABLE XI Comparison of wasteforms[a]

Wasteform	Principal application	Processing temperature[b]	Waste loading[c]	Mechanical properties[d]	Thermal expansion[e]	Thermal conductivity[f]	Chemical durability[g]	Radiation stability[h]	Economics[i]
Hydrated inorganics									
Clay based	LLW–ILW	Low	Intermediate	Low	Low	Low	Low	Low	Low
Cement	LLW–ILW	Low	Intermediate	Low	Low	Low	Low	Low	Low
Concrete	LLW–ILW	Low	Intermediate	Low	Low	Low	Low	Low	Low
FUETAP	IL–HLW–TRU	Low–intermediate	Intermediate	Low	Low	Low	Low	Low	Low–intermediate
Glasses									
Alkali borosilicate	HLW–TRU	High	Intermediate	Intermediate	Intermediate	Low	Intermediate	Intermediate	Intermediate
High-silica	HLW–TRU	Very high	Intermediate	Low–intermediate	Low	Low	High	High	High
Aluminosilicate	HLW–TRU	Very high	Intermediate	Intermediate	Intermediate	Low	High	High	High
Lanthanide silicate	TRU	Very high	Intermediate	Intermediate	Intermediate	Low	High	Intermediate	High
Sintered glass	HLW–TRU	Intermediate	High	Low–intermediate	Intermediate	Low	Intermediate	Intermediate	Low
Alkali phosphate	HLW–TRU	Intermediate	Intermediate	Low	High	Low	Low	Intermediate	High
Aluminophosphate	HLW–TRU	Intermediate	Intermediate	Low	Intermediate	Low	Intermediate	Intermediate	High
Zinc phosphate	HLW–TRU	Intermediate	Intermediate	Low	Intermediate	Low	Low	Intermediate	Intermediate
Iron lead phosphate	HLW–TRU	Intermediate	Intermediate	Low	High	Low	Intermediate	Intermediate	Intermediate
Iron phosphate	HLW–TRU	Intermediate	Intermediate	Low	High	Low	High	Intermediate	Intermediate
Glass-ceramics									
Barium aluminosilicate	HLW	High	Intermediate	Intermediate	Intermediate	Low	Intermediate	Intermediate	Intermediate–high
Magnesium aluminosilicate	HLW	Very high	Intermediate	Intermediate	Intermediate	Low	High	Intermediate	Intermediate–high
Barium titanium silicate	HLW	High	Intermediate	Intermediate	Intermediate	Low	Intermediate	Intermediate	Intermediate–high
Calcium magnesium silicate	HLW	High	Intermediate	Intermediate	Intermediate	Low	High	Intermediate	Intermediate–high
Calcium titanium silicate	HLW	Very high	High	Intermediate	Intermediate	Low	High	Intermediate	Intermediate–high
Basaltic	HLW–TRU	Very high	High	Intermediate	Intermediate	Low	High	Intermediate	Intermediate–high
Phosphate	HLW–TRU	Intermediate	Intermediate	Intermediate	Intermediate	Low	Low	Intermediate	Intermediate
Ceramics									
SYNROC-B	HLW	High	Intermediate	High	Intermediate–high	Intermediate	High	Intermediate	Intermediate–high
SYNROC-C	HLW	High	Intermediate	High	Intermediate–high	Intermediate	High	Intermediate	Intermediate–high
SYNROC-D	HLW	High	Intermediate	High	Intermediate–high	Intermediate	High	Intermediate	Intermediate–high
SYNROC-E	HLW	High	Intermediate	High	Intermediate–high	Intermediate	High	Intermediate	Intermediate–high
SYNROC-F	HLW–TRU	High	Intermediate	High	Intermediate–high	Intermediate	High	Intermediate	Intermediate–high
SYNROC-FA	HLW–TRU	High	Intermediate	High	Intermediate–high	Intermediate	High	Intermediate	Intermediate–high
Calcium silicate	HLW	Intermediate	Intermediate	Intermediate	Intermediate	Intermediate	Intermediate	Intermediate	Intermediate
Titania	HLW	Intermediate–high	Intermediate	Intermediate	Intermediate	Intermediate–high	High	Intermediate	Intermediate–high
Monazite	HLW–TRU	High	Intermediate	Intermediate	Intermediate	Intermediate	Intermediate	High	Intermediate–high
Sodium zirconium phosphate	HLW–TRU	Intermediate	High	Intermediate	–	Intermediate	High	High	Intermediate
Sodium titanium phosphate	HLW–TRU	Intermediate	High	Intermediate	–	Intermediate	High	Intermediate	Intermediate
Rare earth pyrochlore	TRU	High–very high	High	Intermediate	–	Intermediate	Intermediate	Intermediate	Intermediate–high
Lanthanum zirconate	TRU	Very high	High	Intermediate	–	Intermediate	High	High	Intermediate-high
Zirconolite	TRU	High–very high	High	Intermediate	High	Intermediate	High	High	Intermediate
Zircon	TRU	Very high	Low–high	Intermediate	–	Intermediate	High	Intermediate–high	Intermediate

