

**Contract No:**

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

**Disclaimer:**

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

## **Radioactive Waste Conditioning, Immobilisation, and Encapsulation Processes and Technologies: Overview and Advances**

Carol M. Jantzen  
Environmental & Chemical Process Technology  
Savannah River National Laboratory  
Aiken, South Carolina, 29808, USA  
[carol.jantzen@srnl.doe.gov](mailto:carol.jantzen@srnl.doe.gov)

William E. Lee  
Department of Materials  
Imperial College  
London, United Kingdom SW7 2AZ  
[w.e.lee@imperial.ac.uk](mailto:w.e.lee@imperial.ac.uk)

Michael I. Ojovan  
Department of Materials Science and Engineering,  
University of Sheffield, UK  
(Current affiliation: Department of Nuclear Energy  
International Atomic Energy Agency  
Vienna International Centre  
Vienna, 1400, Austria)  
[m.ojovan@sheffield.ac.uk](mailto:m.ojovan@sheffield.ac.uk)

### **ABSTRACT**

The main immobilization technologies that are available commercially and have been demonstrated to be viable are cementation, bituminization, and vitrification. Vitrification is currently the most widely used technology for the treatment of high level radioactive wastes (HLW) throughout the world. Most of the nations that have generated HLW are immobilizing in either alkali borosilicate glass or alkali aluminophosphate glass. The exact compositions of nuclear waste glasses are tailored for easy preparation and melting, avoidance of glass-in-glass phase separation, avoidance of uncontrolled crystallization, and acceptable chemical durability, e.g., leach resistance. Glass has also been used to stabilize a variety of low level wastes (LLW) and mixed (radioactive and hazardous) low level wastes (MLLW) from other sources such as fuel rod cladding/decladding processes, chemical separations, radioactive sources, radioactive mill tailings, contaminated soils, medical research applications, and other commercial processes. The sources of radioactive waste generation are captured in other chapters in this book regarding the individual practices in various countries (legacy wastes, currently generated wastes, and future waste generation). Future waste generation is primarily driven by interest in sources of clean energy and this has led to an increased interest in advanced nuclear power production. The development of advanced wasteforms is a necessary component of the new nuclear power plant (NPP) flowsheets. Therefore, advanced nuclear wasteforms are being designed for robust disposal strategies. A brief summary is given of existing and advanced wasteforms: glass, glass-ceramics, glass composite materials (GCM's), and crystalline ceramic (mineral) wasteforms that chemically incorporate radionuclides and hazardous species atomically in their structure. Cementitious, geopolymer, bitumen, and other encapsulant wasteforms and composites that atomically bond and encapsulate wastes are also discussed. The various processing technologies are cross-referenced to the various types

of wasteforms since often a particular type of wasteform can be made by a variety of different processing technologies.

## **7.1 Introduction**

### **7.1.1 Legacy Wastes**

Most nuclear nations have generated radioactive HLW from nuclear weapons programs and/or commercial nuclear power generation and most store waste materials from a variety of reprocessing flowsheets. The Plutonium and URanium EXtraction (PUREX) process<sup>†</sup> is the baseline for spent fuel reprocessing for most countries with active fuel cycle programs. France and the UK reprocess spent fuel for electric utilities from other countries using the PUREX process to recover uranium ( $^{235}\text{U}$ ) and plutonium ( $^{239}\text{Pu}$ ). Slight modifications to the PUREX process can be made to recover  $^{235}\text{U}$ ,  $^{239}\text{Pu}$ ,  $^{237}\text{Np}$ , and  $^{99}\text{Tc}$  (if desired) and a number of countries (e.g., France, Japan, China, etc.) are developing solvent extraction processes to recover the minor actinides (Am and Cm) from spent fuel. Elimination of these actinides and fission products from the HLW reduces the long-term radio-toxicity and heat generation from an immobilized wasteform once it is entombed in a geological repository.

Most HLW is in either one of two forms: *a*) used nuclear fuel that is destined for direct disposal, or *b*) waste from the reprocessing of commercially generated spent nuclear fuel (SNF or commercial wastes) or from the reprocessing of fuel used to generate  $^{239}\text{Pu}$  for weapons (defense wastes). The SNF retains a high inventory of transuranium elements (~1 atomic %) in its uranium matrix, and the waste from reprocessing is depleted in actinides, mainly  $^{235}\text{U}$  and  $^{239}\text{Pu}$  (~99% removed), having been recovered during chemical processing.

Liquid HLW streams are stored either as neutralized nitric acid streams in mild steel tanks (U.S. and Russia) or as nitric acid streams in stainless steel tanks (France, UK, Japan, Russia). Although borosilicate glasses have become the preferred wasteform for the immobilization of HLW solutions in the majority of the nuclear nations, the chemical variability of the wastes from the different reactor and reprocessing flowsheets coupled with the additional variability imposed by neutralization vs. direct storage or processing of acidic wastes has led to a diverse HLW chemistry, e.g. HLW contains about three fourths of the elements in the periodic table.

Vitrification is currently the most widely used technology for the treatment of high level radioactive wastes (HLW) throughout the world (Table 1). In the United States, more than 3,496 canisters of borosilicate glass contain vitrified, high-level waste from the Savannah River Site (Defense Waste Processing Facility) and 250 canisters at West Valley, New York. In France, approximately 14,000 canisters of HLW-glass have been produced at the La Hague facility (Table 1).

A variety of other radioactive wastes have been generated during the fuel rod cladding/decladding processes, during chemical separations, from radioactive sources, radioactive mill tailings, medical research applications and other commercial processes such as radium for watches and clocks. Many of the sources of radioactive waste generation are captured in other chapters in this book regarding the

---

<sup>†</sup> The PUREX process was developed in the United States in 1950 and the world's first operational full-scale PUREX separation plant, began radioactive operations at the Savannah River Plant in 1954. The process has run continuously at SRP since start-up for defense materials only.

individual practices in various countries (includes legacy wastes, currently generated waste, and anticipated future wastes).

In countries where the HLW waste is neutralized before processing, the HLW has segregated into a Low Activity Waste (LAW) fraction which is an alkali rich supernate and a viscous HLW sludge fraction over time. The LAW fraction of HLW and other medium and low level wastes (MLW and LLW) can be immobilized into a variety of wasteforms, i.e. cements, Ceramicrete, glass, hydroceramics, high temperature ceramic/mineral wasteforms (made by a variety of technologies discussed below), glass-ceramics, and geopolymers and land disposed in safe and specially engineered facilities.

The concept of conditioning waste in order to immobilize it in solid nuclear wasteforms is over 60 years old.[1] Wasteforms can chemically incorporate waste species (glass, GCM's, crystalline ceramics or mineral analogs, and metals), encapsulate waste species in a matrix (cement, geopolymers, hydroceramics, bitumen), or be a combination of both. Wasteforms can be amorphous (glass, bitumen, geopolymers), or crystalline (crystalline ceramics including minerals and zeolites, metals, cements, hydroceramics), or a combination of forms (glass ceramic materials, GCM's; glass beads in a metal matrix; granular crystalline mineral wasteforms in a geopolymer or cement). In particular, GCM's can be formed by controlled cooling, melting above the solubility of certain waste constituents and letting them crystallize out on cooling, or by allowing homogeneous glasses at the melt temperature to cool naturally where some portion of the cooled glass crystallizes.

### ***7.1.2 Future Wastes***

At the turn of the 21<sup>st</sup> century, the interest in sources of clean energy has led to increased interest in advanced nuclear power production, often referred to as the “nuclear renaissance.” The development of advanced wasteforms is a necessary component of this new strategy. Therefore, advanced nuclear wasteforms are being designed for robust disposal strategies. Implicit in the ceramics and glass ceramic wasteform development is the idea of using additives to “tailor” the waste chemically so that the desired host radionuclide phases are produced after consolidation. Implicit in the cements and encapsulant wasteforms is to “design” the encapsulant to retain radioactive and hazardous constituents while being effective in adverse environments.

### ***7.1.3 Overview of Wasteforms and Conditioning Technologies***

A brief summary of glass, glass-ceramic, crystalline ceramic (mineral), cementitious, geopolymer, bitumen, and other encapsulant wasteforms is given below and in Chapter 5. There have been many comprehensive reviews of wasteforms and their properties [2,3,4,5,6,7, 8,9,10,11] and this will not be elaborated on in this chapter except as examples of the different classes of wasteforms discussed in Section 7.4 of this chapter.

This chapter will focus on the various technologies available to create the various types of wasteforms and provide a cross-reference between the various processing technologies and each wasteform. For example, a glass wasteform can be made by Joule heated melting (JHM), advanced Joule heated melting (AJHM), plasma hearth melting (PHM), Hot Isostatic Pressing (HIP), microwave heating, and cold crucible induction melting (CCIM). Thus processing

technologies will be related to conditioning technologies that immobilize radioactive species either by atomic bonding or by encapsulation or a combination of the two (composite wasteforms). The wasteform and technology data is presented in tabulated form for brevity.

## **7.2 Definitions**

For consistency, the definitions given in Chapter 5 of this book, which are from the IAEA, [12,13] are adopted here except for the definitions of encapsulation vs. embedding where examples have been used to make the distinctions clearer.

### **7.2.1 Conditioning**

Conditioning includes those operations that produce a waste package suitable for handling, transport, storage and/or disposal. This may include the following:

- conversion of the waste to a solid wasteform
- enclosure of the waste or wasteform in containers
- providing an overpack if necessary

The wasteform is the waste in its physical and chemical form after treatment and/or immobilization prior to packaging. Thus the wasteform is a component of the waste package.

### **7.2.2 Immobilization**

Waste immobilization is the conversion of a waste into a wasteform by solidification, embedding, or encapsulation. The wasteform can be produced by chemical incorporation of the waste species into the structure of a suitable matrix (typically a glass, GCM, or ceramic) so that the radioactive species are atomistically bound in the structure (chemical or atomic incorporation) or encapsulated.

Chemical incorporation is typical for high-level radioactive waste. Cementation or other encapsulation/embedding technologies are typical for low-level or intermediate-level waste. Immobilization reduces the potential for migration or dispersion of radionuclides during handling, transport, storage and/or disposal.

### **7.2.3 Encapsulation and Embedding**

Encapsulation of waste, on the other hand, is achieved by physically surrounding the waste with or in a material (typically considered a flowable material such as a grout or cement) so the waste particles are isolated and radionuclides are retained. Encapsulation may or may not include some chemical incorporation if the encapsulating phase reacts with the waste, i.e. if hydrating calcium-silicate-hydrates (CSH) incorporate waste species during hydration. The IAEA definition [12] of encapsulation is “immobilization of dispersed solids (e.g. ash or powder) by mixing with a matrix material in order to produce a wasteform,” but also includes emplacement of a solid wasteform (e.g. spent fuel assemblies) in a container.

Embedding is the immobilization of solid waste (e.g. metallic materials) by surrounding it with a matrix material in order to produce a wasteform. Embedding is similar to encapsulation when no chemical interaction is observed between the waste and the encapsulation medium (typically bitumen or polymers).

### **7.2.4 Wasteform**

The IAEA defines a wasteform as “Waste in its physical and chemical form after treatment and/or conditioning (resulting in a solid product) prior to packaging.” The wasteform is a component of the waste package.

A wide range of materials are potentially suitable for immobilizing radioactive waste in a wasteform. For simplicity of describing the types of wasteforms in terms of chemical or atomic incorporation vs. encapsulation/embedding and the various technologies by which these wasteform materials can be made, the wasteforms have been grouped into ten classes:

- Single-phase (homogeneous) glasses
- Multi-phase glass-composite materials (GCM's; heterogeneous glasses)
- Single-phase crystalline ceramic/mineral analogs
- Multi-phase crystalline ceramic/mineral assemblages
- Bitumen
- Metals
- Cements
- Geopolymers and organic polymers
- Hydroceramics
- Ceramicrete

Some wasteforms are considered composites as they both atomically incorporate radionuclides and then these radio-phases are embedded or encapsulated in a secondary matrix.

Each class of wasteform will be discussed in more detail in Section 7.4. Each waste class will have two tables associated with it. One table to discuss the manner in which the radionuclides are sequestered (including a schematic), advantages and disadvantages of the wasteform, and the variety of immobilization technologies by which the wasteform can be made. The second table provides the examples of the wasteform, the technology by which it is made, and references.

## **7.3 Types of Immobilization Processes and Pre-Processes**

Various thermal and non-thermal processes can be used to make various types of wasteforms. The cross-referencing of the various processing technologies that can be used to produce various wasteforms is given in Table 2. In Table 2 the technologies are designated as continuous processes which are more applicable to large volume wastes or batch processes which are more applicable to small to medium volume wastes. Table 2 provides a crosswalk of the processes/technologies (rows) that can be used to form various wasteforms (columns). A list of advantages, disadvantages, and types of wasteform that can be made with a particular technology are given in Table 2. Further discussion of the individual technologies (rows) can be found in Chapter 4 of Reference 11.

The processing and pre-processing technologies by which a wasteform can be made are briefly described below as thermal or non-thermal technologies in keeping with Table 2:

- Thermal Processes

- Calcination – heating at elevated temperature to convert all cations to the oxide form (removes waters of hydration, hydroxides, nitrates in the presence or absence of air, i.e. rotary pyrolytic calciners). May be coupled with other high temperature processes
- Drying – heating at 110°C to remove bound water in preparation for solidification, embedding or other high temperature processes
- Vitrification – the process of solidifying a liquid, sludge, solid, thermal residue, granular wastefrom, or calcine in a glass (borosilicate, iron phosphate, aluminosilicate)
- Metal formation – melting a metallic waste with or without other metal additives
- Pyrolysis – process of destroying organics in the absence of air (more environmentally compliant than Incineration which destroys organics in the presence of air). Pyrolysis can be carried out in calciners, drums, or by Fluidized Bed Steam Reforming (FBSR)
- Hot Isostatic Pressing (HIP) - a manufacturing process used to reduce the porosity of metals and increase the density of many ceramic materials by subjecting the waste/additive mixture to both elevated temperature and isostatic gas pressure in a high pressure containment vessel
- Cold Isostatic Pressing (CIP) and sintering - a manufacturing process used to reduce the porosity of metals and increase the density of many ceramic materials by subjecting the waste/additive mixture to isostatic liquid pressure in a flexible but impervious form such as a balloon before sintering at high temperature
- Hot Uniaxial Pressing (HUP) - a manufacturing process used to reduce the porosity of metals and increase the density of many ceramic materials by subjecting the waste/additive mixture to uniaxial mechanical pressure from above and below in containment form while simultaneously subjecting the form to elevated temperature
- Cold Uniaxial Pressing (CUP) and sintering - a manufacturing process used to reduce the porosity of metals and increase the density of many ceramic materials by subjecting the waste/additive mixture to uniaxial mechanical pressure from above and below in containment form before sintering at high temperature either with or without the containment form
- Non-Thermal Processes
  - Cementation – the process of solidifying a liquid, sludge, solid, thermal residue, granular wastefrom, or calcine in cement matrix of crystalline calcium silicates, aluminates, and ferrate
  - Geopolymerization - the process of solidifying a liquid, sludge, solid, thermal residue, granular wastefrom, or calcine in an amorphous sodium aluminosilicate matrix
  - Bituminization - the process of solidifying a liquid, sludge, solid, thermal residue, granular wastefrom, calcine in bitumen
  - Forming – mixing a waste with cementitious, geopolymeric, bituminous, hydroceramic, or Ceramicrete type additives and mixing in a form, i.e. can, vault, canister, and allowing the material to set or age
  - Pouring – similar to forming but the waste/additive mixture can be poured, extruded, or emptied into a form to set or age
  - Compositing – using metals, glass, cements, geopolymers, etc to encapsulate a waste that has already been solidified for special reasons such as heat dissipation, control of respirable fines in calcined or granular wastefroms, and/or compressive strength requirements.

Often processes are coupled. For example, in France and the UK waste is calcined to remove excess nitrates before vitrification into a final wasteform. This allows free flowing oxides to enter the melter without nitrates being off-gassed or causing the particles to adhere to one another. Organic bearing wastes are often pyrolyzed to remove organics, if needed, before vitrification. [14,15]

Calcining is often performed before HIP, CIP, HUP, or CUP processes are performed so that volatile species are not given off during the hot pressing or during the subsequent sintering. This ensures that the pressed wasteform retains its integrity and form and does not crack during processing from off-gassing of hydrated or nitrated species.

## 7.4 Immobilisation processes and technologies

The major types of wasteforms will be described in regard to the manner in which the radionuclides are immobilized and the methods by which each can be made. Different wasteforms give different durability tests responses. Single phase wasteforms (glass and single phase oxides or crystalline ceramics (minerals) have only one source of radionuclides that can leach during a durability test. In multiphase wasteforms the distribution of the radionuclides amongst the phases present becomes important as each phase has its own rate of leaching for the specific elements that it sequesters. Each wasteform given in Table 3 through Table 10 will be described in terms of the radionuclide immobilization achieved and references given as to which conditioning technologies can be used to make each type of wasteform.

The immobilization of HLW is always achieved by its *atomic-scale* incorporation into the structure of a suitable matrix (typically glass, a GCM, or a crystalline ceramic (also sometimes referred to as mineral analog wasteforms) so that the radionuclides are incorporated into durable structures by any combination of short range order (SRO)<sup>§</sup>, medium range order (MRO)<sup>†</sup> or long range order (LRO)<sup>f</sup>. Glasses incorporate radionuclides and hazardous species into their atomic structure by SRO and MRO. [16] Recent experimentation has shown the existence of large cation rich clusters in glass, e.g. clusters of Ca in CaSiO<sub>3</sub> glasses and clusters of Na<sub>2</sub>MoO<sub>4</sub> in simulated waste glasses (Table 4). These more highly ordered or polymerized regions of MRO, often have atomic arrangements that approach those of crystals and are often referred to as quasi-crystalline species or quasi-crystals. Crystalline ceramics incorporate radionuclides and hazardous species by a combination of SRO, MRO, and LRO. The LRO defines the periodic structural units characteristic of crystalline ceramic structures. In glass, glass-ceramics, glass composite materials (GCM's), and crystalline ceramics the radioactive and hazardous constituents are atomically bonded by a combination of SRO, MRO, and LRO. In GCM's there is additional encapsulation of the ceramic components in the glass matrix.

---

<sup>§</sup> SRO; radius of influence ~1.6–3Å around a central atom, e.g. polyhedra such as tetrahedral and octahedral structural units

<sup>†</sup> MRO; radius of influence ~3–6Å encompasses second- and third-neighbor environments around a central atom. The more highly ordered regions, referred to as clusters or quasicrystals, often have atomic arrangements that approach those of crystals.

<sup>f</sup> LRO extends beyond third-neighbor environments and gives crystalline ceramic/mineral structures their crystallographic periodicity.



## 7.4.1 Solidification by Chemical Incorporation

### 7.4.1.1 Vitrification (Table 3 and Table 4)

Vitrification is currently the most widely used technology for the treatment of high level radioactive wastes (HLW) throughout the world (Table 1). Development of glasses for the solidification of HLW began at different times in the US, Canada, Europe, and the USSR.[17] Different glass formulations (borosilicate, aluminosilicate, and phosphate glasses) and processing strategies were developed. [18] Currently, most of the nations that have generated HLW are immobilizing in either borosilicate glass or aluminophosphate glass. One of the primary reasons that glass has become the most widely used immobilization media is the relative simplicity of the vitrification process, e.g. melt waste plus glass forming additives and cast. There is >50 years processing experience<sup>§</sup> with commercial borosilicate glasses and borosilicate glasses have favorable systems evaluations in terms of both melting and product behavior.

Melting homogenizes the mixture and so this process is easier to perform remotely than a ceramic wastefrom process that requires powder handling, e.g. mechanical mixing of waste and ceramic additives and grinding for particle size control, followed by cold pressing and sintering or hot pressing at elevated temperatures. A second reason that glass has become widely used for HLW is that the amorphous and less rigid structure of glasses (SRO and MRO) compared to ceramics (SRO, MRO, and LRO) enables the incorporation of a very large range of elements that are atomically bonded in the flexible glass structure (see Table 4). Thus glasses can accommodate larger waste composition fluctuations than most ceramics.

The glass forming SRO structural groups are usually tetrahedral Si, B, Al, Fe, P surrounded by four oxygen atoms (tetrahedral coordination) or B surrounded by three oxygen atoms (trigonal coordination) and glasses are named for the predominant tetrahedral species, e.g. borosilicates have primarily B and Si with some Al, Fe, and P and aluminophosphates would have primarily Al, P, and Si. See Table 4 for the attributes of various types of glasses that have been used for a variety of HLW wastes and pertinent references that can be consulted.

The tetrahedra and trigonal species in glass link to each other via bridging oxygen bonds (BO). The remaining non-bridging (NBO) atoms carry a negative charge and, in turn, ionically bond to positively charged cations like  $\text{Cs}^+$ ,  $\text{Sr}^{+2}$ ,  $\text{Ca}^{+2}$  and positively charged waste species. These linkages create the MRO structural groups such as  $(\text{Cs}, \text{K}, \text{Na}, \text{Li})\text{AlO}_2$ ,  $(\text{Cs}, \text{K}, \text{Na}, \text{Li})\text{FeO}_2$ ,  $(\text{Cs}, \text{K}, \text{Na}, \text{Li})\text{BO}_2$ , and  $(\text{Cs}, \text{K}, \text{Na}, \text{Li})\text{SiO}_4$  [19] or  $(\text{Cs}, \text{K}, \text{Na})\text{AlSiO}_4$  [20] which form sheet-like units, chain-like units, and monomers [21] that further bond the waste species ionically.

The tetrahedra define the network regions, while NBO define percolation channels or depolymerized regions (DR) shown in Table 4 that can act as ion-exchange paths for elements that are less well bonded to the NBO. Such percolation channels are also found in rare-earth (lanthanide) alumino-borosilicate (LaBS) glasses as well (see Table 4). Thus, the molecular

---

<sup>§</sup> Phosphate glasses (aluminophosphates and iron-phosphates) are not used commercially as frequently as the borosilicates and hence are not as well studied in HLW stabilization applications.

structure of glass controls radionuclide/contaminant release by establishing the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites through the percolation channels and the mechanisms are similar to those observed in natural analog glasses (basalts) and in mineral analogs.

Moreover, HLW glasses melt at lower temperatures (1050-1150°C) compared to higher ceramic wasteform processing temperatures which minimizes the volatility of radioactive components such as  $^{99}\text{Tc}$ ,  $^{137}\text{Cs}$ , and  $^{129}\text{I}$ . While ceramics are often credited with having higher chemical durability than glasses, if the radionuclides are incorporated in an intergranular glassy phase during processing (see discussion in the next section), they leach at about the same rates as those from glassy wasteforms.[22]

Lastly, nuclear waste glasses have good long term stability including irradiation resistance and excellent chemical durability. In addition, the ease of modeling the durability of a homogeneous rather than a heterogeneous material in terms of having only one radionuclide source term is also an advantage.

A basic assumption in all glass dissolution models is that the solid being modeled is comprised of a single phase and so the durability response has only one source term (see Table 3). Therefore, phase separated glasses (with two source terms) with two distinct glass compositions are avoided as their durability cannot be modeled. Often the two immiscible glass phases have different compositions, e.g. one phase is often boron rich and has a poorer durability than the bulk and/or the matrix phase. Having a poorly soluble second phase is not desirable for HLW glasses where the distribution of the radionuclides in the two glassy phases would have to be known for every waste glass fabricated. Since the volume fraction of each phase is also related to the thermal history of each canister of glass, each canister would be different and this complicates durability modeling to the point that it is virtually impossible.

To ensure that HLW borosilicate glasses are homogeneous (not phase separated), a minimum  $\text{Al}_2\text{O}_3$  limit is applied in the US. The effect of insufficient  $\text{Al}_2\text{O}_3$  was first reported by French researchers [23] who determined that many glass durability models were non-linear, e.g., glasses had release rates far in excess of those predicted by most models, in regions corresponding to low  $\text{Al}_2\text{O}_3$  and in excess of 15 wt%  $\text{B}_2\text{O}_3$ . The phenomena was independently discovered by US researchers and found to exist in natural basalt glass systems as well. [24,25,26]

Additional durability source terms can occur if crystals are present in a glass because crystals create grain boundaries that can (1) selectively undergo accelerated dissolution while the crystals themselves may have a different dissolution response [27] or (2) have compositions not representative of the bulk glass.[28] This will be discussed more in the section on glass ceramics (Section 7.4.1.2)

Glass formulations are generally homogeneous allowing only a few weight percent crystals to form on cooling in the canister. Certain crystals such as iron spinels have little impact on glass durability as they are themselves very durable and cause minimal grain boundary dissolution [27,29]. However, for other phases such as nepheline, acmite, and lithium silicates that are less durable than iron spinels and not isotropic, the impact on glass durability from the crystal and the grain boundaries can be pronounced. This is especially true if the crystal sequesters radionuclides as this gives a secondary source term for radionuclide release. Therefore,

durability testing must be performed to confirm that any crystallization that might occur during canister cooling has minimal impact.[30,31,32,33] This ensures that the last 3 terms in Equation 1 approximate zero and that glass dissolution has a single source for radionuclide and hazardous species release

Equation 1

$$\sum Durability = \underbrace{durability_{(homogeneous)}}_{1st\ term} + \underbrace{durability_{(amorphous\ phase\ separation)}}_{2nd\ term} + \underbrace{durability_{(crystallization)}}_{3rd\ term} + \underbrace{durability_{(accelerated\ grain\ boundary)}}_{4th\ term}$$

This durability equation will be discussed in more detail in reference to other wasteforms where the 3<sup>rd</sup> and 4<sup>th</sup> terms in Equation 1 may become important.

Glasses can be made by JHM, AJHM, CCIM, and HIPing (see Table 3). Extensive reviews on vitrified wasteforms can be found in the references cited in Section 7.8 and in Table 4

#### 7.4.1.2 Glass Ceramics and Glass Composite Materials (GCM's; Table 5 and Table 6)

The distinction between glass-ceramics (a glassy matrix which is allowed to form crystals during cooling) or glassy matrices where controlled cooling is used so that certain crystalline species known to sequester radionuclides are encouraged to form and a Glass Composite Materials (GCM's) [34, 35] is sometimes difficult to determine. In glass-ceramics the precipitating phase may not host any radionuclides and be inert or a radionuclide may be partitioned between a crystalline ceramic (mineral analog) phase and the glass. GCM's are considered a composite material where the long lived radionuclides are atomically bonded in the ceramic (mineral) phase and the glass is an encapsulating matrix phase. The glass can have little or no retention of radionuclides or act as the host for the short lived radionuclides.[36] Glass-ceramics and glass composite materials (GCM's) include glass ceramics where a glassy wasteform is crystallized in a separate heat treatment, GCM's formed by melt crystallization (controlled or uncontrolled), and GCMs in which a refractory waste is encapsulated in glass.[34] Glass ceramics and GCM's offer increased waste loadings, increased wasteform density, and thus smaller disposal volumes.

One such example of a GCM in Table 6 is the glass bonded sodalite as the radionuclide of concern, <sup>129</sup>I, is in the ceramic phases and not in the glassy phase. Other examples of GCM's include the following [36]: (1) glass ceramics in which a glassy wasteform is crystallized in a separate heat treatment[7,37]; (2) GCMs in which, e.g., a refractory waste is encapsulated in glass such as hot-pressed lead silicate glass matrix encapsulating up to 30 volume percent La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore crystals to immobilize minor actinides[38]; (3) GCM formed by pressure-less sintering of spent clinoptilolite from aqueous waste processing[39]; (4) some difficult wastes such as the French HLW U/Mo-containing materials immobilized in a GCM termed U-Mo glass formed by cold crucible melting that partly crystallize on

cooling [40]; (5) “yellow phase”<sup>1</sup> containing wastes are immobilized in Russia in a “yellow phase GCM” containing up to 15 volume percent of sulfates, chlorides, and molybdates [41]; and (6) GCM that immobilizes ashes from incineration of solid radioactive wastes.[42] Note that alkali-rich wastes at the Hanford site that were made by in-container vitrification (ICV)<sup>2</sup> produced an immobilized glassy wasteform with high crystal content that characterize them as GCMs.[43]

Note that yellow phase is composed of species that are poorly soluble in glass such as  $\text{Na}_2\text{SO}_4$  which can sequester Cs and Sr, [44]  $(\text{Na},\text{K},\text{Cs})\text{Cl}$ ,  $(\text{Na},\text{K},\text{Cs})_2\text{Cr}_2\text{O}_7$ , and  $(\text{Na},\text{K},\text{Cs})_2\text{MoO}_4$ . Yellow phase is either (1) prevented from crystallizing (Figure 1) or (2) the glass is heat treated to encapsulate the soluble phase(s) as GCM’s. One such vitrification process given as example 5 in the previous paragraph produces a sulfate-chloride-molybdate GCM by using vigorous melt agitation followed by rapid cooling of the melt to the upper annealing temperature to fix the dispersed “yellow phase” into the host borosilicate or aluminosilicate glass. The sulfate–chloride-molybdate containing GCM (see yellow phase GCM in Figure 1) have only a slightly diminished chemical durability compared with sulfate–chloride-molybdate free aluminosilicate and borosilicate glasses.[36]

In many cases, until a wasteform is made and analyzed for the distribution of radionuclides amongst the crystalline and glassy phases one cannot discern if a glass composite material has been made (see Table 5). In either case, glass-ceramics and GCM’s offer a useful compromise between glasses and ceramics, being easier and less expensive to prepare than conventional ceramics, but offering higher durability than glasses.

Depending on the intended application, the major component may be a crystalline phase with a vitreous phase acting as a bonding agent, or, alternatively, the vitreous phase may be the major component, with particles of a crystalline phase dispersed in the glass matrix. Glass-ceramics and GCM’s may be used to immobilize long lived radionuclides (such as actinide species) by incorporating them into the more durable crystalline phases, whereas the short lived radionuclides may be accommodated in the less durable vitreous phase [36].

Historically, crystallization of vitreous wasteforms has been regarded as undesirable as the crystallization has the potential to alter the glass composition and hence the durability of the remaining continuous glass phase could eventually be compromised when it comes into contact with water. However, there has been a recent trend towards higher crystallinity in vitreous wasteforms so that they are more correctly termed glass-ceramics or GCMs depending on whether the glass or the crystals contain the radionuclides (Table 5).

Table 5 also shows glass ceramics where significant quantities of crystals (arising from higher waste loadings) form, such as in the SRS high iron bearing glasses where spinel crystallizes [27] and the crystals do not incorporate the radioactive species but act as benign or inert “stones” in the glass.

Historically silicate glass-ceramics were developed in the mid 1970’s in Germany. [45] Silicate and phosphate glass ceramics were also developed in the USSR [46], silicate glass ceramics were developed in Japan, [47] and titanium aluminosilicate glass ceramics were developed in Canada.[48] GCM’s represent a second generation, more sophisticated approach to the production of glass-ceramics where the long-lived radionuclides are forced into the more durable crystalline phases by tailoring the waste-

---

1

<sup>2</sup> This is not the baseline AJHM process that will produce a homogeneous glass with minimal crystallization.

additive mixture and/or controlling the crystallization. More recently GCM's such as the glass bonded ceramic wasteforms containing sodalite and alkali halides in a borosilicate matrix have been developed for electrorefiner wastes, specifically the stabilization of  $^{129}\text{I}$  in sodalite and NaI.[49,50,51] while rare-earth oxyapatites, powellite, celsian, and pollucite [52] have been developed for rare-earth lanthanide and Cs, high Mo containing wastes. Excellent reviews of other GCM's, such as SYROC glass ceramics, muratite, and other Ti-based glass ceramics can be found in Stefanovsky, et. al. [3] and Donald, et. al. [4,8,34].

In terms of modeling the durability of glass-ceramics and GCM's the distribution of the radionuclides amongst the crystalline and glassy phase becomes important. Referring back to Equation 1 which gives the needed durability vectors for each phase we see that the second term drops out since the glassy phase should not have glass-in-glass phase separation leaving terms 1, 3, and 4 (Equation 2):

Equation 2

$$\sum \text{Durability} = \underbrace{\text{durability}_{(\text{homogeneous})}}_{1\text{st term}} + \underbrace{\text{durability}_{(\text{crystallization})}}_{3\text{rd term}} + \underbrace{\text{durability}_{(\text{accelerated grain boundary})}}_{4\text{th term}}$$

If the glass contains no radionuclides then the 1<sup>st</sup> term in Equation 2 also drops out. If there are multiple types of phases present and each hosts a different radionuclide then there will be durability vectors for the each phase that hosts that radionuclide as shown in the Table 6 example for the  $^{129}\text{I}$  in glass bonded sodalite wasteforms. If there are no radionuclides in the crystals then the 3<sup>rd</sup> term drops out and it may be possible to demonstrate that the 4<sup>th</sup> term is negligible. If a given radionuclide is present in both the glassy phase and a crystalline phase then the durability response from the glass and the crystalline phase and the grain boundary are additive as shown in Equation 2.

### 7.4.1.3 Ceramic/Mineral Wasteforms (Table 7 and Table 8)

The concept of immobilizing the radioactive elements of nuclear waste in an assemblage of mineral phases was originally introduced by Hatch [1] at Brookhaven National Laboratory in 1953. The feasibility of making a ceramic of natural mineralogically stable phases was demonstrated by McCarthy [53,54] and Roy [2,55] at the Pennsylvania State University between 1973 and 1976. Since that time, a number of other mineralogic-ceramic assemblages have been developed. Among these high temperature (1000-1500°C) processes are the Sandia titanate-based ceramic [56], the Australian titanate-based ceramic "SYNROC" [57,58,59], the silicate-phosphate supercalcine ceramics [60], the alumina based tailored ceramics [61,62], the Pu pyrochlores [63]. Often in ceramics made by cold pressing and sintering or hot isostatic pressing, an intergranular glassy phase is produced during liquid phase sintering on the ceramic grain boundaries and the radionuclides preferentially migrate to the glassy phase(s) [64,65,66,67,68,69,70,71,72]. If the radionuclides are incorporated in the intergranular glassy phase(s), they have been found to leach at about the same rates as those from glassy wasteforms.[22]

Crystalline (ceramic/mineral) wasteforms made by moderate temperature (700-750°C) thermal treatment have not been as intensely investigated as those formed at high temperatures as discussed above [61].

However, crystalline wasteforms made from clay have also been studied almost continuously since the work of Hatch in 1953 [1,61]. Often the high temperatures used for sintering of supercaline ceramics created sodalite-cancrinite mineral assemblages. In 1981, Roy [73] proposed low temperature hydrothermally processed low solubility phase assemblages consisting of the micas, apatite, pollucite, sodalite-cancrinite, and nepheline, many of which could be made from reaction of various clays (kaolin, bentonite, illite) with waste.

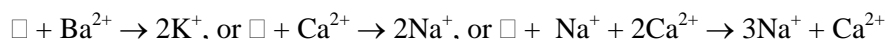
Clay based crystalline (ceramic/mineral) wasteforms were not pursued in the late 1970's and early 1980's because there was no continuous commercial technology available that could process the waste/clay mixtures in a hydrothermal environment [61]. A commercial facility to continuously process radioactive wastes by pyrolysis at moderate temperatures in a hydrothermal steam environment was built by Studsvik in Erwin, Tennessee in 1999 [74,75]. This facility uses a Fluidized Bed Steam Reforming (FBSR) technology to pyrolyze  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  organic resins from commercial nuclear facilities. This technology has the capability to process a wide variety of solid and liquid streams including wastes containing organic ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions at radiation levels of up to 400R/hr. When clay is added as a mineralizing agent, the feldspathoid minerals (sodalite, nosean and nepheline) are formed by nanoscale reaction with the clay. The phases formed act as hosts for high Cl, I, F,  $^{99}\text{Tc}$ , and  $\text{SO}_4$  alkali (Na, K,Cs) bearing wastes [76,77,78,79,80] and organics are destroyed creating steam and  $\text{CO}_2$ . The mineralization occurs at the moderate FBSR temperatures because the FBSR operating temperature is in the range in which most clays become amorphous at the nanoscale level, e.g. kaolin, bentonite (montmorillonite), and illite. The clays lose their hydroxyl ( $\text{OH}^-$ ) groups at the FBSR temperatures which destabilizes the octahedral (6 nearest neighboring atoms that form an octagon)  $\text{Al}^{3+}$  cation in their structure (Figure 2) and they become amorphous as confirmed by X-ray diffraction (XRD) analysis. The alkali in the waste, "alkali activates" the unstable  $\text{Al}^{3+}$  cation to form new mineral phases and the fluidizing agent, steam, catalyzes the mineralization. In the absence of steam many of these mineral phases only form at temperatures of  $>1200^\circ\text{C}$ .

Ceramic wasteforms can be single phase, i.e.  $\text{UO}_2$  or single phase solid solutions like  $(\text{U,Th,Pu})\text{O}_2$  (Table 7). Multiphase ceramics are formulated so that each radionuclide can substitute on a given host lattice in the various phases (see Table 8).

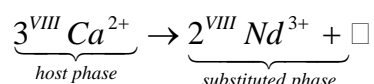
Of great importance when relying on the LRO (size and coordination of the crystallographic site which will act as host to a given radionuclide or its decay product upon transmutation) is that the crystal-chemical substitutions must be electrically balanced. [81,82] When a monovalent cation transmutes to a divalent cation, the substitutions must be coupled to retain the electrical balance of the host phase without destroying the integrity of the phase: the lattice site must be of suitable size and bond coordination to accept the transmutation. The bonding in crystalline ceramic or mineral phases can only maintain charge balance in one of two ways: (1) if sufficient lattice vacancies exist or (2) if a variable valence cation like Fe or Ti is present in a neighboring lattice site for charge balance. Both scenarios assume that the variable valence cations do not change lattice sites and that the charge balancing cations are in the same host phase in nearby lattice sites. The lattice site must be of sufficient size or flexible enough to accommodate the transmuting cation. It is advantageous if the lattice site of the desired host phase has irregular coordination or is distorted as will be shown in some examples below:

The solubility or flexibility of a ceramic or mineral phase(s) as hosts for a substituted cation of a different valence can be studied by performing coupled substitutions on the phase pure mineral host phase. If the

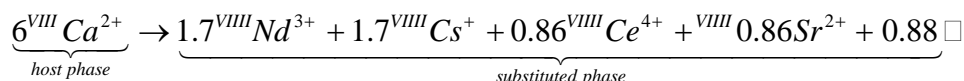
number of cations changes during the substitution, a vacancy is either created or consumed and the substitution must maintain electrical neutrality. These types of substitution are most often seen in polymorphic substitutions [83] of the type



where  $\square$  denotes a vacancy. Implicit in these coupled substitutions is the fact that the exchanging cations occupy the same lattice sites, have the same coordination, and thus the crystallographic symmetry is maintained. Therefore, substitutions as described above should be written with roman numerals that designate the number of oxygen atoms that coordinate around a given cation, e.g.  $^{\text{VIII}}\text{Ca}$  designates the octahedral VIII-fold coordination for the  $\text{Ca}^{2+}$  lattice site in oxyapatites:

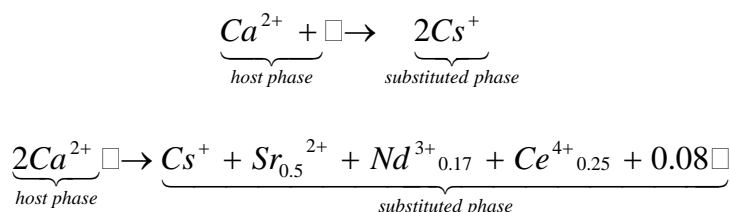


Calcium-neodymium coupled substitutions have been successful [81,82] in the oxyapatite ( $\text{Ca}_6[\text{SiO}_4]_3$ ) structure forming completely substituted  $\text{Nd}_4\square_2[\text{SiO}_4]_3$  where 2/3 of the lattice sites have  $\text{Nd}^{3+}$  and 1/3 are vacant. In the oxyapatite structure the  $\text{Ca}^{2+}$  is normally in VIII-fold coordination and has a 1.12 Å [84,85,86] atomic radius. The  $\text{Nd}^{3+}$  cation in VIII-fold coordination also has an atomic radius of 1.11 Å [86] very close to the  $\text{Ca}^{2+}$  atomic radius in VIII-fold coordination. Felsche showed that the rare earth elements  $\text{La}^{3+}$  through  $\text{Lu}^{3+}$  can substitute for  $\text{Ca}^{2+}$  and form oxyapatites,  $\text{RE}_{4.67}\square_{0.33}[\text{SiO}_4]_3\text{O}$ . [87]; see Table 8] McCarthy and Davidson [54], showed that even more complex, but coupled, substitutions were possible in the oxyapatite structure such as

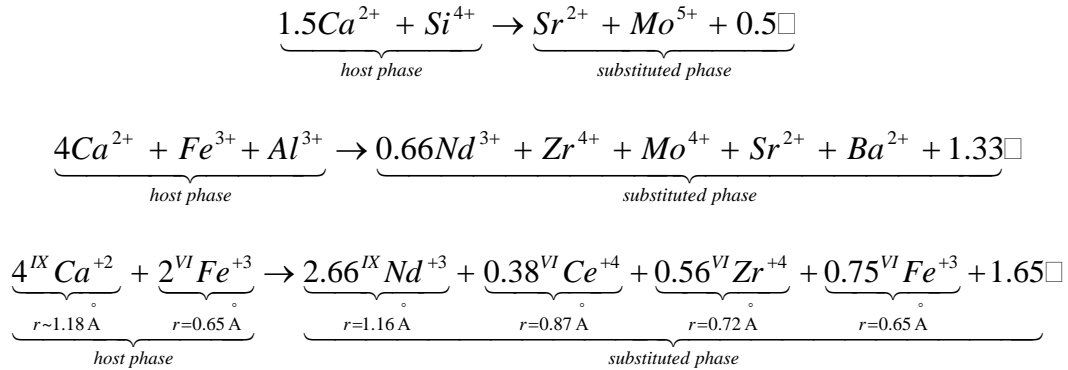


where the atomic radius,  $r$ , of  $\text{Cs}^+$  in VIII-fold coordination is 1.74 Å,  $\text{Ce}^{4+}$  in VIII-fold coordination is 0.97 Å, and  $\text{Sr}^{2+}$  in VIII-fold coordination is 1.26 Å. In this case small radii cations such as  $\text{Ce}^{4+}$  are mixed with large radii cations like  $\text{Cs}^+$  so that individual lattice sites can distort without perturbing the entire crystal structure. Note that the exchanging cations are always in the same lattice site of the same host phase [54,81,82,87].

The substitutions such as given above for the oxyapatites were also demonstrated [81,82] to be possible in many other Ca-bearing cementitious mineral phases such as Iarnite ( $\text{Ca}_2\text{SiO}_4$  or  $\beta\text{-C}_2\text{S}$ ), alite (calcium trisilicate or  $\text{Ca}_3\text{SiO}_5$  or  $\text{C}_3\text{S}$ ),  $\text{C}_3\text{A}$  ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ), and  $\text{C}_4\text{AF}$  ( $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ ). This allowed Jantzen, et. al. [88,89] to make substitutions for  $\text{Ca}^{2+}$  in each phase (up to ~ 15 mole%) and the following additional substitutions<sup>f</sup>:



<sup>f</sup> Note that the number of lattice sites have to be equivalent on the left hand side and right hand side of the equation.



These types of crystal-chemical substitutions have been studied in (1) SYNROC (SYNthetic ROCK) titanate phases such as zirconolite ( $CaZrTi_2O_7$ ), perovskite ( $CaTiO_3$ ), and hollandites (nominally  $Ba(Al,Ti)_2Ti_6O_{16}$ ) [90] and (2) in high alumina tailored ceramic phases such as magnetoplumbites (Table 8). The magnetoplumbites (discussed below) are also found as a minor component in SYNROC when the waste being stabilized is high in Al.[91]

In the SYNROC phase assemblages, the hollandite phase is the  $Cs^+$  host phase. The structure can be written as  $Ba_xCs_y(Al,Fe)_{2x+y}Ti_{8-2x-y}O_{16}$  where  $x+y$  must be  $<2$ . [92] There are two types of octahedral sites. One accommodates trivalent cations like  $Al^{3+}$ ,  $Ti^{3+}$ , and  $Fe^{3+}$  while the other accommodates  $Ti^{4+}$ . The  $Cs^+$  is accommodated in tunnels that normally accommodate the  $Ba^{2+}$  cation. The Cs-Ba lattice sites are VIII-fold coordinated [90, 92]. The substitution is ordered upon fabrication and incommensurate superstructures result when  $Cs^+$  substitutes for  $Ba^{2+}$ . [91]

Cesium has been experimentally substituted for Ba when  $Fe^{3+}$  is substituted for  $Ti^{3+}$  in the VI-fold sites of hollandite. The species  $\underbrace{\overset{VIII}{Cs}_{0.28}}_{A \text{ site}} \underbrace{\overset{VIII}{Ba}_{1.00}}_{B \text{ site}} \underbrace{\overset{VI}{Al}_{1.46} \overset{VI}{Fe}_{0.82}}_{B \text{ site}} \underbrace{\overset{VI}{Ti}_{5.72}}_{C \text{ site}} O_{16}$  has been fabricated by

sintering in air at  $1320^\circ C$ . [92] A Ba-Al hollandite ( $Ba_{1.16}Al_{2.32}Ti_{5.68}O_{16}$ ) was electron irradiated (1-2.5 MeV) and  $\beta$ -irradiated ( $4 \times 10^8$  to  $7 \times 10^9$  Gy) and found to contain  $Ti^{3+}$  centers and  $O_2^-$  superoxide ions which confirmed the mechanism of charge balance during transmutation. [92] Theoretically, the limiting y value in hollandite is 0.81 Cs which corresponds to a 9.54 wt% waste loading of  $Cs_2O$ . [93]

Single phase and multiphase ceramics can be made by many of the thermal treatment technologies given in Table 2. Examples include melting in smelters instead of melters, cold pressing (CIP or CUP) and sintering, hot isostatic pressing (HIP), or hot uniaxial pressing (HUP). Mineral wasteforms made from clays can be made by FBSR. The clay minerals act as a template: kaolin templates the feldspathoid minerals (sodalite and nepheline) while illite clays template the micas (see Table 8).