Inorganic ion-exchange media									
Titanate	ILW–HLW	Intermediate	High	–	Intermediate–high	Intermediate	Intermediate	Intermediate	Intermediate
Zeolite	ILW–HLW	Intermediate	High	–	Intermediate–high	Intermediate	Intermediate	Intermediate	Intermediate
Sodalite	ILW–HLW	Intermediate	High	–	Intermediate–high	Intermediate	Intermediate	Intermediate	Intermediate
Encapsulants									
Cement matrix	HLW–TRU	Low	High	Low	Low	Low	Low	Low	Low
Metal matrix	HLW–TRU	Intermediate	High	Intermediate	High	High	High	Low–intermediate	Intermediate
Ceramic matrix	HLW–TRU	Intermediate–high	High	Intermediate	Intermediate	Low–intermediate	High	Intermediate	Intermediate–high
Glass matrix	HLW–TRU	Intermediate	High	Intermediate	Intermediate	Low–intermediate	Intermediate	Intermediate	Intermediate
Coated particles	HLW–TRU	Intermediate	High	Intermediate	Intermediate	Low–intermediate	Intermediate	Intermediate	Intermediate
Sol–gel particles	HLW–TRU	Intermediate	High	Intermediate	Intermediate	Low–intermediate	Intermediate	Intermediate	Intermediate

[a] Data from [6, 8–14, 38, 82–84, 112, 114, 123, 127, 157, 170, 178, 256].

[b] *Processing temperature*: low, $\leqslant 200\,^{\circ}\mathrm{C}$; intermediate, 200–1000 °C; high, 1000–1250 °C; very high, $>1250\,^{\circ}\mathrm{C}$.

[c] *Waste loading*: low, $<10\%$; intermediate, 10–20%; high, 20–40%; very high $>40\%$.

[d] *Mechanical properties* (*MOR*): low, <50 MPa; intermediate, 50–200 MPa; high, >200 MPa.

[e] *Thermal expansion*: low, $<5\times10^{-6}\,^{\circ}\mathrm{C}^{-1}$; intermediate, $5\text{–}10\times10^{-6}\,^{\circ}\mathrm{C}^{-1}$; high, $>10\times10^{-6}\,^{\circ}\mathrm{C}^{-1}$.

[f] *Thermal conductivity*: low, $<2.0\,\mathrm{W\,m^{-1}\,K^{-1}}$; intermediate, $2.0\text{–}5.0\,\mathrm{W\,m^{-1}\,K^{-1}}$; high, $>5.0\,\mathrm{W\,m^{-1}\,K^{-1}}$.

[g] *Chemical durability*: low, <borosilicate glass; intermediate, comparable to borosilicate glass; high, >borosilicate glass.

[h] *Radiation stability*: low, <borosilicate glass; intermediate, comparable to borosilicate glass; high, >borosilicate glass.

[i] *Economics*: low, <borosilicate glass; intermediate, comparable to borosilicate glass; high, >borosilicate glass.

many of them are not well characterized at the present time. The most widely studied include zirconolite-rich SYNROC wasteforms and iron phosphate based glasses. Lesser studied candidates include a number of phosphate and rare earth pyrochlore ceramics. In general, high temperatures are required for the fabrication of the pyrochlore type materials, and this may be a disadvantage, particularly if dealing with active wasteforms. The newer iron phosphate based glasses are a significant improvement on the earlier alkali phosphate compositions, being considerably more durable, less corrosive and exhibiting greater thermal stability.