In terms of modeling the durability of multiphase ceramics the distribution of the radionuclides amongst the crystalline phases and in any intergranular glassy phase is important. Referring back to Equation 1 which gives the needed durability vectors for each phase we see that the second term drops out since the glassy phase should not have glass-in-glass phase separation leaving terms 1, 3, and 4 (Equation 3) where the 1<sup>st</sup> term should have a minimal durability impact unless large concentrations of the intergranular glass exist or large amounts of radionuclides have been sequestered in the glassy phase compared to the ceramic phase.



Equation 3

$$\sum Durability = \underbrace{durability_{(homogeneous)}}_{1st\ term} + \underbrace{durability_{(crystallization)}}_{3rd\ term} + \underbrace{durability_{(accelerated\ grain\ boundary)}}_{4th\ term}$$

If there are multiple types of phases present in the ceramic and each hosts a different radionuclide then there will be durability vectors for the each phase that hosts that radionuclide as shown in the Table 6 example for the  $^{129}\text{I}$  in glass bonded sodalite wasteforms.

#### 7.4.1.4 Metals

A metal wasteform (MWF) has been under development for stabilization of the metallic fuel hulls from spent nuclear fuel processed pyrochemically. As the spent fuel is chopped and the fuel materials are removed by the pyrochemical processing and a stainless steel shell (called a hull or cladding hull) is left in the basket of the bath system. The process removes uranium, actinides, and most fission products, leaving behind the hulls, fuel alloy material (generally zirconium), and any noble metal fission products (like technetium) in the basket.[94] The noble metal fission products remain somewhat adhered to the surface of the stainless steel hulls and the hulls are coated with salt from the salt bath.

The basket is processed to remove the salt and solidify the hulls, alloy, and other metals into a consolidated wasteform. The hulls are solidified by melting the metal into a uniform, homogeneous wasteform (1,560°C). Once homogeneous the metal alloy should cool to a single phase. Typically, some zirconium (in addition to that remaining from the alloy) is added to bring the metal to about 15 wt% zirconium and lower the melting point of the mass. With the exception of the zirconium to control melting temperature, very few additives are made to the primary waste (cladding hulls), and the overall waste loading is typically above 90%.[95]

The metallic waste seems to be a simple wasteform with little development necessary. It has high waste loading, durable, and fairly straightforward to process. The only development that might make a difference would be an evaluation of whether the cladding could be removed from the process before electrorefining and disposed of separately as a low-level wasteform that is potentially greater than Class C. However, the cladding is the host form for the noble metal fission products (notably technetium), and separate disposition would probably require developing a different wasteform for those radionuclides.

Likewise, MWF are under study by ANSTO for applications in the United Kingdom by HIPing. In this case metal encapsulation is to be used for immobilizing debris waste streams that are uneconomic to handle separately, e.g. cermet, SiC, graphite, broken fuel pins, fuel hulls etc. The process is the same as that used to make glass-ceramic and full-ceramic wasteforms and so the processing method is multipurpose.

In spent nuclear fuel (SNF) epsilon metal ( $\epsilon$ -metal) which is composed of Mo-Tc-Ru-Pd-Rh is generated from the fission process and heat. The  $\epsilon$ -metal phase in SNF forms in the same manner that  $\epsilon$ -metal formed in the natural reactors in Gabon, Africa some 2 billion years ago and has survived largely unchanged except for the decay of  $^{99}\text{Tc}$ . Therefore,  $\epsilon$ -metal has shown long-term stability in nature. This metal does not dissolve during the acid dissolution of SNF but forms solid particles with dimensions of ~10  $\mu\text{m}$  in the dissolver sludge. This sludge was formed

into a monolithic wastefrom, by arc melting at 1800°C into an alloy pellet containing Ru, Re (standin for <sup>99</sup>Tc), Mo, Pd, and Rh in the appropriate masses of each metal. [96] Dissolution rates of  $4 \cdot 10^{-5}$  g/(m<sup>2</sup>·d) and  $4 \cdot 10^{-3}$  g/(m<sup>2</sup>·d) were reported for synthetic ε-metal phase and ε-phase harvested from SNF under reducing and oxidizing conditions in static durability testing. [97,98]

## **7.4.2 Solidification by Encapsulation**

This section primarily discusses non-thermal methods of encapsulation. The thermal encapsulation by glass is covered in Section 7.4.1.2 in the section on Glass Ceramic Materials.

### **7.4.2.1 Cements Including Grouts**

Stabilization and solidification with cement-based binders has been used to immobilize radioactive wastes since the beginning of the nuclear age. The process has been used to encapsulate solid waste, solidify liquid waste (including tritiated water), stabilize contaminated soils, stabilize tank-heel residues after tanks are emptied, and as low-permeability barriers. Cements have also been used as binders and to encapsulate granular or cracked wastefroms.

Cements microencapsulate wastes, although there is recent evidence that during hydration three binding mechanisms can also occur between the cement and metal ions in the waste [99,100,101]:

- Precipitation of metal ions into the alkaline matrix as an oxide, mixed oxide, or as another discrete solid phase.
- Adsorption or (co-)precipitation of metal ions onto the surface of cement minerals.
- Incorporation of metal ions into hydrated cement minerals as they crystallize.

Both these mechanisms are shown as examples in Table 9 with the binding mechanisms (reaction of the waste with the cement or grout particles) which are shown as encapsulation and without the binding mechanism which are shown as embedding.

These processes are not mutually exclusive (so both encapsulation and embedding both take place) and the above classification partly reflects slow kinetics; previously adsorbed species may be incorporated as cement pastes mature. Nevertheless, it does allow some generalized guidelines to be formulated. The solubility of discrete heavy metal solid phases is a limiting factor with regard to the second and third mechanisms [102], so that only ions that do not precipitate as basic oxides tend to be incorporated in or surface adsorbed to hydrated cement minerals to a significant degree.

The principal minerals available in the hydrated Portland Cement matrix are calcium silicate hydrate (C-S-H, 50 wt%), portlandite (Ca(OH)<sub>2</sub>, 20 wt%) and Ca aluminates. The most important Ca aluminates are ettringite (3CaO·Al<sub>2</sub>O<sub>3</sub>·3CaSO<sub>4</sub>·32H<sub>2</sub>O, 4 wt%), calcium aluminate monosulphate (3CaO·Al<sub>2</sub>O<sub>3</sub>·CaSO<sub>4</sub>·12H<sub>2</sub>O, 7 wt%) and Ca carboaluminate (3CaO·Al<sub>2</sub>O<sub>3</sub>·CaCO<sub>3</sub>·11H<sub>2</sub>O, 7 wt%) [103]. Together they make up almost 90 wt% of the mineral suite in hydrated Ordinary Portland Cement (OPC) paste and thus, have the greatest potential for metal(loid)-ion binding. The relative importance of the above processes for selected metals can be found in a recent review [104].

OPC is the most common type of cement used for immobilizing liquid and wet solid wastes worldwide [6]. Composite cement systems were developed in the UK for ILW encapsulation using additional powders as well as OPC such as blast furnace slag (BFS) and pulverized fuel ash (PFA). These offered

cost reduction, energy saving and potentially superior long-term performance. BNFL e.g. use a 9:1 ratio of BFS to OPC to reduce heats of hydration which for OPC cements would otherwise limit container volumes. Large containers (e.g. Figure 3) can therefore be safely used without concern over heat from setting reactions causing water to boil off.

Modeling has shown that cements can be “designed” to retain radioactive and hazardous constituents [105]. In fact, much research has focused on improving the effectiveness of grout in adverse environments associated with the disposal of radioactive waste [106,107,108]. As discussed in these references, a variety of cement-polymer composites have been investigated as a means of making grouts more compatible with the radioactive and chemical constituents in waste.

For example, the addition of blast furnace slag to the Saltstone cement<sup>3</sup> being used to solidify Cs-decontaminated salt supernate at the Savannah River Site (SRS), provides a chemical reductant [iron(II)] and a precipitating agent (sulfide) that chemically binds contaminants such as chromium and technetium as insoluble species, thus reducing their tendency to leach from the wasteform. Experimentation has shown that leaching of chromium and technetium was effectively reduced to levels that would allow all projected future salt solution compositions to be processed into Saltstone [109]. Long-term lysimeter studies have shown that the addition of slag essentially stopped technetium-99 leaching, although it did not reduce nitrate leaching [109]. Because the SRS Saltstone admixture that is blended with 45% liquid waste is only 10wt% OPC, 25 wt% fly ash, and 25 wt% slag, it is a geopolymeric cement as the alkali in the salt supernate reacts with the fly ash in geopolymer like chemical reactions.

The water in the hydrated cement blends may generate H<sub>2</sub> by radiolysis in high radiation fields and require vented canisters [110] when containerized. While this study concentrated on Transuranic (TRU) wastes containing <sup>238</sup>Pu oxide which is primarily alpha radiation there are other studies that demonstrate the radiolysis of concrete with <sup>60</sup>Co (gamma radiation) and <sup>3</sup>H (beta radiation) [111,112,113].

A recent comprehensive review of cement systems for radioactive waste disposal can be found in Pabalan et al.[114,115] Long-term cement durability comparisons have been made using ancient cements, geopolymers, and mortars [116,117,118,119,120,121,122, 123], some of which may also serve as natural analogues for geopolymer wasteforms. [124,125]

The cements and grout formulations are too extensive to list as examples. The durability response is complex due to the relative response of encapsulation with some chemical reaction and embedding. Therefore, the durability is usually modeled as a diffusion rate with respect to the element(s) of interest.

### **7.4.2.2 Geopolymers**

Forming geopolymers is a process that is very similar to cementation. Geopolymers are inorganic ceramic polymers made from aluminosilicates and cross-linked with alkali metal ions. [126,127,128] During fabrication a low water content is used (H<sub>2</sub>O/M<sub>2</sub>O ~ 10-25 wt%) so that an amorphous geopolymer forms instead of crystalline zeolites which would technically form hydroceramic wasteforms discussed below. A nominal composition of 4SiO<sub>2</sub>•Al<sub>2</sub>O<sub>3</sub>•M<sub>2</sub>O is used to represent the geopolymer matrix although the Si:Al ratio varies according to the application from 1 to 3. For cements and concrete like applications a ratio of 2:1 is nominally used [129]. The alkali can be Na, K, or Cs. Geopolymers appear to be excellent low temperature binders and environmentally more acceptable than cement

---

<sup>3</sup> Saltstone contains 5 weight percent cement, 25 weight percent flyash, 25 weight percent blast furnace slag, and 45 weight percent salt solution.

wasteforms as the starting materials only need to be heated to ~700°C instead of clinkering at 1400-1500°C..

Geopolymers and geopolymeric cements, including but not limited to fly ash based geopolymeric concretes, are ideal for environmental applications, such as the permanent encapsulation of radioactive species [130,131] and other hazardous wastes. [132] Geopolymers can be used as sealants, capping, barriers, and other structures necessary at containment sites. Pilot scale demonstrations have been performed in Europe on both mining wastes and uranium mill tailings [133,134,135]. Geopolymers were investigated for the disposal of radioactive wastes in Europe in the mid to late 1990's [136,137] and the following applications have more recently been investigated.

- Geopolymers with Si:Al ratios of 1:1 and 2:1 for the stabilization of hazardous Resource Conservation and Recovery Act (RCRA) metals such as Ni, Se, Ba, Hg, Cd, Cr, Pb. A simulant RCRA spike was made that contained the RCRA components at 60X the concentration of the RCRA treatment standards known as the Universal Treatment Standards or UTS limits. [138] The mixture was very acidic (pH<1). The RCRA simulant was substituted for ½ of the 10 wt% water in the geopolymer formulation and the geopolymers met the EPA TCLP test limits at less than the UTS limits even though the geopolymer contained 60X the UTS concentrations. It is not known whether the RCRA components interacted with the geopolymer or not, i.e. if this was encapsulation or embedding (Table 9).
- Geopolymers derived from metakaolin and alkaline silicate solutions and having nominal Na/Al and Si/Al molar ratios of 1 and 2 were studied at ANSTO for the stabilization of <sup>137</sup>Cs and <sup>90</sup>Sr. [139] These geopolymers were studied by transmission electron microscopy and found to be amorphous on the ~1 nm scale after curing at 40°C. The Cs inhabited the amorphous phase, whereas Sr was incorporated only partly, being preferentially partitioned to crystalline SrCO<sub>3</sub>. This study implies that the geopolymer components do interact with some species and not with others providing both encapsulation and embedding (Table 9).
- Special geopolymer formulations, marketed under the name DuraLith, have been patented [140] for stabilization of <sup>129</sup>I and <sup>99</sup>Tc. Testing [141] showed great promise for retention of technetium with rhenium used as a surrogate for the Tc but not for iodine.
- Removal of radiolytic H<sub>2</sub> production (and freeze-thaw problems) can be carried out by heating geopolymers at ~300°C without any serious effects on strength or leachability [142]
- Geopolymers have demonstrated excellent fire resistance [142]

#### **7.4.2.3 Hydroceramics**

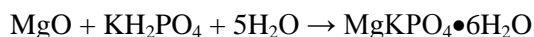
Hydroceramics are another concrete-type material that is similar to zeolitized rock. It is made by curing a mixture of inorganic waste, calcined clay, vermiculite, and Na<sub>2</sub>S, NaOH with water under hydrothermal conditions (60 to 200°C) to form a matrix containing crystalline zeolites embedded in a sodium aluminosilicate matrix [143]. The solidification process occurs as a result of hydration reactions. The NaOH solution dissolves the metakaolin (Al<sub>2</sub>O<sub>3</sub>•2SiO<sub>2</sub>) much the same as in geopolymers but abundant

water or hydroxides provide the water to create crystalline silicates instead of an amorphous matrix. The hydroceramic process takes advantage of the sodalite and cancrinite structures in immobilizing oxyanion salts such as nitrate, nitrite, chloride, fluoride, and iodide within the physical cage like structures of the crystals created.

Hydroceramic wasteforms have been shown to be effective on low-activity sodium-bearing waste. The technology is still under investigation with studies focused on optimization of waste pretreatment (calcination), waste stream-specific optimization of the formulations, and a study of scale-up factors to insure viability for full-scale operation. [143] In cases where the waste has a high nitrate-nitrite composition, the waste must first be denitrified in some manner, such as calcination, to remove the nitrates and nitrites from the waste. If sodium-nitrate-based waste is pretreated with metakaolin, sucrose, and then calcined, it can be used to make a hydroceramic wasteform. [143] Successful wasteforms have been achieved with waste loadings of 40 to 60 wt% waste.[144,145] Hydroceramic wasteforms have been made with Idaho National Laboratory's HLW calcine. [146]

#### **7.4.2.4 Ceramicrete**

Phosphate-bonded ceramics, also known as chemically bonded phosphate ceramics, form through the reaction of magnesium oxide with mono-potassium phosphate in water according to the following reaction:



The reaction product ( $\text{MgKPO}_4 \bullet 6\text{H}_2\text{O}$ ) is Ceramicrete, a rapid setting phosphate ceramic [147] that contains a considerable amount of bound water. The reaction takes place at room temperature, although there is some heat generation from the reaction, to form a hard, insoluble ceramic. Some waste components react to form insoluble phosphates, and others are encapsulated in the matrix. The patented technology [148] has been licensed to treat mixed and low-level wastes and is being used for macro-encapsulation and containerization of uranium. In the U.S. this low temperature wasteform has also been investigated for both micro- and macro-encapsulation of radioactive and hazardous waste streams. [141].

The waste-treatment process includes neutralizing the waste to a pH of 5; adding sodium sulfide, tin chloride, and silver zeolite to precipitate insoluble compounds of Hg and Cr, Tc(Re), and I, respectively; evaporating water to reduce the volume; and adding the binder mix ( $\text{MgO}$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{CaSiO}_3$ ). Adding silica as wollastonite ( $\text{CaSiO}_3$ ) or fly ash improves the waste-form performance [141].

#### **7.4.2.5 Bitumen**

There are several processes for solidifying bitumen with waste streams.[6] The most common bituminization process embeds wastes in molten bitumen and the waste becomes encapsulated when the bitumen cools. The process combines heated bitumen and a waste concentrate, usually in slurry form, in a heated extruder containing screws that mix the bitumen and waste. Water is evaporated from to ~0.5% moisture.[149] The final product is a homogeneous mixture of extruded solids and bitumen.

Bituminization has proven to be effective in treating low-level radioactive waste. Radionuclides are effectively controlled and Ojovan et al [150] have recently shown that as the bitumen ages it becomes harder and more thermally stable. These assessments of aged bitumen had been made after 12 years in an open (wet) repository. The bitumen was found to age into asphaltenes, saturated hydrocarbons and

aromatic hydrocarbons. The asphaltene fraction was found to increase as the bitumen aged and the asphaltene was found to be responsible for retaining the major part of the radioactivity. Thus bitumen was found to be as durable as some glasses. This is in keeping with the much earlier findings of Westsik [151] who showed that bitumen was more durable than cement wasteforms with very low fractional release rates of  $<10^{-5}$  fraction/day. Bitumen has been used in Europe, Canada, Russia and to a lesser extent in the United States.

### ***7.4.3 Solidification in Composites (chemical incorporation & encapsulation)***

Composites can be thought of as multi-barrier wasteforms. Usually a composite wasteform is required to meet a specific wasteform criterion, e.g. heat loading, respirable fines, compressive strength, etc. A single phase or multiphase crystalline ceramic or even a glass can further be encapsulated in a metal, a glass, or an encapsulant wasteform such as cement, geopolymers, hydroceramics, bitumen etc. The encapsulant phase offers a second level of protection to the release of radionuclides or hazardous components in the wasteform as shown in Table 10. Composites include many GCM's such as glass bonded sodalites that have already been discussed in Section 7.4.1.2. Composites can also include deteriorated cement wasteforms that are remediated by encapsulation (see Table 10). A few examples are given below and a few examples are shown in Figure 3.

#### **7.4.3.1 Metal Matrix**

In metal matrix wasteforms a metal is used as the encapsulant for either glass or crystalline materials in which the radionuclides or waste species are already atomically bonded. The advantages of this type of encapsulation include (1) improved thermal conductivity of the waste package, (2) potentially decreased leach rates of radionuclides because of the metal matrix encapsulation, (3) improved mechanical strength and decreased dispersability on impact, and (4) improved radiation protection during handling. [152,153] The encapsulation of wasteforms in metal matrices was pursued in the U.S. and developed full scale in PAMELA which was a joint Belgium-German project located in Belgium.

Vitromelt is a composite wasteform in which glass beads (0.5 cm) are embedded in a metal matrix (usually a Pb alloy). [154,155,156] For example, waste immobilized in calcium silicate pellets was encapsulated in a lead matrix. In one variation of the commercial PAMELA vitromet process phosphate glass beads containing HLW were produced by passing molten glass through nozzles. The beads were subsequently fed into a container and infiltrated with molten lead alloy to produce a composite wasteform ('vitromet'). The beads, with a diameter of 0.5cm, 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.

In studies related to vitromelts immobilized waste pellets have been coated with pyrolytic graphite, before encapsulating in a metal matrix, in order to improve the leach resistance. 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. Metal matrices have included Pb-based alloys (e.g. Pb—Sb, Al, Sn), Al-based alloys (e.g. Al—Si, Cu, Ti), and Cu. Particles can be coated by conventional

ceramics (e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  or  $\text{SiO}_2$ ) or by carbon products (e.g.  $\text{PyC}$ ,  $\text{Cr}_7\text{C}_3$  or  $\text{SiC}$ , glass (borosilicate or aluminosilicate, or metals (e.g. Ni, Si, or Fe before being encapsulated). Uncoated, sintered supercalcine pellets have been encapsulated in vacuum-cast Al-12Si and glass-coated, sintered supercalcine pellets encapsulated in vacuum-cast Al-12Si. Supercalcine pellets have also been  $\text{PyC}/\text{Al}_2\text{O}_3$  coated before encapsulation in gravity-sintered Cu.

Cermets are related composite wasteforms in which radionuclides in the form of small oxide or silicate particles +1 mm in size that are dispersed in a metal matrix.[152] The unique aspects of the wasteform are the very fine scale on which the radionuclide-containing phases are dispersed, the fact that the alloy is primarily comprised of hydrogen reducible metals which are already in the waste, the high thermal conductivity, and reduced leach rates due to the alloy encapsulation. Developmental work on cermet was performed using simulated wastes, radionuclide-containing simulated wastes, West Valley acid THOREX wastes and SRS HLW sludge and un-neutralized SRS wastes. Waste loadings of up to around 30% were been reported. The addition of elements in excess of stoichiometric requirements is used to insure the formation of specific ceramic phases, e.g. excess Al and Si to insure the formation of pollucite.

#### **7.4.3.2 Ceramic/Mineral Wasteforms made by FBSR in Geopolymer or Cement**

Use of the FBSR process to produce a highly leach resistant mineralized wasteform from Hanford Low Activity Waste (LAW) has been investigated since 2001 (see Section 7.4.1.3). Initial studies focused on producing and testing the granular mineral product created by processing high sodium waste feeds with clays at  $\sim 720^\circ\text{C}$  to produce nepheline ( $\text{NaAlSiO}_4$ ) and nepheline-based minerals such as the sodalites to host I, F, Cl and nosean to host sulfate and sulfide. Numerous studies (74,75,76,77,78,79,80) have shown that it is possible to produce a mineral wasteform that effectively immobilizes both radionuclides and hazardous constituents.

To be accepted for near-surface disposal, the wasteform is required to meet an acceptance criterion for compressive strength of 500 psi. This requirement is derived from a Nuclear Regulatory Commission Branch Technical Position on low level waste (LLW) forms in the U.S. which somewhat arbitrarily specifies 500 psi to preclude subsidence in the waste disposal system. It is also noted that a monolithic wasteform reduces the impact to human health for the intruder scenario in the waste site Performance Assessments. While a monolith is desirable there are other means by which this requirement can be met, e.g. waste stabilization in high integrity containers (HICs).

In 2005-2006 the Savannah River National Laboratory (SRNL) performed a monolith feasibility study for granular FBSR product. [157] Monoliths were made out of ordinary portland cement (OPC) at 80-87 wt% FBSR loading, out of ceramicrete (a blend of  $\text{MgO}$  and monopotassium phosphate ( $\text{KH}_2\text{PO}_4$ )) at an FBSR loading of 35.7 wt%, and out of hydroceramics (aluminosilicate zeolite phases formed from metakaolin plus  $\text{NaOH}$ ) at FBSR loadings of 50-80 wt%. The hydroceramics had the best durability as they had a similar chemical makeup to the FBSR product (see Figure 4) but the hydroceramics required hydrothermal processing. Therefore, geopolymers were used to bind the granular mineral wasteform due to the similarity of the chemical makeup (see Figure 4) to the FBSR product and the fact that the geopolymers did not require hydrothermal processing. Up to 70 wt% granular product was stabilized in the geopolymer. The granular mineral stabilized geopolymer were shown to be more durable than the granular product alone. [158]

## **7.5 Wasteforms, Waste packages, and the Geologic Environment**

The long-term behavior of a waste disposal facility is a function of the entire disposal system, including the wasteform, engineered barriers, and surrounding environment. In order to assess the ability of a given disposal concept to meet regulatory requirements it is necessary to consider the influence of each of these system components on short-and long-term performance. This is accomplished through the performance assessment (PA) process. For HLW many countries are proposing long storage life for the canistered glass wasteforms during geological repository siting and preparation. During that time a great many of the radionuclides will decay leaving the long lived radionuclides as the primary sources that need be considered in a PA.