9.4. The future

For the immobilization of conventional HLW, borosilicate glass is well established as the preferred wasteform. The future is directed towards the identification of similar glasses with improved durability and processing characteristics, which will mainly be achieved through compositional modification of existing wasteforms. The identification of related wasteform compositions exhibiting wider processing windows and that are more tolerant of waste stream compositional variations is also an area for future study. Other types of glass wasteforms with lower manufacturing temperatures and easier processing routes also offer potential for further study; for example sintered glass.

With the recent emergence of various new types of waste, together with the requirement for immobilizing surplus fissile material, many of the alternative wasteforms are currently being re-examined and new wasteforms are being identified. As outlined in previous sections, those showing particular promise include SYNROC ceramics with zirconolite as the major crystalline phase, together with phosphate and rare earth pyrochlore ceramics. Wasteforms for the newer applications in which high concentrations of Pu may be incorporated require the addition of modifiers; for example, neutron absorbing elements to prevent criticality. Elements with high neutron absorbing cross-sections include many of the rare earths, in particular Gd, Sm and Eu, together with a variety of other elements including B and Cd. In the case of pyrochlore ceramics, including zirconolite, the rare earth elements can substitute for Zr or its equivalent and can therefore be incorporated directly into the wasteform in the amount required. In the case of glass wasteforms, these elements (and in particular B) can be incorporated as the appropriate oxide within the glass structure. The iron phosphate glasses are particularly promising candidates for the immobilization of actinide rich wastes and surplus materials. Considerable work is required, however, before any of these materials can be seriously considered as viable candidates. Areas requiring particular attention include larger scale manufacture, and production and characterization of active wasteforms.

In general, more detailed characterization of wasteforms, in particular chemical durability, also needs to be addressed for alternative wasteforms, with the aim of producing a comprehensive data base in this area. This should include more fundamental structural studies of candidate wasteforms, using a variety of techniques, e.g. electron microscopy, X-ray diffraction and extended X-ray absorption fine structure EXAFS [271]. The influence of radiolysis on susceptible wasteforms also requires additional attention. Ultimately, by establishing a comprehensive data base for wasteform materials, it will be possible to select and tailor individual candidates for specific immobilization applications. This will include the immobilization not only of radioactive materials, but also of other highly toxic or environmentally aggressive wastes, including asbestos, heavy metal contaminated residues, and related waste or surplus products.

A final area of potential concern relates to the influence of organic and bacteriological activity on wasteforms and waste repositories. This has only received limited attention to date, but has been shown to be important in some cases (e.g. [272–275]). It would seem reasonable that additional studies be undertaken in this area.

10. Conclusions

1. Until recently, the major impetus worldwide has been on the immobilization of HLW from the reprocessing of spent nuclear fuel and from certain defence processing operations; however, increasing interest is now also being shown in the immobilization of *surplus* nuclear materials, including U and Pu, from both civil and military operations.

2. A large amount of information is available on the immobilization of conventional HLW using glass, ceramic and glass-ceramic wasteforms, with work in these areas spanning more than 30 years. Currently, however, borosilicate glass is the only accepted wasteform for the immobilization of HLW. Many commercial waste vitrification plants have been constructed and are operational worldwide; for example, in the USA, UK, France, Belgium, Italy, the former USSR, the People's Republic of China, India and Japan.

3. With the emergence of additional sources of highly radioactive materials for immobilization, many of the alternatives to borosilicate glass are now being re-examined as potential second-generation wasteforms. More recently, novel wasteforms are also being identified. These include various titanate-based SYNROC formulations, together with zircon, zirconolite and monazite, primarily as candidate hosts for actinide phases. Alternative glass compositions are also being reconsidered, including rare earth silicate and iron phosphate compositions, again primarily as actinide hosts. Iron-enriched basaltic glass-ceramics may also offer the prospect of improved hosts for actinide phases.

4. With the exception of SYNROC, the majority of alternative wasteforms have only been studied on a small, non-radioactive scale. Much work is therefore required on the scaling-up of both materials and processes, in addition to examining the influence of loading with active materials. It is also essential that comprehensive data bases are established for all potential alternative candidate wasteforms.

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