Figure 5 is a schematic of a generic high level waste repository. It shows the relative role of the wasteform, the role of the multiple barriers (canisters, containers, overpacks, and casks) in the waste disposal system. It is the concept of the “Russian doll” – a barrier within a barrier within a barrier as discussed in Chapter 1. Ultimately the role of the repository or disposal environment is to isolate the waste from the biosphere until all the barriers have failed at which time almost all of the radionuclides will have decayed.

While the wasteform is the source term and should be as durable as reasonably possible, multiple barriers must corrode before the wasteform will be exposed to groundwater. Due to research programs over the past several decades, there is now an extensive data-base and substantial understanding of the behavior of nuclear waste glasses in a variety of disposal environments. [159] The present challenge is to model glass behavior in the near-field of specific geologic repository environments and to develop a fundamental understanding of the long-term corrosion rate. [160]

## **7.6 Recent Advances in Wasteform Processing**

Historically, the crystallization of vitreous wasteforms has always been regarded as undesirable, as it has the potential to alter the composition (and hence, durability) of the remaining continuous glass phase, which would (eventually) come into contact with water. However, there has been a recent trend toward higher crystallinity in ostensibly vitreous wasteforms so that they are more correctly termed GCMs. This is particularly apparent in the development of hosts for more difficult waste or where acceptable durability can be demonstrated even where significant quantities of crystals (arising from higher waste loadings) are present. Acceptable durability will result if the active species are locked into the crystal phases that are encapsulated in a durable, low-activity glass matrix. The GCM option is being considered in many countries including Australia, France, Russia, South Korea, the United Kingdom, and the United States. The processing, compositions, phase assemblages, and microstructures of GCMs may be tailored to achieve the necessary material properties.

Joule heated melters are relatively intolerant of crystal growth in the melt which causes slag formation. [161] Recently, Sellafield has shown the ability to go to 38 wt% waste loading [162] from 25 wt% waste loading [163] by allowing spinel formation in the melt but the Sellafield melter is induction heated not a JHM design. However, 1-2% crystallization of spinels is planned for Hanford’s HLW AJHM and it is anticipated that the spinel crystals will stay buoyant



from the melt pool agitation afforded by the bubblers.[164, 165] This strategy will likely work unless during long maintenance outages, the crystals grow larger than the size that the agitation can sustain or the melt pool will have to be diluted with components that dilute the spinel forming tendencies because JHM's and AJHM's cannot be drained without causing damage to the electrodes. Either that or cold crucible induction-heated melters (CCIM), which are already being pursued in Russia, France, and the U.S. will have to be substituted as an alternative to JHM and AJHM melter technology. The major advantages of CCIM over JHM/AJHM are higher productivity, higher temperatures, longer lifetime, smaller dimensions, and higher waste loadings while maintaining the same product quality while at the same time being robust in terms of producing GCM's and mineral wasteforms by a melt and controlled crystallization route.

Advances in the techniques to measure and quantify how and where radionuclides are bonded in glasses and glass ceramics will enable GCM's to be tailored to sequester the desired radionuclides in the ceramics phases and either minimize or prevent the radionuclides from migrating to the glassy encapsulating phase. This will allow the crystalline and glass structures based on MRO and LRO to be used to model glass and GCM behaviour and properties.

Mineral wasteforms will advance using novel processing techniques like templating. Hybrid wasteforms, e.g. glass-ceramics instead of glass vs. ceramic, geopolymeric cements combining geopolymers and cement or methods that combining thermal treatment (calcining, FBSR) with encapsulation in geopolymers or cements will provide double barrier composites for troublesome waste species.

## **7.7 Radiation Damage in Glasses and Ceramics**

No discussion of the relative attributes of glass, glass-ceramics, and ceramic/mineral wasteforms is complete without a discussion of the relative radiation stability of the various wasteforms. The effects of radiation damage due to self-irradiation of various wasteforms have been studied for decades and a few of the more recent reviews of this field are given in Section 7.9.2.

Radiation damage is not only important because it impacts the stability of the wasteform but if the material swells or is otherwise degraded by self-irradiation this impacts the long term durability of the wasteform (see discussion in Section 7.8). While glasses undergo radiation damage that can cause density variations, careful durability experiments have shown that the radiation damage does not affect the dissolution rate as studied by Single Pass Flow Through (SPFT) and Soxhlet durability tests. Many pertinent examples are given in Reference 4.

In ceramic/mineral wasteforms the crystalline structure may become amorphous, a phenomena observed in nature and known as metamictization (the formation of amorphous metamict phases). This phase change from a crystalline structure to a partially or completely amorphous structure is accompanied by macroscopic swelling of the structure. An interesting study by Weber, Ewing and others [166] has shown that the SYNROC crystalline phases (zirconolite and perovskite) are susceptible to macroscopic swelling at high dosages (Figure 6). Moreover, the swelling in the titanium based SYNROC phases is greater than the swelling in the silicate based supercalceine ceramics at lower dosages which in turn is greater than the swelling in glass ceramics (Figure 6). Additional references regarding the swelling of individual mineral/ceramic phases can be found in the references in the annotated Table 6 and Table 8.

## 7.8 Leach Testing and It's Role in The Waste Acceptance Process

The most important requirement for a wasteforms is the chemical durability, expressed as a dissolution rate. It should be noted that for some radionuclides solubility limits the dissolution rate while others are completely soluble, e.g.  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ , or  $^{135}\text{Cs}$ . These soluble radionuclides are released at the maximum forward rate of dissolution. For the production of durable nuclear wasteforms, it is desirable for the wasteforms to be highly insoluble in the long-term to minimize release to the environment, i.e. to have the slowest forward dissolution rate possible. Since no “durability test” can be carried out on these geologic time scales, dual approaches are taken:

- 1 durability test parameters such as surface area (SA), time (t), temperature (T), or a combination such as (SA)•(t) are used to “accelerate” dissolution as long as the acceleration parameter(s) used does not change the dissolution mechanism
  - to ensure that the mechanism is not “altered” by the acceleration modes of the experiments natural analogs are usually tested simultaneously.
- 2 models are used to predict wasteform dissolution from parameters that can be measured such as the activation energy of dissolution, forward rate of dissolution, and from an understanding of the dissolution mechanisms.
  - predictive and/or transport models for wasteform performance on extended time scales (1000-1,000,000 years) has led to various thermodynamic and kinetic models (see 160, 187 ).

Thus, there are no “wasteform specific” durability tests, but a suite of tests that must be performed to understand the leaching mechanism(s) of a wasteform and to derive the parameters necessary for the particular predictive or transport model(s) being applied.

In order to determine if a particular wasteform is acceptable it must demonstrated that the wasteform performance in the disposal system is adequate. Such evaluations, in the US are known as total system performance assessments (TSPA) for HLW and PA's for ILAW. The TSPA or PA includes all of the testing and performance modeling that has been gathered on the wasteform and the TSPA is intended to provide a technical basis that a wasteform is acceptable for deep geological disposal.

For HLW in many countries the geological disposal sites have not been determined while wasteform producers have already made many canisters of vitrified waste (see Table 1). Due to the mismatch in timing between the need to stabilize HLW and when a geological repository will be chosen and ready to receive the wasteforms, the US devised a strategy to addresses vitrified waste acceptance based on Production Control. Production Control is intended to determine how the production of a wasteform material affects (or controls) its performance and identify the ranges for processing variables that result in an acceptable wasteform. The primary role of most of the waste acceptance product specifications (WAPS) developed in the US for vitrified HLW wasteforms verify that the properties of a specific wasteform product are consistent with the existing regulations and thus will be acceptable for disposal, either by direct measurement or through process control.

Therefore, waste acceptance testing is, for the most part, focused on comparing a specific wasteform product to the range of wasteforms that are (1) considered to have acceptable performance based on performance modeling and (2) produced within the production control limits. What will be acceptable with respect to wasteform performance and processability will depend on the disposal site and engineered system and cannot be completely quantified at the time the waste form is made. The range of acceptable wasteform compositions will depend on the required performance. [167]

While the predicted long term durability of a waste form is a necessity for its “qualification for shallow land burial” or “deep geologic disposal” there is also a need for short term testing that can be related to acceptable performance by the following linking relationships [168]:

process control ↔ composition control ↔ dissolution rate control ↔ performance control  
↔ acceptable performance.

This approach allows a wasteform producer to ensure that the waste form that they are producing on a tonnage per year basis will be acceptable to long term performance instead of having to test each and every canister or form produced. For high level waste glass (alkali borosilicate glass) in the US the manner in which this was done is given below in a brief stepwise fashion and explained in more detail in References 11, 169,170 ,171, 172, 173:

- 1 develop an acceptable wasteform durability based on HLW performance modeling (fractional dissolution rates between  $10^{-4}$  to  $10^{-6}$  parts per year (i.e., the glass wasteform would take 10,000 to 1,000,000 years to totally dissolve [174])
- 2 the middle of the range determined by HLW performance modeling was adopted as the wasteform specification; if the long-term fractional dissolution rate of a wasteform was  $\leq 10^{-5}$  parts per year for the most soluble and long-lived radionuclides then borosilicate glass would provide acceptable performance for any repository site or concept
- 3 develop an understanding of the glass durability mechanisms from a combination of the test protocols (ASTM C1220 which was previously known as MCC-1, ASTM C1285 which is known as the Product Consistency Test (PCT) [175,176], ASTM C1662 which is the SPFT test and ASTM C1663 which is the Vapor Hydration Test or VHT)
- 4 develop a glass standard, the Environmental Assessment (EA) glass [177,178] that bounded the upper release rate found to be acceptable from the HLW repository modeling from step 1 above
- 5 generate databases for modeling the maximum radioactive release rate(s) by relating the release of  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ , and  $^{135}\text{Cs}$  to the release of non-radioactive species such as Na, Li, and B which leach at the same rate (congruently); this is part of the ASTM C1285 (PCT) test protocol
- 6 develop a short term test and process control strategy for ensuring that every glass produced had a dissolution rate less than that of the EA glass at the L95% confidence level based on Na, Li, B which in turn ensures acceptable performance control
- 7 Continue to qualify that the radionuclide response of production glasses verify that production glass radionuclide releases are consistent with the releases predicted by Na, Li, and B

Therefore, a suite of the existing durability tests (those for affinity control, solubility control, and/or diffusion control) must be performed on a wasteform to determine the mechanisms, and determine the parameters necessary for the mechanistic model(s) being developed, e.g. the transition state theory (TST) models used in the TSPA for HLW geological disposal or the PA's for shallow land burial. Different durability tests are used for a diffusion model for example for cement. However, one cannot apply a glass standard that leaches by an affinity limited mechanism to cement that leaches by diffusion nor can one apply a borosilicate glass standard to non-borosilicate type glasses since it is not known whether the radionuclides in non-borosilicate glasses leach by the same degradation mechanism and whether the leaching of Na, Li, and B remain congruent with the leaching of the radionuclides. In these cases, new standards need to be developed and qualified and the leaching mechanisms understood.

For glasses the advances in the measurement of medium range order (MRO) in glass wasteforms has led to the understanding that the molecular structure and composition of a glass like the molecular structure and composition of minerals, controls the wasteform durability by establishing the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites. During the early stages of glass dissolution, a "gel" layer resembling a membrane forms through which ions exchange between the glass and the leachant (Figure 7). The hydrated gel layer exhibits acid/base properties which are manifested as the pH dependence of the thickness and nature of the gel layer. Advances in the understanding of the dissolution mechanisms of borosilicate glasses proposed for nuclear waste solidification were extensively studied in the 1980's-1990's [22, 179,180,181,182,183,184,185,186] and such mechanisms are still being studied.[160,187,188,189,190] At least four operative mechanisms have been shown to control the overall glass durability as shown in Figure 7. These four mechanisms are ion exchange, matrix dissolution, accelerated matrix dissolution, and surface layer formation (possibly of a protective or passivating nature).

One can bound or model the shorter term durability of a glass using kinetic or thermodynamic models to describe the impacts of ion exchange and matrix dissolution or hydrolysis by examining either time-temperature data (Figure 8) or release vs time or accelerated release, expressed as  $SA/V \bullet \text{time}$  Figure 9, but these underlying mechanisms become modified if surface layers form and/or if, at very long times when the gel layer ages *in situ* into clay or zeolite minerals or the leachate becomes saturated with respect to a clay or zeolite phase. If zeolite mineral assemblages (higher pH and  $Al^{3+}$  rich glasses) form, the dissolution rate increases (Figure 9) which is undesirable for long-term performance of glass in the environment.

The current theories of glass dissolution [159] suggest that all glasses typically undergo an initial rapid rate of dissolution denoted as the "forward rate" (Figure 8 and Figure 9). However, as the contact time between the glass and the leachant lengthens some glasses come to "steady state" equilibrium and corrode at a "steady state" rate while other glasses undergo a disequilibrium reaction with the leachant solution that causes a sudden change in the solution pH or the silica activity in solution [191]. The "return to the forward rate" (Figure 9) after achieving "steady state" dissolution is undesirable as it can cause a glass to return to the rapid dissolution characteristic of initial dissolution.

The initial rate is often referred to as Stage I dissolution in the U.S. literature but it encompasses zones where multiple mechanisms are operative including regimes that are interdiffusion controlled, hydrolysis controlled, and a rate drop that is diffusion or affinity controlled [159]. The “steady state” rate (also known as the residual or final rate) that signals the end of the alteration phase and/or a pseudo-equilibrium between the alteration and re-condensation reactions [159, 192] is known as Stage II dissolution, and the return to a forward rate (or resumption of alteration) is known as Stage III dissolution. Diffusion controlled dissolution of network modifiers and/or radionuclides during Stage I and Stage II normally follow a mathematical function related to the square root of the test duration as observed in many burial studies [190] while other radionuclides are solubility limited, entrapped in the gel layer, or complexed in secondary alteration phases that form from the leachate solution.

A reaction zone is formed as the leached layer solution interface progresses into the glass (Figure 7a). The front of the reaction zone represents the region where the glass surface sites interact with the ions in solution [193]. The top of the gel reaction zone represents the leached layer-glass interface where a counter-ion exchange occurs [193]. The glass dissolution rate is modified by the formation of the hydrated amorphous gel layers and/or secondary precipitates, e.g., metal hydroxo and/or metal silicate complexes that have reached saturation in the leachate and can precipitate on the surface of the gel layer [22,179,181,182,194,195]. These “back reactions” have been attributed to formation of silanol bonds as surface adsorption sites which were modified by changes in solubility of the species in solution and surface (zeta potential) considerations.[22,196]

The gel layer may, under certain conditions, act as a selective membrane [194,197] or as a protective/passivating layer [22,159, 180,181, 182,184,185,186,198,192]. The slowing of glass dissolution to a steady state rate by solution saturation (affinity) of glass matrix elements or reaction through a surface layer has been referred to as Stage II dissolution including residual rate dissolution, steady state dissolution, or the final dissolution rate. Recent mechanistic modeling of glass durability including the slowing of the dissolution rate due to affinity and/or surface layer effects was first modeled by Grambow and Muller [199] and is referred to as the GM2001 model. The GM2001 model combines the effect of glass hydration by water diffusion with ion exchange and affinity-controlled glass network corrosion (Figure 8 and Figure 9). The slowing of dissolution due to the effect of a growing surface gel layer is represented by a mass transfer resistance for silica by this layer. At the interface between the glass and the gel layer a different “gel layer” is assumed to be hydrated glass that allows diffusion of H<sub>2</sub>O in and boron and alkali atoms out of the glass (similar to Figure 7). A 2003 modification of the GM2001 model, known as the GM2003 model [159], treats silica dissolution and silica diffusion through the gel separately from water diffusion and boundary conditions are specified at the gel/diffusion layer and the gel/solution interfaces. Recently, the GRAAL (Glass Reactivity with Allowance for the Alteration Layer) model [187,189] has been proposed which is dependent on the composition and the passivating nature of the gel layer, called the Passivating Reactive Interphase (PRI). The leached layer has been found experimentally to be zoned (5-7 zones) and the GRAAL model assigns various mechanisms to different zones within the PRI.

The resumption of alteration (Stage III) causes the long term dissolution rate to reaccelerate to a rate that is similar to the initial forward dissolution rate for some glasses. This unexpected and poorly understood return to the forward dissolution rate has been shown to be related to the formation of the  $\text{Al}^{3+}$ -rich zeolite, analcime, and/or other calcium silicate phases. Moreover, the presence of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  in the HLW glass, in the leached layer, and in the leachant has been shown to influence whether a glass maintains Stage II dissolution or reverts to the forward rate of dissolution, e.g., Stage III dissolution. Van Iseghem and Grambow [191] demonstrated that an  $\text{Al}^{3+}$ -rich zeolite (analcime) formed on certain glasses during dissolution but not on others. Van Iseghem and Grambow also demonstrated that a change in solution pH accompanied the return to the apparent forward rate when analcime formed. Likewise, Inagaki [200] demonstrated that solution pH and solution concentrations of Na and K were also involved in the formation of undesirable analcime versus Na-bedellite (a smectite clay). Other zeolites and smectite clays that are rich in  $\text{Fe}^{3+}$  compared to  $\text{Al}^{3+}$  do not appear to accelerate glass corrosion [191,201,202]. Since many long term durability models are still being refined and an international study group [203] is actively working on a refined understanding of the PRI, a variety of leaching tests are being used to facilitate an integrated understanding of these stages of durability.

## **7.9 Sources of further information**

### **7.9.1 Reviews of Wasteforms:**

E.R. Vance, M.W.A. Stewart and S. Moricca, “**Advanced Ceramics and Glass-Ceramics for Immobilisation of ILW and HLW**,” Materials Research Society Symp. Proc., v. 1475, Cambridge University Press, Cambridge, UK, 163-172 (2012).

M.I. Ojovan, “**Handbook of Advanced Radioactive Waste Conditioning Technologies**,” Woodhead Publishing Ltd, Cambridge, UK 488pp. (2011).

National Research Council, “**Waste Forms Technology and Performance**,” National Academies Press, Washington, DC 294pp (2011).

I.W. Donald, “**Waste Immobilization in Glass and Ceramic Based Hosts**,” John Wiley Ltd, West Sussex, UK, 507 pp. (2010).

R.C. Ewing and W.J. Weber, “**Actinide Waste Forms and Radiation Effects**,” Chapter 35 In: **The Chemistry of the Actinides and Transactinide Elements**, vol. 6, L. R. Morss, N.M. Edlestein, and Jean Fuger (Eds.) Springer, Amsterdam, 3813-3888 (2010).

D. Caurant, P. Loiseau, and O. Majerus, V. Aubin-Chevaldonnet, I. Bardez, and A. Quintas, “**Glasses, Glass-Ceramics and Ceramics for Immobilization of Highly Radioactive Nuclear Wastes**,” Nova Science Publishers, Inc., New York, 359p. (2009).

R.T. Pabalan, F.P. Glasser, D.A. Pickett, G.R. Walter, S. Biswas, M.R. Juckett, L.M. Sabido, and J.L. Myers, “**Review of Literature and Assessment of Factors Relevant to Performance of Grouted Systems for Radioactive Waste Disposal**,” Center for Nuclear Waste Regulatory Analysis, San Antonio Texas Report # CNWRA 2009-001 (April 2009).

M.I. Ojovan and W.E. Lee, **“New Developments in Glassy Nuclear Wasteforms,”** Nova Science Publishers, New York, 131 p. (2007).

W. E. Lee, M. I. Ojovan, M. C. Stennett, and N. C. Hyatt, **“Immobilisation of Radioactive Waste in Glasses, Glass Composite Materials and Ceramics,”** Advances in Applied Ceramics, 105[1], 3-12 (2006).

M.I. Ojovan and W.E. Lee, **“An Introduction to Nuclear Waste Immobilization,”** Elsevier, Amsterdam, 315pp. (2005).

S.V. Stefanovsky, S. V. Yudintsev, R. Giere, and G. R. Lumpkin, **“Nuclear Waste Forms,”** Geological Society of London Special Publications, v. 236, 37-63 (2004).

I.W. Donald, B.L. Metcalfe, and R.N.J. Taylor, **“The Immobilization of High Level Radioactive Wastes Using Ceramics and Glasses,”** J. Materials Science, V. 32, 5851-5887 (1997).

W. Lutze and R.C. Ewing, **“Radioactive Waste Forms for the Future,”** North-Holland Publishers, Amsterdam, 778pp. (1988).

### ***7.9.2 Reviews of Radiation Effects in Waste Forms:***

R.C. Ewing and W.J. Weber, **“Actinide Waste Forms and Radiation Effects,”** Chapter 35 In: **The Chemistry of the Actinides and Transactinide Elements**, vol. 6, L. R. Morss, N.M. Edlestein, and Jean Fuger (Eds.) Springer, Amsterdam, 3813-3888 (2010).

B.E. Burakov, M.I Ojovan, W.E. Lee. **“Crystalline Materials for Actinide Immobilisation”, Chapter 6 “Radiation damage”,** Imperial College Press, London, 198 pp. (2010).

M.I. Ojovan, W.E. Lee. **“Role of Self-Irradiation in Corrosion of Nuclear Waste Glasses”,** *Proc. WM’06 Conference*, February 27 – March 3, 2006, Tucson, Arizona, WM-6239, 13p. (2006).

W.J. Weber, R.C. Ewing, C.R.A. Catlow, T. Diaz de la Rubia, L.W. Hobbs, C. Kinoshita, HJ. Matzke, A.T. Motta, M. Nastasi, E.H.K. Salje, E.R. Vance and S.J. Zinkle, **“Radiation Defects in Crystalline Ceramics for the Immobilization of High-level Nuclear Waste and Plutonium,”** Journal of Materials Research, 13 (6), 1434-1484 (1998).

W.J. Weber, R.C. Ewing, C.A. Angell, G.W. Arnold, A.N. Cormack, J.M. Delaye, D.L. Griscom, L.W. Hobbs, A. Navrotsky, D.L. Price, A.M. Stoneham and M.C. Weinberg, **“Radiation Effects in Glasses used for Immobilization of high-level Waste and Plutonium Disposition,”** Journal of Materials Research, 12(8), 1946-1978 (1997) .

R.C. Ewing, W.J. Weber, and W.J. Clinard, **“Radiation Effects in Nuclear Waste Forms,”** Progress in Nuclear Energy, 29 (2), 63-127 (1995).

### ***7.9.3 Reviews of Natural Analogs:***

W. Miller, R. Alexander, N. Chapman, I. McKinley, J. Smellie. **“Geological disposal of radioactive wastes & natural analogues”**. Elsevier, Oxford, 316 pp. (2000).

W.R. Alexander. **“Natural cements: how can they help us safely dispose of radioactive waste?”** Radwaste Magazine, September, 62-69 (1995).

R.F. Haaker and R.C. Ewing, R. C., **“Naturally Occurring Crystalline Phases: Analogues for Radioactive Waste Forms,”** U.S. DOE Report PNL-3505, Pacific Northwest Laboratory, Richland, WA (1981).

R.C. Ewing, **“Natural Glasses: Analogues for Radioactive Waste Forms,”** Scientific Basis for Nuclear Waste Management, I, G.J. McCarthy (Ed)., Plenum Press, New York, 57-68 (1979).  
Other references cited in the text for glasses and cements.



## **7.10 Acknowledgements**

This work was sponsored by the Department of Energy and the Savannah River National Laboratory in connection with work done under Contract No. DE-AC09-08SR22470. The authors would also like to acknowledge the helpful suggestions of Connie Herman of SRNL.

The authors would also like to thank Dr. Delbert Day of the Missouri University of Science and Technology and Dr. Adrian C. Wright of the J.J. Thomson Physical Laboratory in Reading UK for providing the schematics and data for the structure of iron phosphate glass. The authors would like to thank Michael J.D. Rushton of Imperial College for the structure of magnetoplumbite.

The lead author would also like to thank the National Academy of Science for permission to update and modify several tables and figures from their 2011 “Waste Forms Technology and Performance Final Report.” The lead author also acknowledges the assistance of Dr. Rodney Ewing of the University of Michigan, Dr. Tina M. Nenoff of Sandia National Laboratories, and Dr. David W. Johnson retired from Bell Laboratories for assisting with the collection of the extensive lists of waste form references.

**Table 1. Data on HLW Glass Production**

Vitrification Plant	Location	Melting Process	Waste Glass Produced (metric tons)	Waste Loading Range (wt%)	Size of Canisters (meters)	Number of Canisters	TBq <sup>‡</sup>
Defense Waste Processing Facility (DWPF), Savannah River Site	Aiken, South Carolina, USA	JHCM	6169*	28-40 <sup>c</sup>	0.6 x 3	3,496	1.7 x 10 <sup>6</sup>
West Valley Demonstration Project (WVDP)	West Valley, New York, USA	JHCM	~500**	~20.4-23.5 <sup>b</sup>	0.6 x 3	275	8.9 x 10 <sup>5</sup>
Waste Vitrification Plant (WVP), BNFL	Sellafield, UK	Induction, hot crucible	~2,200 <sup>†</sup>	~25-32 <sup>a</sup>	0.43 x 1.34	5627 <sup>††</sup>	2.4 x 10 <sup>7</sup>
Areva NC (R7/T7) <sup>d</sup>	La Hague, France	Induction, hot crucible	6,642 <sup>f</sup>	12-18 <sup>§§</sup>	0.43 x 1	16,334	2.51 x 10 <sup>8</sup>
AVM or Atelier de Vitrification de Marcoule <sup>d</sup>	Marcoule, France	Induction, hot crucible	1,138 <sup>ξ</sup>	12-18 <sup>§§</sup>	0.43 x 1	3,159	1.69 x 10 <sup>6</sup>
Pamela	Mol, Belgium	JHCM	500 <sup>§</sup>	15-25 <sup>§§</sup>	0.30 x 1.2 0.43 x 1.34	2200	4.5 x 10 <sup>5</sup>
Tokai Vitrification Facility <sup>c</sup> (TVF)	Japan	JHCM	>100	20-30 <sup>§§</sup>	0.43 x 1	247 <sup>ff</sup>	1.5 x 10 <sup>4</sup>
Mayak Vitrification Facility <sup>f</sup> (EP-500)	Ural Region, Russia	JHCM	~8000	33 <sup>§§</sup>	0.57 x 1	17,600	3.33 x 10 <sup>7</sup>

<sup>‡</sup> 1 Tera-Becquerel (TBq) = 10<sup>12</sup> atoms decaying per second or transmutations per second

\* 1996-June 2012

\*\* 1996-2002 – mission complete

<sup>†</sup> 1991 to April 2012 at 142L glass per canister and an assumed glass density of 2.75 g/cc (390 kg glass per container)

<sup>††</sup> Maximum total is 10,000 (capacity of vitrified product store), of which ~2,200 will be returned to overseas customers. Actual total is expected to be less depending on post-operation clean-out strategy.

<sup>f</sup> 1989-2011

<sup>ξ</sup> 1978-2008

<sup>§</sup> 1985-1991

<sup>ff</sup> 1995-2012

<sup>§§</sup> acidic waste loadings are comprised of fission products and minor actinides – corrosion products and alkali are not included as for neutralized wastes

a A. Riley, S. Walker, N.R. Gribble, “Composition Changes and Future Challenges for the Sellafield Waste Vitrification Plant,” Sci. Basis for Nuclear Waste Mgt, XXXIII, Materials Research Society, Pittsburgh, PA, 267-273 (2009).

b J.M. Perez, Jr., D.F. Bickford, D.E. Day, D.S. Kim, S.L. Lambert, S.L. Marra, D.K. Peeler, D.M. Strachan, M.B. Triplett, J.D. Vienna, R.S. Wittman, “High-Level Waste Melter Study Report,” PNNL-13582 (2001).

**Chapter 7 in Radioactive Waste Management and                      SRNL-STI-2012-00407**  
**Contaminated Site Clean-up: Processes, Technologies and International Experience**

- c. C.M. Jantzen, A.D. Cozzi, and N.E. Bibler, “High Level Waste Processing Experience with Increased Waste Loadings,” Environmental Issues and Waste Management Technologies X, J.D. Vienna, C.C. Herman, and S.L. Marra (Eds), Ceramic Transactions 168, 31-49 (2005).
- d. Catherine Veyer of AREVA, personnel communication (2010).
- e. Seiichiro Mitsui of JAEA, personnel communication (2010).
- f. P.P. Poluektor, private communication (2010).

Table 2. Waste Form Processing Technologies (adapted from Reference 11)

	Processing Technology	Process Mode	Treatment and Waste Stream Scale	Waste Forms Produced	Advantages	Disadvantages
THERMAL TECHNOLOGIES	Joule Heated Melter (JHM)	Continuous	Large	Borosilicate glass, other glasses (LaB's, FeP, AIP, chalcognide, etc.)	Proven technology; typically operates with a "cold cap" to minimize volatility of species of concern	Electrode and refractory erosion may be a problem; solubility control of certain species (Cr, Mo, and SO <sub>4</sub> ) critical
	Advanced Joule Heater Melter (AJHM)	Continuous	Large	Borosilicate glass, GCM's, other glasses (LaB's, FeP, AIP, chalcognide, etc)	Increased capacity, throughput, and melt rate compared to JHM	Operates with minimal or no "cold cap" with associated increases in volatility of species of concern
	Cold Crucible Induction Melter (CCIM)	Continuous	Large	Borosilicate glass, GCM's, other glasses (LaB's, FeP, AIP, chalcognide etc), crystalline ceramics, simple oxides, metal matrix	Allows processing of corrosive glasses; no refractories; no electrodes; water cooled; can be stirred if needed; increased capacity compared to JHM and AJHM; can operate at higher temperatures than JHM and AJHM; operates with a "cold cap" to minimize volatility	Higher temperature operation can increase volatilization of species of concern but "cold cap" coverage minimizes these impacts
THERMAL TECHNOLOGIES	In-Container Vitrification (ICV); also known as "Bulk Vitrification"	Batch	Depends on container size (could be medium to large)	Borosilicate glass; GCM's, Other Glasses (LaB's, FeP, AIP, chalcognide etc.)	Inexpensive and simple for low activity wastes or contaminated soils; not applicable to HLW	Inhomogeneous waste forms produced; no temperature control so radionuclide vaporization is high; little or no convection

	<b>Processing Technology</b>	<b>Process Mode</b>	<b>Treatment and Waste Stream Scale</b>	<b>Waste Forms Produced</b>	<b>Advantages</b>	<b>Disadvantages</b>
						in melt
	Self-Sustaining Vitrification (SSV)	Batch	Small	GCM's	Inexpensive; can be used to process small amounts of wastes at remote locations	May require some pre-processing, i.e. grinding of the waste and pre-mixing
	Cold Press and Sinter (Cold Uniaxial Pressing, CUP: Cold Isostatic Pressing, CIP)	Batch	Small	GCM's, crystalline ceramics, simple oxides, metal matrix, zeolites, hydroceramic	Higher Waste Loadings; Minimum disposal volume	Usually small scale; may require pre-calcining or pre-treating waste to an oxide to avoid shrinkage of form
	Hot Isostatic Pressing (HIP)	Batch	Small	Borosilicate glass (lab scale only), GCM's, crystalline ceramic/simple oxides, metal matrix, zeolites, hydroceramics	Zero off-gas emissions; higher waste loadings; minimum disposal volume; mature flexible technology; no major secondary wastes; mature industrial process	Processes small quantities; can overpressurize if large amounts of volatiles (e.g. nitrates/hydrates) are present; may require pre-calcining or pre-treating waste to an oxide (shrinkage handled by bellows like canisters)

	Processing Technology	Process Mode	Treatment and Waste Stream Scale	Waste Forms Produced	Advantages	Disadvantages
THERMAL TECHNOLOGIES	Hot Uniaxial Press (HUP)	Batch	Small	Borosilicate glass (lab scale only); GCM's, crystalline ceramic, simple oxides, metal matrix, zeolites, hydroceramic	Higher Waste Loadings; minimum disposal volume, mature flexible technology; mature industrial process	Usually small scale; may require pre-calcining or pre-treating waste to an oxide for shrinkage control
	Cyclone Furnaces	Continuous	Large	Borosilicate glass, GCM's, other glasses (LaB's, FeP, AIP, chalcognide, etc.), crystalline ceramics, simple oxides, metal matrix	Suitable for soils containing low volatility radionuclides;	Secondary recovery process needed to treat off gases
	Fluidized Bed Steam Reforming (FBSR)	Continuous	Large	Crystalline ceramic, simple oxides, zeolites	Pyrolysis (not incineration); immobilizes halides, sulfates, <sup>99</sup> Tc sequestered in sodalite; moderate temperature; ≥85% volatile species contained; wastes processed without neutralization; destroys organics and nitrates; industrially proven technology; no secondary liquid waste stream	Product is granular and requires a high integrity container (HIC) or encapsulation in a binder to make a glass ceramic material, a geopolymer, or a hydroceramic; Radionuclide partitioning amongst the phases needs to be further studied

	Processing Technology	Process Mode	Treatment and Waste Stream Scale	Waste Forms Produced	Advantages	Disadvantages
THERMAL TECHNOLOGY	Electric Arc Furnaces	Batch	Medium/ Large	High temperature glasses, GCM's, crystalline ceramics, simple oxides, metal matrix	Established Industrial Practice; Similar technology is used for ICV	No large scale practice; high temperatures; volatilization of radionuclides
	Plasma Furnaces	Batch	Small	Borosilicate glass, high temperature glasses, GCM's, crystalline ceramics, simple oxides, metal matrix	Plasma generating electrode erosion; efficient for the destruction of organics	
	Microwave Heating	Batch	Small	Borosilicate glass, GCM's, other glasses (LaB's, FeP, AIP, chalcognide, etc.), crystalline ceramics, simple oxides, metal matrix	Suitable for mixed wastes; Can be used as a heat source in other equipment (e.g fluidized bed)	Limited to small scale; process scale up; inhomogeneous heating (need a susceptor material); no large scale practice
NON-THERMAL TECHNOLOGIES	Cement	Continuous or Batch	Large	Ordinary portland cement (OCP), High Alumina Cements, Geopolymeric Cements with Fly Ash, slag, or meta-kaolin	Simple technology; design formulation for best waste retention; fly ash and slag additives keep <sup>99</sup> Tc and Cr in reduced oxidation state to prevent leaching	Formulations waste specific; some sequestering of radionuclides in hydration products vs. grain boundaries needs more study; radiolytic production of H <sub>2</sub> in high radiation; pH of pore water alkaline and promotes leaching

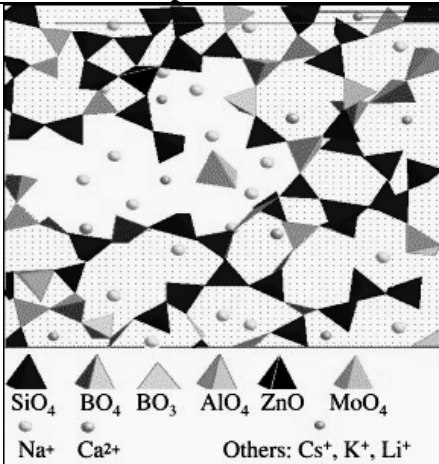
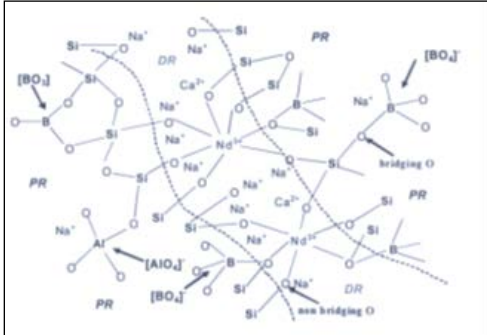
	Processing Technology	Process Mode	Treatment and Waste Stream Scale	Waste Forms Produced	Advantages	Disadvantages
NON-THERMAL TECHNOLOGIES	Geopolymer	Batch	Large or Small	Geopolymers incorporate liquid waste encapsulate incinerated, pyrolyzed, or calcined wastes, geopolymeric cements	Minimal water so radiolytic H <sub>2</sub> generation is limited, fire resistant, pore water less alkaline than cements	Formulations waste specific; distribution of radionuclides among the phases needs more study; batches are thick and require extrusion
	Hydroceramics	Batch	Small	Zeolite, crystalline ceramic	High capacity for high sodium or calcium containing wastes; stabilize halides and sulfates.	Require hydrothermal set; requires more water than geopolymers so radiolytic H <sub>2</sub> generation; batches are thick and require extrusion; wastes with >25 wt% nitrate must be pre-treated
	Ceramicrete	Batch	Small	Crystalline ceramic incorporates liquid waste or encapsulates	Very dense; room temperature curing; high waste loading	High heat of hydration; bubble formation which can be vibrated out of mixture during set
	Bitumen	Continuous or batch	Large to small	Encapsulated or Embedded Waste Forms	Simple; low operating cost; leach resistant characteristics	Flammable; requires heat to make bitumen molten; poor performance with salts; thick even when molten; requires extrusion

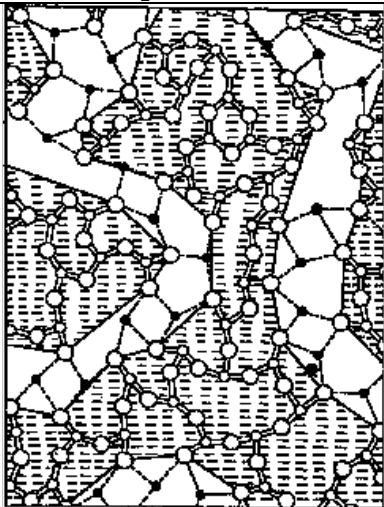


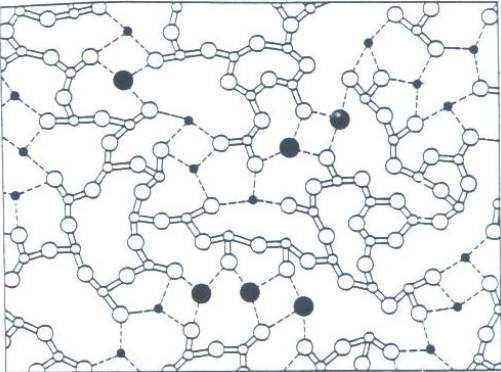
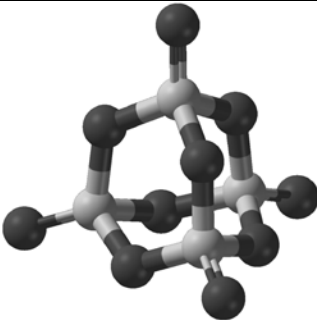
Table 3. Attributes of Homogeneous vs. Inhomogeneous Glass Waste Forms (adapted from Reference 11)

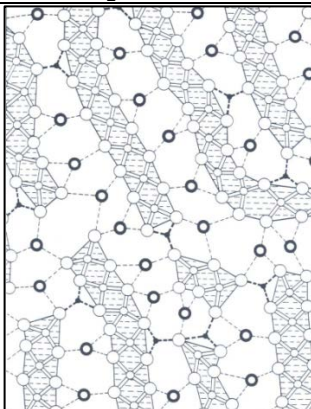
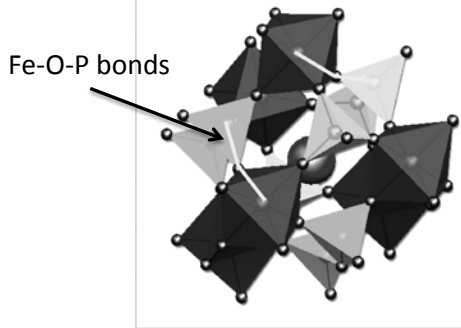
Waste Form	Homogeneous Glass	Inhomogeneous Glass
<b>Description</b>	Radionuclides and hazardous species are atomically bonded in a durable glass structure usually to oxygen atoms that are also bonded to the matrix elements, Si, Al, B, P, etc. by short range order (SRO) and medium range order (MRO).	Some radionuclides and hazardous species are atomically bonded in a durable glass structure as with homogeneous glass but other radionuclides reside in a very soluble immiscible glass phase (glass-in-glass phase separation)
<b>Radionuclide Immobilization Mechanism</b>	Chemical Incorporation	Chemical Incorporation
<p>Key</p> <p>Cs U Tc Pu xl.</p>		
<b>Waste Loading(s)/Durability</b>	<p>a. moderate waste loading</p> <p>b. good overall durability</p> <p>c. easy to model radionuclide release from a single phase</p>	<p>a. moderate waste loading</p> <p>b. poor durability for certain radionuclides</p> <p>c. impossible to model radionuclide release as the fraction of the second phase is dependent on thermal history</p>
<b>Immobilization Technologies</b>	<p>Joule Heated Melters (JHM)</p> <p>Advanced Joule Heated Melters (AJHM)</p> <p>Cold Crucible Induction Melters (CCIM)</p> <p>Hot Isostatic Pressing (HIP)</p> <p>Hot Uniaxial Pressing (HUP)</p>	<p>Joule Heated Melters (JHM)</p> <p>Advanced Joule Heated Melters (AJHM)</p> <p>Cold Crucible Induction Melters (CCIM)</p> <p>Hot Isostatic Pressing (HIP)</p> <p>Hot Uniaxial Pressing (HUP)</p>

Table 4. Examples of Homogeneous Glass Waste Forms Demonstrating their SRO and MRO Structure (adapted from Reference 11)

Type of Glass	Major Structural Components		Comments
Alkali Borosilicate [3,4, 5,6, 7,8, 18,34,61]	$(\text{SiO}_4)^{-4}$ , $(\text{BO}_4)^{-5}$ , $(\text{BO}_3)^{-3}$ and some $(\text{AlO}_4)^{-5}$ and $(\text{FeO}_4)^{-5}$ structural units to which alkali, alkaline earth, and waste species bond.	 <p>Atomic structure of a French nuclear waste glass: unshaded region shows formation of a <math>(\text{Na,Cs})_2\text{MoO}_4</math> cluster [204].</p>	Ease of processing, melt temperatures 1150-1200°C to minimize volatility; cold cap production if feasible minimizes volatility; most waste cations highly soluble in glass; overall waste solubility 25-40 wt%; made by JHM, AJHM, CCIM or HIP.
Lanthanide Borosilicate (LaBS) [5,6, 18,205, 206,207, 208, 209]	$(\text{SiO}_4)^{-4}$ , $(\text{BO}_4)^{-5}$ , $(\text{BO}_3)^{-3}$ and some $(\text{AlO}_4)^{-5}$ structural units to which lanthanides, alkaline earth, and other waste species bond	 <p>Atomic structure of a French HLW rare earth bearing borosilicate glass. <math>\text{Na}^+</math>, <math>\text{Ca}^{2+}</math> and <math>\text{Nd}^{3+}</math> exist in the percolation channels. PR is the polymerized region and DR is the depolymerized region.[7]</p>	Higher waste loading (16-59 wt%) for actinides/lanthanides than alkali borosilicates; lanthanides serve as neutron absorbers; 1300-1500°C melting causes volatilization of some radio-nuclides; corrosion similar to alkali boro-silicates; made by CCIM, HIP, or induction melting.


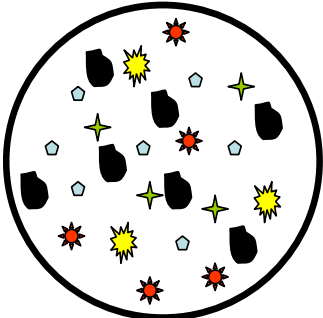
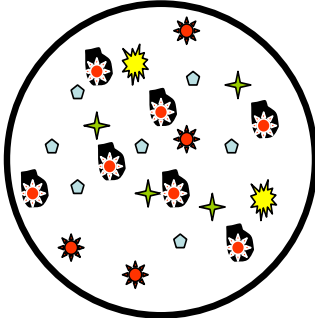
Type of Glass	Major Structural Components		Comments
Aluminosilicate glasses and/or alkali aluminosilicate glasses  [4,8,61]	$(\text{SiO}_4)^{-4}$ and $(\text{AlO}_4)^{-5}$ structural units to which alkali, alkaline earth, and waste species bond – (similar structure to borosilicate glasses when $(\text{BO}_4)^{-5}$ are present)	 <p>Atomic structure of a simple generic <math>\text{M}_2\text{O}_3(\text{G}_2\text{O}_3)_2</math> glass (M is modifying cations, G represents tetrahedral cations). The shaded regions are the PR regions. The un-shaded regions represent the percolation channels or DR regions (from 210).</p>	Melt temperature of $\sim 1600^\circ\text{C}$ causes volatilization of radionuclides; waste loading dependent on rapid cooling, e.g. 20 wt% $\text{UO}_2$ if cooled rapidly while $<10$ wt% if cooled slowly; improved durability over borosilicate glass; CCIM, HIP
Aluminoborate glasses	$(\text{BO}_4)^{-5}$ , $(\text{BO}_3)^{-3}$ and some $(\text{AlO}_4)^{-5}$	Not used for waste vitrification.	

Type of Glass	Major Structural Components		Comments
High Silicate Glasses (Sintered Glasses) [4,8,61]	$(\text{SiO}_4)^{-4}$	 <p>Atomic structure of sodium silicate glass. Glass formers are small open circles, oxygen atoms are large open circles, modifier cations are small filled circles, U atoms which form clusters are large filled circles. [211]</p>	Requires hot pressing and sintering at 600-800°C in order to retain volatile fission elements such as Cs, Ru, Mo and Tc; waste solubility 5-35 wt%.
Alkali Alumino-phosphate [3,4,8, 5,6,7,34,212, 213, 214, 215]	$(\text{PO}_4)^{-3}$ and $(\text{AlO}_4)^{-5}$ structural units to which alkali, alkaline earth, and waste species bond	 <p>Atomic structure of phosphate glass with <math>\text{P}_4\text{O}_{10}</math> cagelike structures which provides the basic building block for phosphate glass formers.</p>	Melts at lower temperatures than silicate or borosilicate systems; most cations readily incorporated; accommodates >10 wt% sulfate; corrosive to materials of construction; tendency to devitrify; durability comparable to borosilicate glass if alumina content is sufficient; composition ~ 24-27 $\text{Na}_2\text{O}$ , 20-24, $\text{Al}_2\text{O}_3$ + $\text{Me}_m\text{O}_n$ , 50-52 $\text{P}_2\text{O}_5$ ; JHM, AJHM, CCIM.

Type of Glass	Major Structural Components		Comments
<p>Lead Iron Phosphate (LIP)</p> <p>[4,8,61,216,217,218, 219,220,221,222]</p>	<p><math>(\text{PO}_4)^{-3}</math> and <math>(\text{FeO}_4)^{-5}</math> structural units to which alkali, alkaline earth, and waste species bond</p>	 <p>Atomic structure of LIP glass. Polyphosphate chains are cross-linked by lead atoms (open circles) and iron atoms (small filled circles) which form “knots” in the percolation pathways that inhibit cation diffusion. [223].</p>	<p>40-66 PbO; 30-55 P<sub>2</sub>O<sub>5</sub>; 0-10 Fe<sub>2</sub>O<sub>3</sub> dependant on amount of iron oxide in waste; melts 850-1050°C; waste loading (~20 wt%); abandoned due to regulatory issues with PbO component poor solubility of certain species, devitrification, poorer waste solubility than borosilicate glasses, etc.; JHM, AJHM, CCIM.</p>
<p>Iron Phosphate (IP)</p> <p>[224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236,237,238,239, 240,241,242]</p>	<p><math>(\text{PO}_4)^{-3}</math> and <math>(\text{FeO}_4)^{-5}</math> tetrahedral structural units to which alkali, alkaline earth, and waste species bond; Fe-O-P bonds have shown to be hydration resistant whether iron is Fe<sup>2+</sup> or Fe<sup>3+</sup> [243]</p>	 <p>Atomic structure of IP glasses are nano-heterogeneous, with FePO<sub>4</sub>-like regions and phosphate chains that incorporate Fe<sup>2+</sup>/Fe<sup>3+</sup> network-modifying cations. Large atom in center of cage like structure is a waste cation. [244,245]</p>	<p>Good chemical durability; high solubility for many heavy metals (U,Cr, Zr,Cs,Mo, noble metals, rare earths); melts 950°C to 1100°C; viscosity typically &lt;1 poise; low corrosion of oxide refractories and Inconel alloys; waste loadings 25- 50 wt%; tendency to devitrify; JHM, AJHM, CCIM.</p>

Type of Glass	Major Structural Components	Comments
<p>Chalcogenide and Chalcohalide</p> <p>[96,246,247]</p>	<p>Glasses obtained by melting chalcogen elements (S, Se, and Te) with Group V and IV elements</p> <p><math>\text{TeO}_2\text{-XCl-B}_2\text{O}_3</math>  <math>\text{TeO}_2\text{-XCl-Li}_2\text{O}</math>  <math>\text{TeO}_2\text{-XCl-Na}_2\text{O}</math></p> <p>XCl = “mixed chlorides” waste simulant at ~19 wt%</p> <div data-bbox="842 293 1409 727" data-label="Chemical-Block"> </div> <p>[from 248]</p>	<p>S, Se, and Te glasses for radionuclides difficult to immobilize in borosilicate glass systems, i.e. <math>^{129}\text{I}</math>. Gels such as <math>\text{Pt}_2\text{Ge}_4\text{S}_{9.6}</math> are used to immobilize actinides, noble gases, and carbon dioxide, and mixed chlorides.</p>

**Table 5. Attributes of Glass-Ceramics and Glass Composite Material (GCM's) Waste Forms (Adapted from Reference 11)**

Waste Forms	GCM (secondary crystalline phase contains no radionuclides and/or is inert)	GCM (secondary crystalline phase contains radio-nuclides and should be durable)
Description	Radionuclides can be chemically incorporated in the glassy matrix (same as single phase glasses) and crystals such as spinels (Cr, Ni, and Fe species) crystallize that do not contain radionuclides and are inert.	Radionuclides can be chemically incorporated in the glass matrix and in the crystalline phases. Example shows Cs in the glass and in a secondary phase. Secondary phases need to be durable like pollucite (Cs,Na) <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> and soluble phases such as (Na,Cs) <sub>2</sub> SO <sub>4</sub> should be avoided as they are not GCM's.
Radionuclide Immobilization Mechanism	Chemical Incorporation	Chemical Incorporation and Encapsulation
<p>Key</p>  <p>Cs U Tc Pu xl.</p>		
Waste Loading(s)/Durability	<p>a. higher waste loadings \</p> <p>b. secondary phases have no radionuclides</p> <p>c. good overall durability</p> <p>d. easy to model radionuclide release from single phase glass once grain boundary dissolution is experimentally shown to be minimal</p>	<p>a. higher waste loadings</p> <p>b. secondary phases contain long lived radionuclides</p> <p>c.glassy phase can contain the shorter lived radionuclides or no radionuclides</p> <p>d. more complex to model radionuclide release from multiple phases and grain boundaries</p>
Immobilization Technologies	<p>Joule Heated Melters (JHM- crystals form on cooling)</p> <p>Advanced Joule Heated Melters (AJHM ~1-3 vol% crystals probable)</p> <p>Cold Crucible Induction Melters (CCIM 10-50 wt% crystals)</p> <p>Hot Isostatic Pressing (HIPing &gt;40 wt% crystals)</p> <p>Hot Uniaxial Pressing (HUPing &gt;90 wt% crystals)</p> <p>Press and sinter (&gt; 90 wt% crystals)</p>	



**Table 6. Examples of Glass-Ceramics and Glass Ceramic Materials (GCM's) as Waste Forms (adapted from Reference 11)**

Name	Glass Phase	Crystalline Phase(s)	Comments
<b>Borosilicate Based</b>			
Alkali Borosilicates [44,45,249,250,251,252]	Borosilicate	NiFe <sub>2</sub> O <sub>4</sub> spinels ZrSiO <sub>4</sub> Al <sub>2</sub> O <sub>3</sub>	Glasses which are allowed to partially crystallize in a stirred melt pool or upon cooling; crystals are inert; crystallized glass viscosity is non-newtonian; secondary phases must be inert; AJHM or CCIM.
Glass Bonded Sodalites [49,50,51,253]	Borosilicate	<sup>129</sup> I in NaI; <sup>129</sup> I in sodalite Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> (I) <sub>2</sub> ; Cl in sodalite Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> (Cl) <sub>2</sub>	Electrorefiner wastes; radio-nuclide release from each phase is measured, e.g: Si, Al, Na, Li (sodalite and glass), B (glass), Cl, I (sodalite and halite); HIP or cold pressing/sintering
Synroc Alumino-borosilicates [11]	Alumino-borosilicate	Zirconolite CaZrTi <sub>2</sub> O <sub>7</sub>	Zirconolite is major crystalline phase for Pu and Gd (neutron absorber); for low purity actinide wastes; Pu partitions into crystalline phase over the glass phase by a factor of 100:1; accommodates actinides and any associated impurities; HIP
Barium Aluminosilicates Celsian [4,8,61,254]	Borosilicate (sodium aluminosilicate with 2-7 wt% B <sub>2</sub> O <sub>3</sub> and 3-4 wt% TiO <sub>2</sub> )	Celsian, BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> Pyrochlore (RE <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub> ; RE"rare earth), Scheelite (BaMoO <sub>4</sub> ), Pollucite (CsAlSi <sub>2</sub> O <sub>6</sub> ) molybdenum-nosean [Na <sub>8</sub> Al <sub>6</sub> MoO <sub>4</sub> (SiO <sub>4</sub> ) <sub>6</sub> ] Perovskite CaTiO <sub>3</sub> Diopside CaMgSi <sub>2</sub> O <sub>6</sub> Eucryptite LiAlSi <sub>2</sub> O <sub>6</sub> spodumene LiAlSi <sub>2</sub> O <sub>6</sub> Nepheline, NaAlSi <sub>3</sub> O <sub>8</sub>	Pyrochlore host for actinides and Sr; pollucite host for Cs and Rb; Noble metal fission products form small metallic droplets. Melt temperatures from 1100-1400°C; Controlled crystallization between 530-720°C; leaching characteristics have been noted to be comparable to the borosilicate glasses affording no significant advantages; additional work in this area has been limited, melt and control crystallization or press and sinter.
Diopside Borosilicates [4,8,61,254,255]	Borosilicate	Diopside CaMgSi <sub>2</sub> O <sub>6</sub> Powellite CaMoO <sub>4</sub> Perovskite CaTiO <sub>3</sub>	Waste loadings ~ 30 wt% for European and Japanese commercial wastes which is usually ~16 wt%; Melted at 1300°C; controlled crystallization in the range 800-1100°C; Cs was in the diopside; La, Ce, Nd, Pr in the perovskite, Sr and Sm were in the glass; noble metals were metallic.



Name	Glass Phase	Crystalline Phase(s)	Comments
<b>Titania Based</b>			
Synroc and sphene  [4,8,61,256, 257, 258,259,260, 261,262,263, 264,265]	Sodium aluminosilicate with TiO <sub>2</sub> and CaO	Sphene CaTiSiO <sub>5</sub> Pyrochlore Ca(Re,U)Ti <sub>2</sub> O <sub>7</sub> Zirconolite CaZrTi <sub>2</sub> O <sub>7</sub> Perovskite (Ca,Re,U,Sr)TiO <sub>3</sub> Anorthite CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	Sphene and Synroc crystalline ceramic forms, mainly zirconolite, can also be formulated. Formation at 1300-1500°C. Actinides and REEs, and Sr are in zirconolite; Cs and the remaining Sr into the vitreous phase; CCIM and cool, press and sinter,
Alkali titanium silicate  [4,8,61,266]	Sodium Titanium silicates	Corundum Al <sub>2</sub> O <sub>3</sub> Cristobalite SiO <sub>2</sub> Albite NaAlSi <sub>3</sub> O <sub>8</sub> Zirconolite CaZrTi <sub>2</sub> O <sub>7</sub> Perovskite (Ca,Re,U,Sr)TiO <sub>3</sub> Zircon ZrSiO <sub>4</sub>	Formed by HIPing calcine (70 wt%) with Si, Ti, Al metal and alkali oxides; for high Zr containing Idaho National Laboratory wastes.
Barium titanium silicate Fresnoite  [4,8,61, 256]	Barium silicates with TiO <sub>2</sub>	Fresnoite, Ba <sub>2</sub> TiSi <sub>2</sub> O <sub>8</sub> Ba priderite BaFe <sub>2</sub> Ti <sub>6</sub> O <sub>16</sub> Pyrochlore RE <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub> Scheelite BaMoO <sub>4</sub>	Form at 1200°C. Fresnoite hosts Ba and Sr, Priderite hosts Ba, pyrochlore hosts RE, actinides, RE and Sr. Cs remains in the glassy phase. Glass is 50% and crystalline phases are 50%.
<b>Silicate Based</b>			
Basalt  [4,8,61, 256,267, 268]	complex natural oxide based on Si, Ca, Mg, Fe, Al and Ti	For Purex wastes: augite (Ca, Mg, Fe) <sub>2</sub> Si <sub>2</sub> O <sub>6</sub> powellite (Ca, Sr) MoO <sub>4</sub> spinel (NiFe <sub>2</sub> O <sub>4</sub> ).	Glasses melt in the range 1300-1400°C. Crystallization is carried out at temperature ranges 670-700°C and 900-950°C. The chemical durability superior to that of borosilicate glasses; JHM, CCIM
Iron Enriched Basalt (IEB)  [4,8,61, 256]	Alumino-silicate glass	iron spinel; feldspars NaAlSi <sub>3</sub> O <sub>8</sub> to CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ; augite (Ca,Mg, Fe) <sub>2</sub> Si <sub>2</sub> O <sub>6</sub> ; fluoroapatite, Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F; zircon, ZrSiO <sub>4</sub> ; fluorite CaF <sub>2</sub> ; cristobalite SiO <sub>2</sub> ; hematite, Fe <sub>2</sub> O <sub>3</sub> , mullite Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub>	Applications to commercial and defense wastes, including decontamination of Three Mile Island containment water together with core debris; Melt at 1400-1500°C and controlled cooling after casting the glass into containers; JHM, CCIM; arc melting

<b>Name</b>	<b>Glass Phase</b>	<b>Crystalline Phase(s)</b>	<b>Comments</b>
Iron Enriched Basalt (IEB) with TiO <sub>2</sub> and ZrO <sub>2</sub> [4,8,61,256]	Aluminosilicate glass	Same as above plus: zirconolite pseudobrookite Fe <sub>2</sub> TiO <sub>5</sub> chevkinite Ce <sub>4</sub> Fe <sub>2</sub> Ti <sub>3</sub> Si <sub>4</sub> O <sub>22</sub>	Cast glasses crystallized by holding at 1200°C for 16 h; Ti phases retain the actinides; JHM, CCIM; arc melting
Magnesium aluminosilicate (MAS) [4,8]	Magnesium aluminosilicate	Enstatite MgSiO <sub>3</sub> Indialite/Corderite Mg <sub>2</sub> Al <sub>4</sub> Si <sub>5</sub> O <sub>18</sub>	Used as an encapsulant for Zr alloy cladding wastes; accommodates 20% ZrO <sub>2</sub> ; press and sinter
<b>Phosphate Based</b>			
Apatite/monazite glass ceramics [269,270,271]	Calcium phosphate	Apatite Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (F,Cl) Monazite (Ce,U)PO <sub>4</sub>	Apatite hosts Ca,P,F, Cl, S, Sr, Cs, As, Pb, Ba, Hg, Cd, Cr, U, and Ce, Melted at 1400°C, crystallized at 1150°C and allowed to furnace cool; investigated primarily for phosphate rich or fluoride rich waste streams including Idaho National Laboratory CaF <sub>2</sub> wastes; JHM, AJHM, CCIM.

Table 7. Attributes of Homogeneous and Multiphase Ceramic (Mineral) Waste Forms







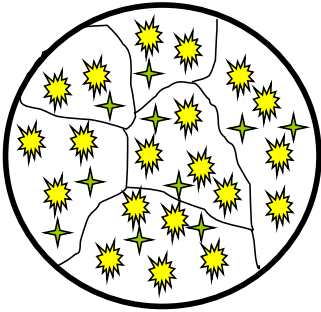
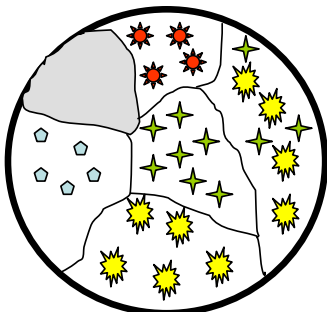
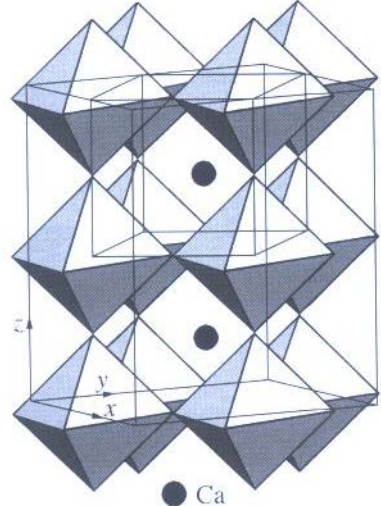
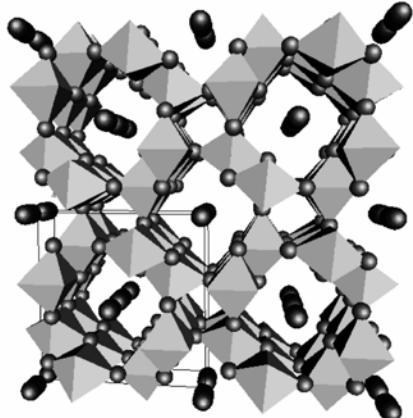
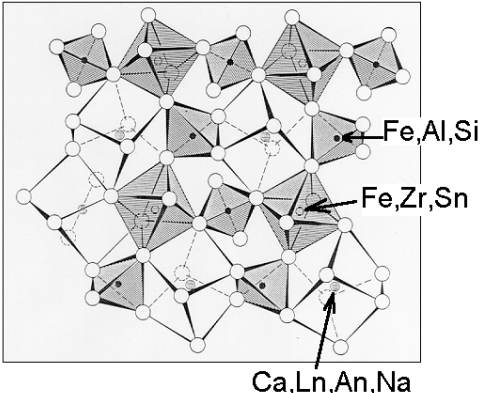
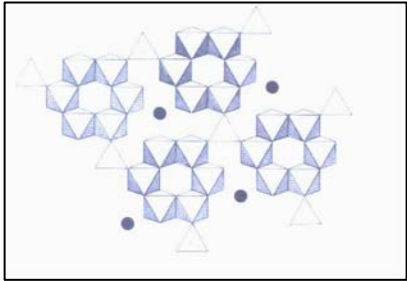
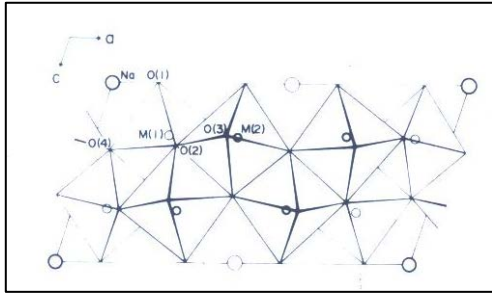
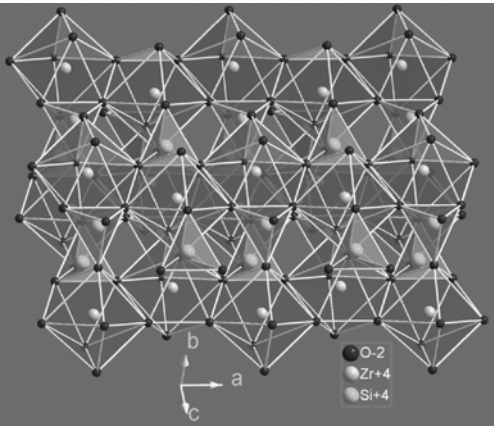
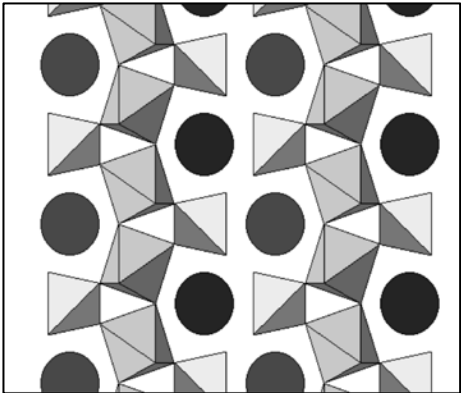
Waste Form(s)	Single Phase Oxides/Minerals/Metals (granular or monolithic)	Multiphase Oxides/Minerals/Metals (granular or monolithic)
Description	Individual phases contains one radionuclide or hazardous species or a solid solution, i.e. $\text{UO}_2\text{-ThO}_2$ (shown).	Individual phases contain different or multiple radioactive or hazardous species (see solid solution indicated between $\text{UO}_2\text{-ThO}_2$ ). Some phases do not incorporate radionuclides or hazardous species at all.
Radionuclide Immobilization Mechanism	Chemical Incorporation	Chemical Incorporation
<p><b>Key</b></p>  <p>phase or binder without radionuclides</p> <p>      </p> <p>Cs U Tc Pu xl.</p>		
Waste Loading(s)/Durability	<p>a. high waste loading for single radionuclide or hazardous species</p> <p>b. good overall durability</p> <p>c. easy to model species released from a single phase</p> <p>d. may require precalcining for certain technologies to work efficiently</p>	<p>a. high waste loadings</p> <p>b. superior overall durability</p> <p>c. difficult to model durability of species released from multiple phases and grain boundaries</p> <p>d. need to tailor for species partitioning amongst phases</p> <p>e. need to determine species partitioning and source terms from each phase</p> <p>f. may form an intergranular glassy phase that sequesters species of concern</p> <p>e. may require precalcining for certain processes to work efficiently</p>
Immobilization Technologies	<p>Hot Isostatic Pressing (HIPing &gt;40 wt% crystals)</p> <p>Hot Uniaxial Pressing (HUPing &gt;90 wt% crystals)</p> <p>Press and sinter (&gt; 90 wt% crystals)</p> <p>Fluidized Bed Steam Reforming (&gt;90 wt% crystals)</p>	

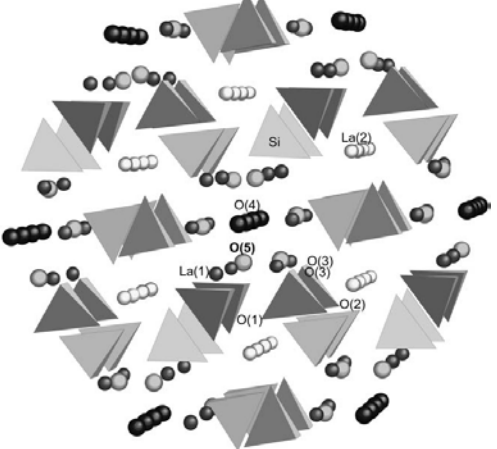
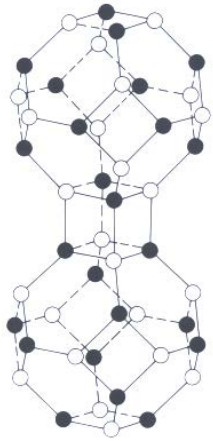
Table 8. Examples of Single and Multiple Crystalline Ceramic (Mineral) Waste Forms (adapted from Reference 11)

Crystalline Ceramic Phase	Comments	Structure	
SIMPLE OXIDES			
XO <sub>2</sub> Oxides [272,273,274,275]	ZrO <sub>2</sub> , UO <sub>2</sub> , ThO <sub>2</sub> ,HfO <sub>2</sub> , PuO <sub>2</sub> have the simple fluorite CaF <sub>2</sub> cubic Structure; make by HIP, HUP, press and sinter, melt and crystallize.	<div><div>Cubic Zirconia, 1C</div><div>Murataite, 3C</div><div>Pyrochlore, 2C</div><div><div><div>Zr<sup>4+</sup></div><div>Y<sup>3+</sup></div><div>Ti<sup>4+</sup></div><div>Zn<sup>2+</sup></div><div>Gd<sup>3+</sup></div><div>Fe<sup>3+</sup></div><div>O<sup>2-</sup></div></div><div><div>b</div><div>a</div><div>c</div></div></div></div> <div>Projection along [111] direction for zirconia, pyrochlore, and murataite structures [from 279]</div>	
COMPLEX OXIDES			
Pyrochlore [276, 277, 278, 279]	A derivative of the fluorite structure type, A <sub>2</sub> B <sub>2</sub> O <sub>7</sub> , where A-site contains large cations (Na, Ca, U, Th, Y and lanthanides) and the B-site contains smaller, higher valence cations (Nb, Ta, Ti, Zr, Fe <sup>3+</sup> ).		
Murataite [3,7,280,281, 282, 283,284,285,286, 287, 288]	Also a derivative of the isometric fluorite structure A <sub>6</sub> B <sub>12</sub> C <sub>5</sub> TX <sub>40-x</sub> . with multiple units of the fluorite unit cell; hosts U, Pu, Cm, and RE's including Gd a neutron absorber. Forms in solid solution with pyrochlore.		
Zirconolite [289; 290, 291, 292,293, 294]	Monoclinic CaZrTi <sub>2</sub> O <sub>7</sub> , has a fluorite-derived structure closely related to pyrochlore, where Pu, U, Gd and Hf may be accommodated on the Ca/Zr-sites, as in the case of Ca(Zr,Pu)Ti <sub>2</sub> O <sub>7</sub>	<div><div><div><div>Ca<sup>2+</sup></div><div>Zr<sup>4+</sup></div></div><div><div><div>c</div><div>a</div><div>b</div></div><div><div>Ca/Zr layer (CaO<sub>6</sub>, ZrO<sub>7</sub>)</div><div>Ti layer (TiO<sub>6</sub>, TiO<sub>5</sub>)</div><div>Ti(2)</div></div></div></div><div>[from 7]</div></div>	

Crystalline Ceramic Phase	Comments	Structure
Perovskite [291, 295]	<p><math>\text{CaTiO}_3</math> has a wide range of compositions as stable solid-solutions; orthorhombic; consists of a 3-dimensional network of corner-sharing <math>\text{TiO}_6</math> octahedra, with Ca occupying the large void spaces between the octahedra (the corner-sharing octahedra are located on the eight corners of a slightly distorted cube). Plutonium, other actinides, and rare-earth elements can occupy the Ca site in the structure, as in <math>(\text{Ca,Pu})\text{TiO}_3</math>. The octahedra can also tilt to accommodate larger cations in the Ca site [from 296]</p>	 <p>[from 296]</p>
Ba-Hollandite [297, 298]	<p><math>\text{Ba}_{1.2}(\text{Al,Ti})_8\text{O}_{16}</math> tunnels between <math>\text{TiO}_6</math> octahedra accommodate <math>^{133}\text{Ba}</math>, <math>^{137}\text{Cs}</math> and <math>^{90}\text{Sr}</math>.</p>	

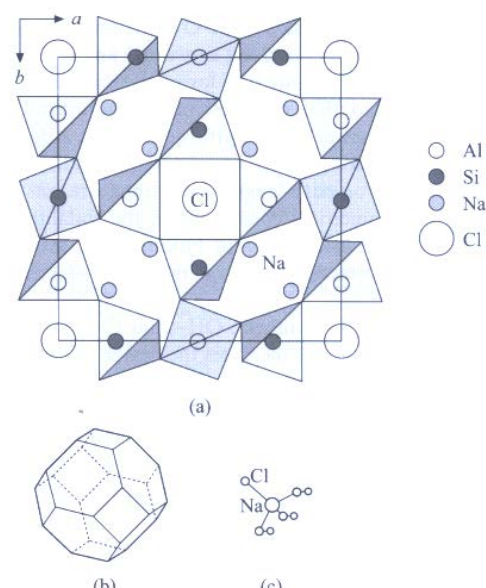
Crystalline Ceramic Phase	Comments	Structure
Ferrite garnet [278]	$^{[8]}A_3^{[6]}B_2[TiO_4]_3$ , e.g. $^{[8]}(Ca,Gd, \text{actinides})^{[6]}Fe_2^{[4]}Fe_3O_{12}$	
Garnet [299, 300, 301, 302]	$A_3B_2(XO_4)_3$ ; distorted cubic structure; $BO_6$ octahedra and $XO_4$ tetrahedra establish a framework structure alternately sharing corners; A and B sites can host actinides, RE's, and $X = Si^{4+}, Fe^{3+}, Al^{3+}, Ga^{3+}, Ge^{4+}$ and $V^{5+}$ making silicate, ferrite, aluminate, gallate, germinate, and vanadate garnets	
Crichtonite [303]	$(Sr,La,Ce,Y)(Ti,Fe^{3+},Mn,Mg, Zn, Cr, Al, Zr, Hf, U, V, Nb, Sn, Cu, Ni)_{21}O_{38}$	 <p>Sr, La, Ce, Y positions are indicated by the solid circles. Other cations are in the octahedral positions. [from 304]</p>
Freudenbergite [305]	$Na_2Al_2(Ti,Fe)_6O_{16}$ a spinel based phase suitable for incorporating Al rich wastes from Al fuel cladding/decladding. The A site can accommodate Na,K while the different octahedral sites can accommodate Mg, Co, Ni, Zn, Al, $Ti^{3+}$ , Cr, Fe, Ga, Si and Nb.	 <p>[from 306]</p>

Crystalline Ceramic Phase	Comments	Structure
<b>SIMPLE SILICATES</b>		
Zircon/Thorite [307, 308]	$\text{ZrSiO}_4/\text{ThSiO}_4$ ; zircon is an extremely durable mineral that is commonly used for U/Pb age-dating, as high uranium concentrations (up to 20,000 ppm) may be present; the $\text{PuSiO}_4$ end member is known and Ce, Hf and Gd have been found to substitute for Zr.	
Titanite (sphene) [256, 309]	$\text{CaTiSiO}_5$ can sequester cations such as Ba, Sr, and fission product oxides (~15 wt%), U, Cr, and Ni in the Ca sites (dark circles). Tetrahedra are Si and octahedral are Ti.	

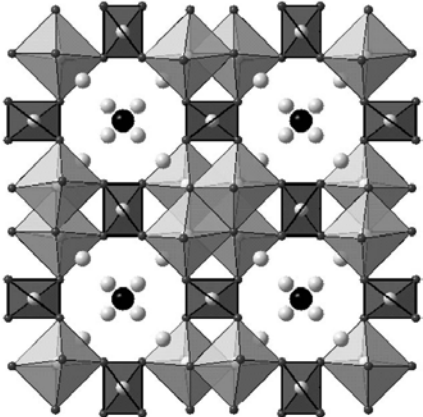
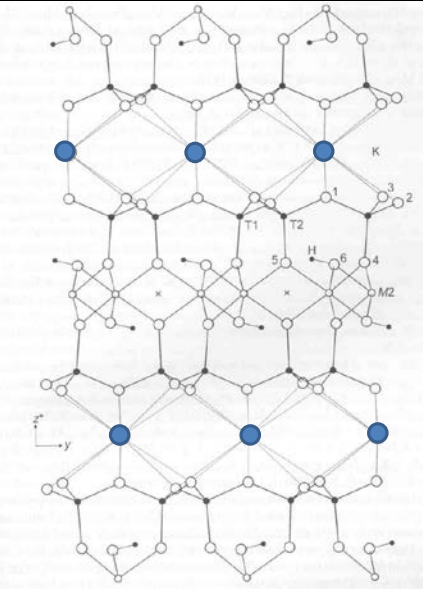
Crystalline Ceramic Phase	Comments	Structure
<p>Britholite (silicate apatite)</p> <p>Also known as oxy-apatites in the literature.</p> <p>[54,82,87,310,311,312,313]</p>	<p><math>(\text{REE}, \text{Ca})_5(\text{SiO}_4, \text{PO}_4)_3(\text{OH}, \text{F})</math>; i.e. <math>\text{Ca}_2\text{Nd}_8(\text{SiO}_4)_6\text{O}_2</math>, <math>\text{Ca}_2\text{La}_8(\text{SiO}_4)_6\text{O}_2</math>; based on ionic radii of <math>\text{Nd}^{3+}</math>, <math>\text{La}^{3+}</math>, and <math>\text{Pu}^{3+}</math>, an extensive range of solubility for <math>\text{Pu}^{3+}</math> substitution for the Nd or La, particularly on the 6h site, is expected. Since there is an extensive range in the Ca/RE ratio in these silicate apatites, a fair amount of <math>\text{Pu}^{4+}</math> substitution may be possible; <math>\text{La}^{3+}</math> through <math>\text{Lu}^{3+}</math> can substitute for <math>\text{Ca}^{2+}</math> and form oxyapatites, <math>\text{RE}_{4.67}\square_{0.33}[\text{SiO}_4]_3\text{O}</math>; can also accommodate Sr and Cs, Th, U, Np.</p>	 <p>[from 314]</p>
<b>FRAMEWORK SILICATES</b>		
<p>Zeolites [315, 316, 317, 318, 319,320]</p>	<p><math>(\text{X}_{x/n}[(\text{AlO}_2)_x (\text{SiO}_2)_y]</math> where X is the charge balancing counter-ion, n is the charge of the counter-ion, x is the number of charge-deficient alumina sites, and y is the number of charge-neutral silica sites; characterized by internal voids, channels, pores, and/or cavities of well-defined size in the nanometer range, <math>\approx 4\text{-}13 \text{ \AA}</math>; channels and/or cavities may be occupied by charge-compensating ions and water molecules. Zeolites like Ag-Mordenite selectively sorbs <math>\text{I}_2</math> (<math>^{129}\text{I}</math>); certain zeolites can be converted to condensed oxide ceramics by heating. This process is particularly attractive for waste form fabrication because capture and storage is performed with minimal steps.</p>	 <p>Structure of Zeolite-A [321] showing alternate Al and Si atom ordering but omitting the tetrahedral oxygens around each Al and Si.</p>

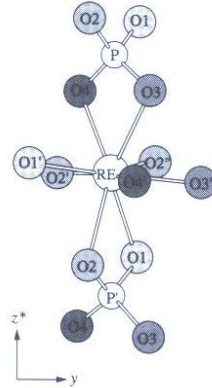
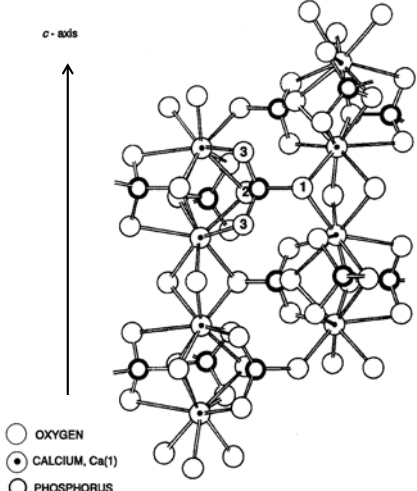


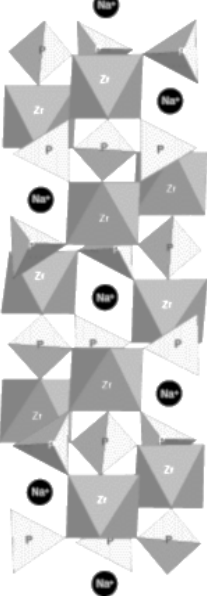
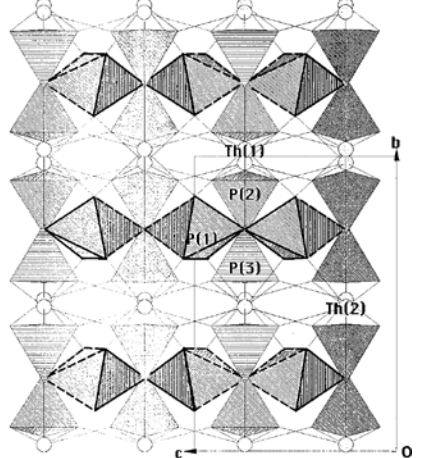


Crystalline Ceramic Phase	Comments	Structure
Sodalite Group (name of mineral changes with anions sequestered in cage structure)  [49, 338, 344, 346, 342, 343,344,345,346, 347, 348, 349, 350,351]	Sodalite $\text{Na}_8\text{Cl}_2\text{Al}_6\text{Si}_6\text{O}_{24}$ also written as $(\text{Na},\text{K})_6[\text{Al}_6\text{Si}_6\text{O}_{24}]\bullet(2\text{NaCl})$ to demonstrate that 2Cl and associated Na atoms are in a cage structure defined by the aluminosilicate tetrahedra of six adjoining $\text{NaAlSiO}_4$ ; a naturally occurring feldspathoid mineral; incorporate the alkali, alkaline earths, rare earth elements, halide fission products, and trace quantities of U and Pu (sodalite was and is being investigated as a durable host for the waste generated from electro-refining operations deployed for the reprocessing of metal fuel); minor phases in High Level Waste (HLW) supercalcine waste forms* where they retained Cs, Sr, and Mo, e.g. $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{NaMoO}_4)_2$ ; sodalite structures are known to retain B, Ge,I,Br, and Re in the cage like structures	 <p>Structure of Sodalite showing (a) two-dimensional projection of the (b) three- dimensional structure and (c) the four fold ionic coordination of the Na site to the <math>\text{Cl}^-</math> ion and three framework oxygen bonds. [352]</p>
	Nosean, $(\text{Na},\text{K})_6[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{Na}_2\text{SO}_4)$ , silica “stuffed derivative” sodalite cage type structure host mineral for sulfate or sulfide species.	
	Hauyne, $(\text{Na})_6[\text{Al}_6\text{Si}_6\text{O}_{24}]((\text{Ca},\text{Na})\text{SO}_4)_{1-2}$ sodalite family; can accommodate either $\text{Na}_2\text{SO}_4$ or $\text{CaSO}_4$	
	Helvite $(\text{Mn}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S})$ : Be can be substituted in place of Al and $\text{S}_2$ in the cage structure along with Fe, Mn, and Zn	
	Danalite $(\text{Fe}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S})$	
	Genthelvite $(\text{Zn}_4[\text{Be}_3\text{Si}_3\text{O}_{12}]\text{S})$	
	Lazurite, $(\text{Ca},\text{Na})_6[\text{Al}_6\text{Si}_6\text{O}_{24}]((\text{Ca},\text{Na})\text{S},\text{SO}_4,\text{Cl})_x$ ; can accommodate either $\text{SO}_4$ or $\text{S}_2$ ,Ca or Na and Cl	
Cancrinite [353]	$(\text{Na},\text{Ca},\text{K})_6[\text{Al}_6\text{Si}_6\text{O}_{24}]((\text{Na},\text{Ca},\text{K})_2\text{CO}_3)_{1.6}\bullet 2.1\text{H}_2\text{O}$ Only found in hydroceramic waste forms	

\* Supercalcines were the high temperature silicate based “natural mineral” assemblages proposed for HLW waste stabilization in the United States (1973-1985).

Crystalline Ceramic Phase	Comments	Structure
Crystalline SilicoTitanate (CST) [331,354, 355,356,357, 358]	[(Ca,Na,K,Ba)AlSiO <sub>4</sub> incorporates Ca, Na, K, Ba, Cs, and Sr	 <p>Crystal structure of Cs exchanged Nb–titanium silicate. The dark and light grey spheres represent Cs<sup>+</sup> cations and water molecules, respectively.[from 359]</p>
Micas (Dehydroxylated) [360,361,362]	<p>The following dehydroxylated micas have been synthesized phase pure: LiAl<sub>3</sub>Si<sub>3</sub>O<sub>11</sub>, NaAl<sub>3</sub>Si<sub>3</sub>O<sub>11</sub>, KAl<sub>3</sub>Si<sub>3</sub>O<sub>11</sub>, RbAl<sub>3</sub>Si<sub>3</sub>O<sub>11</sub>, CsAl<sub>3</sub>Si<sub>3</sub>O<sub>11</sub>, TlAl<sub>3</sub>Si<sub>3</sub>O<sub>11</sub>, Ca<sub>0.5</sub>□<sub>0.5</sub>Al<sub>3</sub>Si<sub>3</sub>O<sub>11</sub>, Sr<sub>0.5</sub>□<sub>0.5</sub>Al<sub>3</sub>Si<sub>3</sub>O<sub>11</sub>, Ba<sub>0.5</sub>□<sub>0.5</sub>Al<sub>3</sub>Si<sub>3</sub>O<sub>11</sub>, La<sub>0.33</sub>□<sub>0.66</sub>Al<sub>3</sub>Si<sub>3</sub>O<sub>11</sub>. In the Cs-mica up to 30 wt% Cs<sub>2</sub>O can be accommodated, in the Rb-mica up to 22 wt% Rb<sub>2</sub>O can be accommodated, and in the Ba-mica up to 19 wt% BaO can be accommodated. Mg, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mn, Li, Cr, Ti and V can substitute for VI-fold coordinated Al<sup>3+</sup>.</p>	 <p>[from 363]</p>

Crystalline Ceramic Phase	Comments	Structure
<b>PHOSPHATES</b>		
Monazite [213,269, 364,365,366,367, 368]	CePO <sub>4</sub> or LaPO <sub>4</sub> ; very corrosion resistant and can incorporate a large range of radionuclides including actinides and toxic metals into its structure; it has been proposed as a potential host phase for excess weapons plutonium and as a host phase for radionuclides and toxic metals in glass-ceramic waste forms for low-level and hazardous wastes.	 <p>Alternating chains of PO<sub>4</sub> tetrahedra and REO<sub>9</sub> polyhedra. [from 369]</p>
Xenotime [213]	YPO <sub>4</sub>	
Apatite [10,54,45, 213,312,313, 269, 368,370, 371,372, 373,374, 375,376,377, 378,379]	Ca <sub>4-x</sub> RE <sub>6+x</sub> (SiO <sub>4</sub> ) <sub>6-y</sub> (PO <sub>4</sub> ) <sub>y</sub> (O,F) <sub>2</sub> ; actinide-host phases in HLW glass, glass-ceramic waste forms, ceramic waste forms and cement; actinides can readily substitute for the rare-earth elements in the crystal structure, as in Ca <sub>2</sub> (Nd,Cm,Pu) <sub>8</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub> , and fission products are also readily incorporated. However, the solubility for tetravalent Pu may be limited without other charge compensating substitutions; has been proposed as a potential host phase for Pu and high-level actinide wastes.	 <p>[from 380]</p>

Crystalline Ceramic Phase	Comments	Structure
Sodium zirconium phosphate (NZP) [21381, 382,383, 384,386]	<p><math>\text{NaZr}_2(\text{PO}_4)_3</math>; structure can incorporate a complex variety of cations, including plutonium; three-dimensional network of corner-sharing <math>\text{ZrO}_6</math> octahedra and <math>\text{PO}_4</math> tetrahedra in which plutonium can substitute for Zr, as in <math>\text{Na}(\text{Zr,Pu})_2(\text{PO}_4)_3</math>. Complete substitution of <math>\text{Pu}^{4+}</math> for Zr has been demonstrated in NZP. Cs and Sr can substitute for Na while fission products and actinides substitute for Zr in octahedral positions. P is tetrahedral.</p>	 <p>[from 384]</p>
Thorium phosphate Diphosphate (TPD) [213,387, 388, 389]	<p><math>\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7</math>; a unique compound for the immobilization of plutonium and uranium; partial substitution of Pu for Th has been demonstrated (up to 0.4 mole fraction), complete substitution is not possible.</p>	 <p>[from 390]</p>

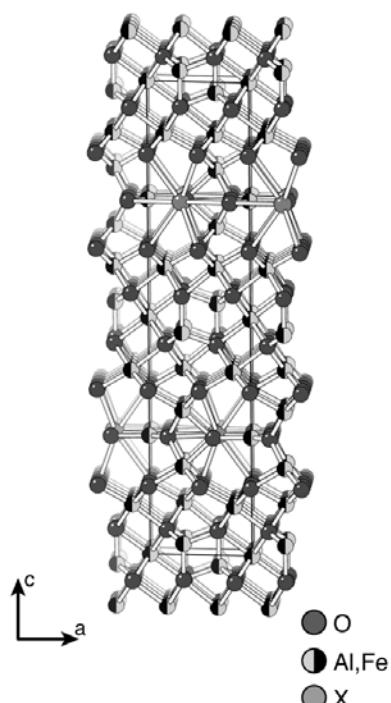
Crystalline Ceramic Phase	Comments	Structure
<b>ALUMINATES</b>		
Magnetoplumbites [22, 62, 391,392, 393, 394]	Nominally $X(\text{Al,Fe})_{12}\text{O}_{19}$ where $X = \text{Sr, Ba, (Cs}_{0.5} + \text{La}_{0.5})$ and $(\text{Na}_{0.5} + \text{La}_{0.5})$ . The X site is XII-fold coordinated and both $\text{Cs}^+/\text{Ba}^{2+}-\text{Fe}^{3+}/\text{Fe}^{2+}$ or $\text{Cs}^+/\text{Ba}^{2+}-\text{Ti}^{4+}/\text{Ti}^{3+}$ type substitutions can occur. Accommodating structures because they are composed of spinel blocks with both IV-fold and VI-fold coordinated sites for multivalent cations and interspinel layers which have unusual V-fold sites for small cations. The interspinel layers also accommodate large cations of 1.15-1.84 Å, replacing oxygen in XII-fold sites in the anion close packed structure. The large ions may be monovalent, divalent, or trivalent with balancing charge substitutions either in the interspinel layer ( $\text{Na}_{0.5} + \text{La}_{0.5}$ ) or between the interspinel layer and the spinel blocks ( $\text{Cs}^+/\text{Ba}^{2+}-\text{Fe}^{3+}/\text{Fe}^{2+}$ or $\text{Cs}^+/\text{Ba}^{2+}-\text{Ti}^{4+}/\text{Ti}^{3+}$ ).	

Table 9. Attributes and Examples of Encapsulant and Embedded Waste Forms (Cements, Geopolymers, Ceramicrete, Hydroceramics, and Bitumen)

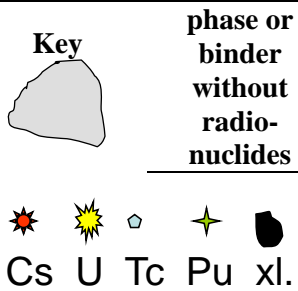
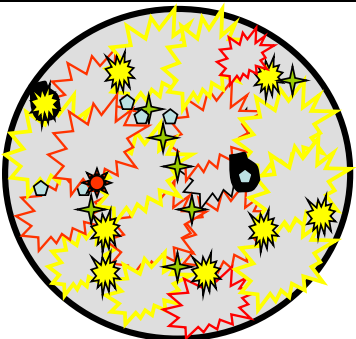
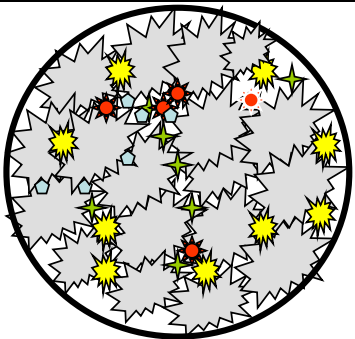
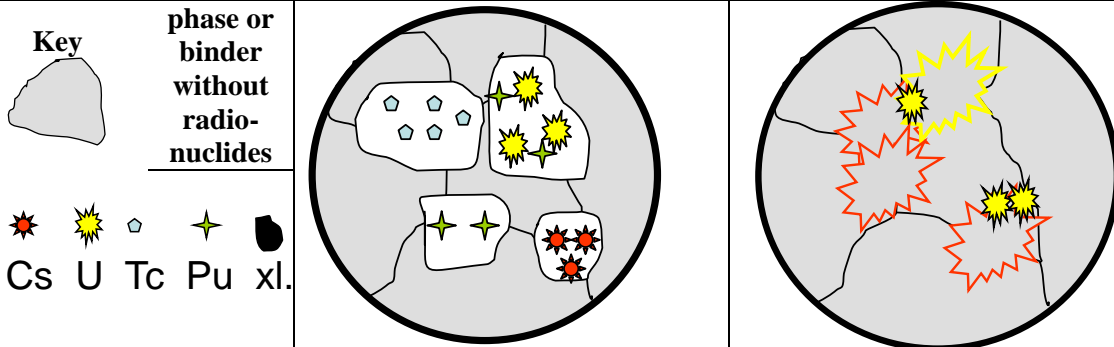
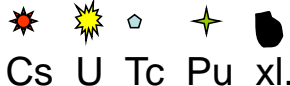
Waste Form(s)	Encapsulated Waste Forms	Embedded Waste Forms
<b>Description</b>	Liquid waste is mixed with concrete or other binder – hydrated phases occur that can incorporate the radionuclides or hazardous species weakly or retain them by sorption. Example Cs and U sequestered by C-S-H hydrates and U and Tc sequestered by secondary fly ash granules. The remaining species are trapped on the grain boundaries of the interlocking C-S-H phases.	Liquid waste is mixed with concrete or other binder – primary phases and any secondary phases created by hydration (if an active mechanism) do not retain or sorb the radionuclide or hazardous species. Example shows Tc, Cs, U, and Pu all on the grain boundaries.
<b>Radionuclide Immobilization Mechanism</b>	Encapsulation and some chemical incorporation	Encapsulation and no chemical incorporation
<p><b>Key</b></p>  <p>phase or binder without radionuclides</p> <p>Cs U Tc Pu xl.</p>		
<b>Waste Loading(s)/Durability</b>	<ul style="list-style-type: none"> <li>a. low waste loadings</li> <li>b. lower overall durability</li> <li>c. difficult to model radionuclide release from hydrated secondary phases and grain boundaries</li> <li>d. easy to process – usually mix and cast</li> </ul>	<ul style="list-style-type: none"> <li>a. low waste loadings</li> <li>b. lower overall durability</li> <li>c. difficult to model radionuclide release from grain boundaries</li> <li>d. easy to process – usually mix and cast</li> <li>e. in case of bitumen must be heated to flow so embedding can occur</li> </ul>
<b>Immobilization Technologies</b>	<p>Mix and pour (cement, geopolymer, ceramicrete) Heat, mix, and pour (bitumen) Mix, pour, cure at slightly elevated temperatures (hydroceramics)</p>	



Table 10. Attributes and Examples of Composite Waste Forms

Waste Form(s)	Composite	Composite
<b>Description</b>	<b>Multiphase granular Oxides/Minerals/Metals</b> (must be monolithed due to disposal requirements if not containerized)	<b>Previously made waste forms in need of remediation</b> (monolithing agents can be numerous and include glass – see GCM's above)
<b>Radionuclide Immobilization Mechanism</b>	Chemical Incorporation and Encapsulation/Embedding	Chemical Incorporation and Encapsulation/Embedding
<p><b>Key</b></p>  <p>phase or binder without radionuclides</p> <p>   Cs U Tc Pu xl.         </p>		
<b>Waste Loading(s)/Durability</b>	<ul style="list-style-type: none"> <li>a. high waste loadings only if binder (monolithing agent) is minimized</li> <li>b. superior overall durability-double containment</li> <li>c. difficult to model radionuclide release from multiple phases</li> <li>d. need to tailor for and determine radionuclide partitioning amongst phases</li> <li>e. may require precalcining for certain processes to work efficiently</li> </ul>	<ul style="list-style-type: none"> <li>a. high waste loadings only if binder (monolithing agent) is minimized</li> <li>b. superior overall durability-double containment</li> <li>c. difficult to model radionuclide release from multiple phases</li> <li>d. need to determine radionuclide partitioning amongst phases</li> </ul>
<b>Immobilization Technologies for Matrix Phase</b>	<ul style="list-style-type: none"> <li>Mix and pour (cement, geopolymers, ceramicrete)</li> <li>Heat and pour (glass or metal)</li> <li>Heat, mix, and pour (bitumen)</li> <li>Mix, pour, cure at slightly elevated temperatures (hydroceramic)</li> </ul>	



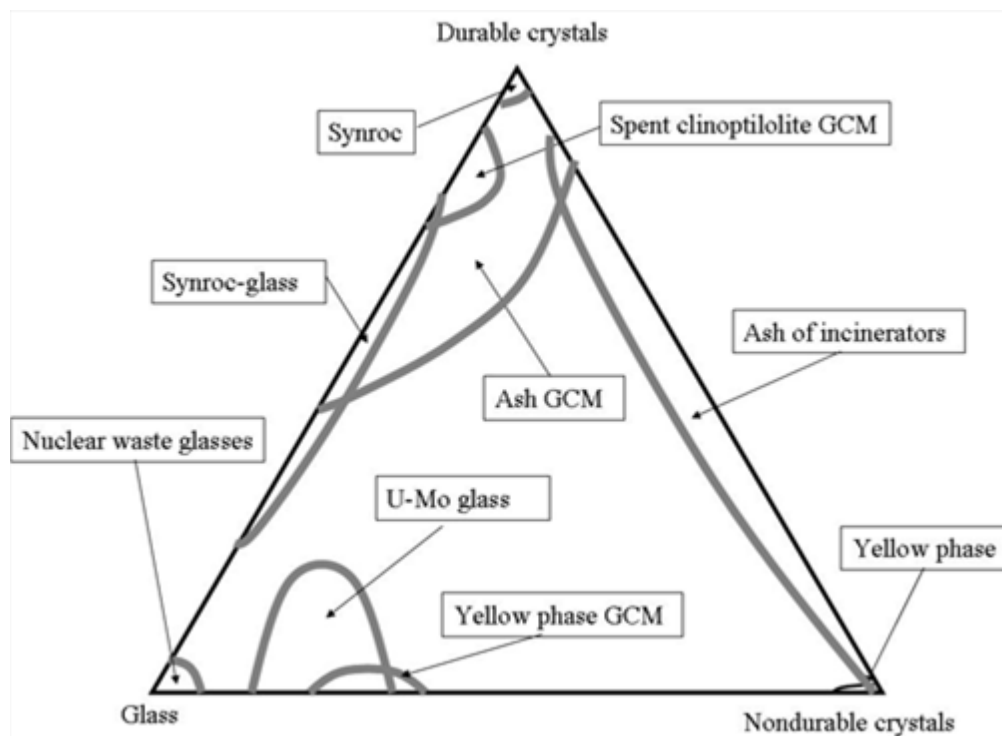


Figure 1. Current homogeneous glass formulations are limited to the lower left hand corner of this triangular diagram. If the homogeneous glasses crystallize durable crystals shown at the apex of the triangle, e.g. spinels,  $ZrO_2$ , apatite,  $TiO_2$ , etc, then waste loading can be increased and glass-composite materials (GCM's) produced by changing the melter technology (e.g. CCIM's) or invoking a different technology such as HIPing. Ceramic wasteforms are at the apex and are considered exceptionally durable wasteforms but may be more appropriate for small volume wasteforms as processing is more difficult. Some ceramic wasteform formulations can be melted in advanced melters like CCIM's and then allowed to crystallize into GCM's. While certain species such as Mo, S, and P can create non-durable secondary phases (lower right apex of the triangle), these should be avoided or macroencapsulated which moves their durability closer to the lower left apex of the triangle.[36]

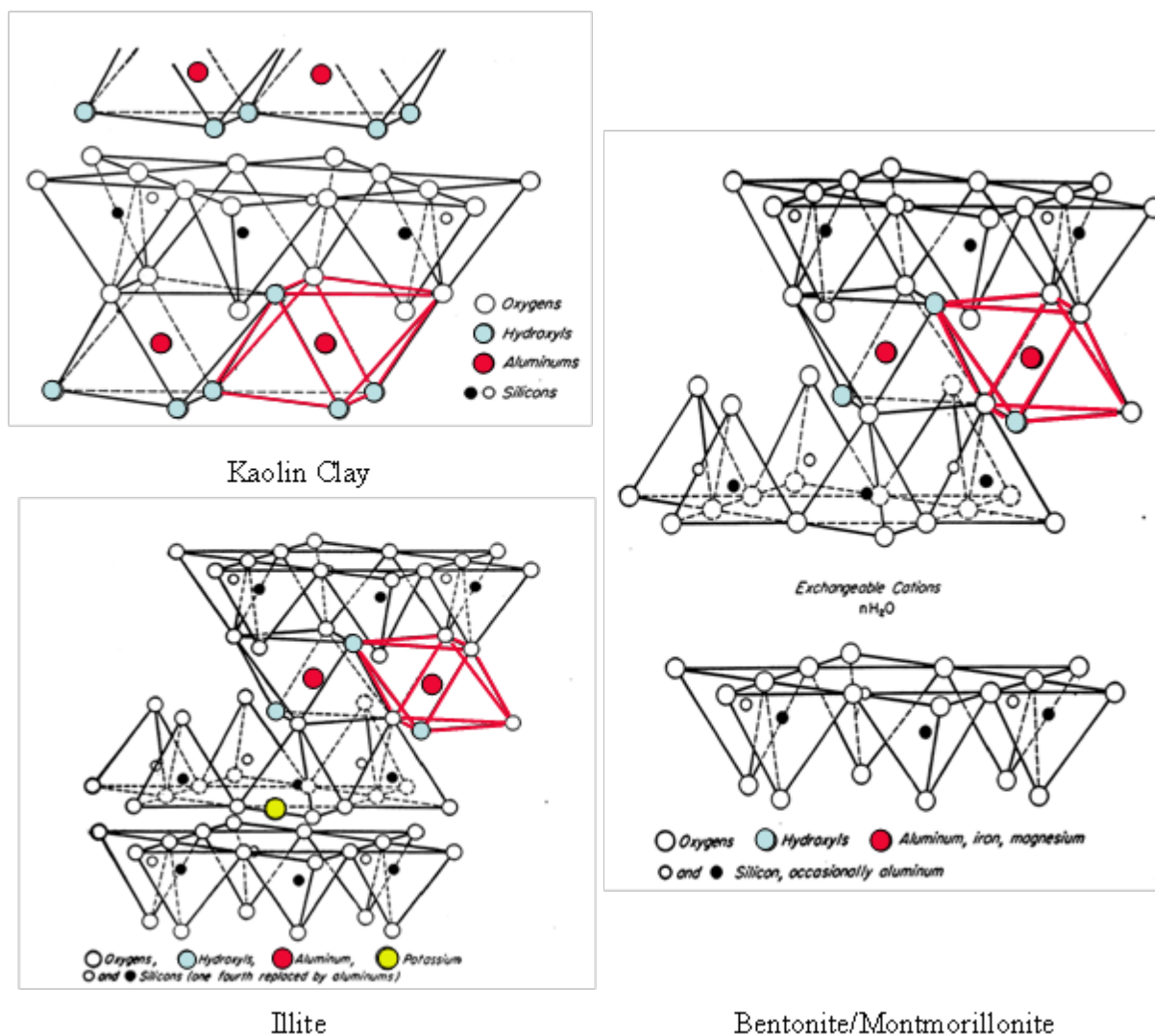


Figure 2. Atomic structures of various clays (kaolin, bentonite-montmorillonite, illite). After Grim [395,396].



(a)



(b)



(c)

Figure 3. Examples of composite wastefoms using encapsulation in cements where the cement physically surrounds the waste and the radionuclides may be immobilized by being incorporated into the cement phases. ILW in (a) is compacted ILW solids, in (b) is Magnox [Mg alloy] fuel cladding swarf and in (c) is ceramic fuel zircalloy cladding hulls.

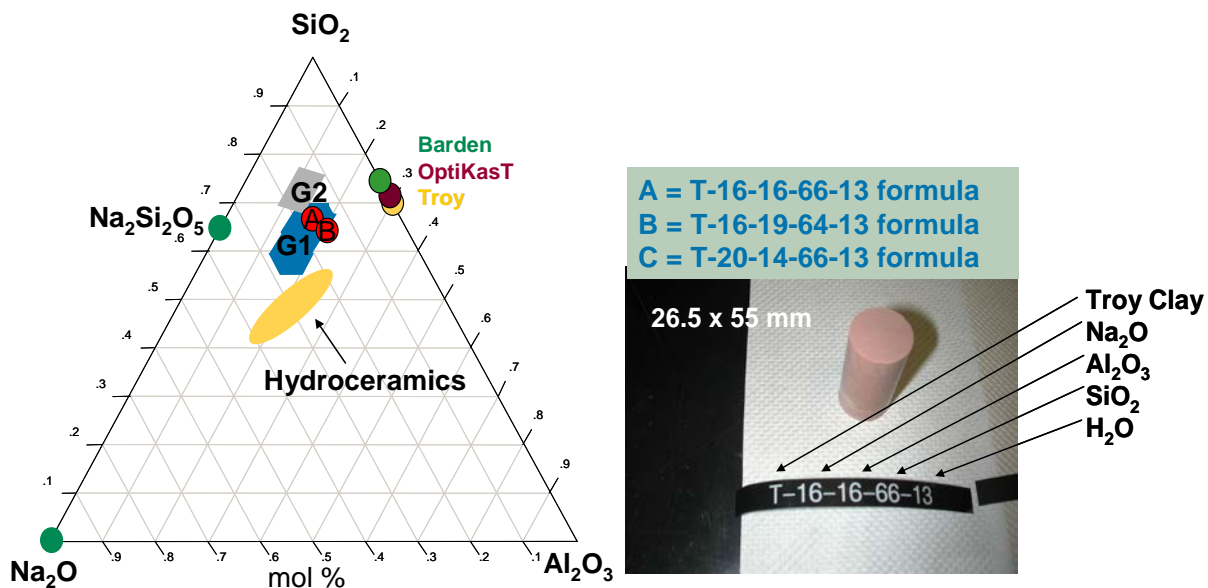


Figure 4. Formulation region for geopolymers compared to hydroceramics in the  $\text{Na}_2\text{O}$ - $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  (mol%) ternary. Note that the fourth dimension is water content and not shown on the ternary mol% diagram. The geopolymer region labeled as G1 is the target range. Optimum formulations are designated as A and B and a 1" x 2" cylindrical monolith made with composition A is shown in the photograph.

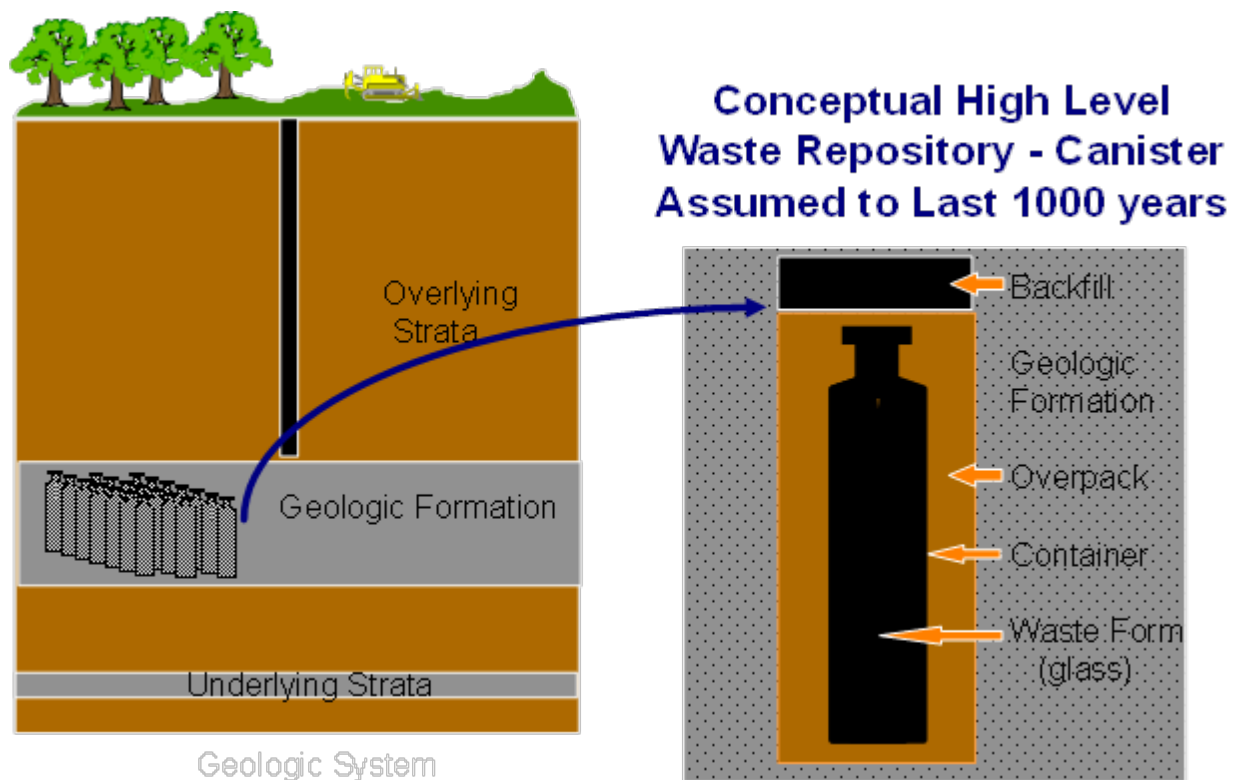


Figure 5. A generic HLW waste disposal system.

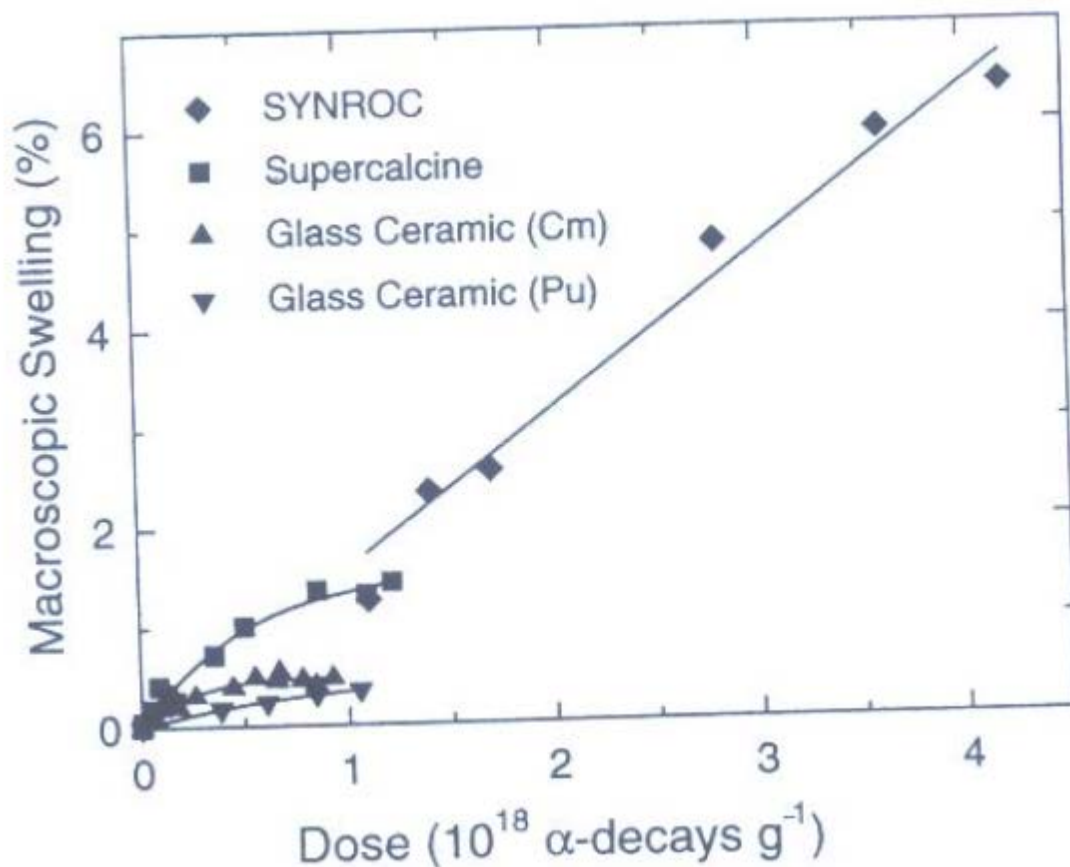
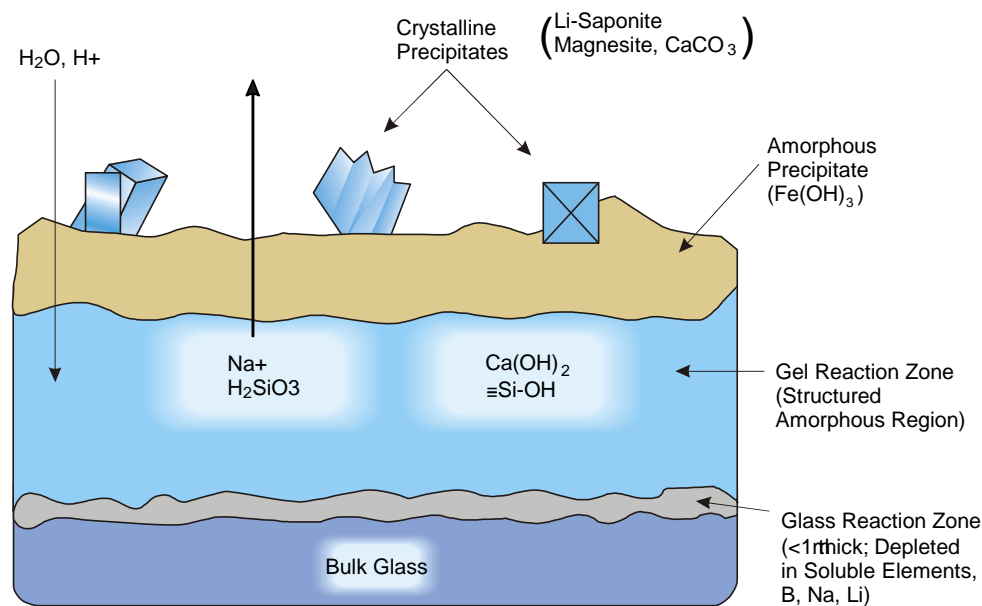
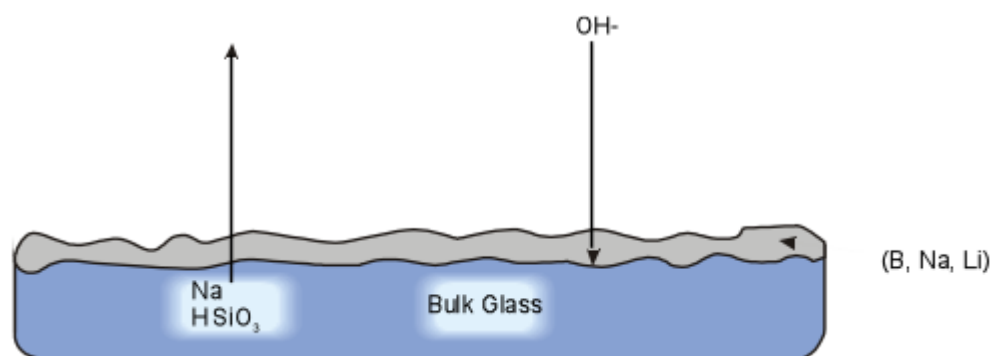


Figure 6. Macroscopic swelling in Pu-doped Synroc, Cm-doped supercalcine, and Cm-doped and Pu-doped glass-ceramics [ Reprinted with permission from “Radiation Effects in Crystalline Ceramics for the Immobilization of High-level Nuclear Waste and Plutonium” by W.J. Weber, R.C. Ewing, et. al, Journal of Materials Research, 13 (1998) MRS.



(a)



(b)

Figure 7. a Schematic diagram of glass dissolution mechanisms (ion exchange and matrix dissolution) in aqueous solution, coupled with both hydrated amorphous surface layer formation and crystallization/precipitation from solution [179,397].

b Schematic diagram of the glass dissolution mechanism known as “accelerated matrix dissolution.” In this mechanism, the excess strong base in the leachate released by the ion exchange mechanisms attacks the glass surface layers, including the gel layer, and makes the glass appear to have little or no surface layer.

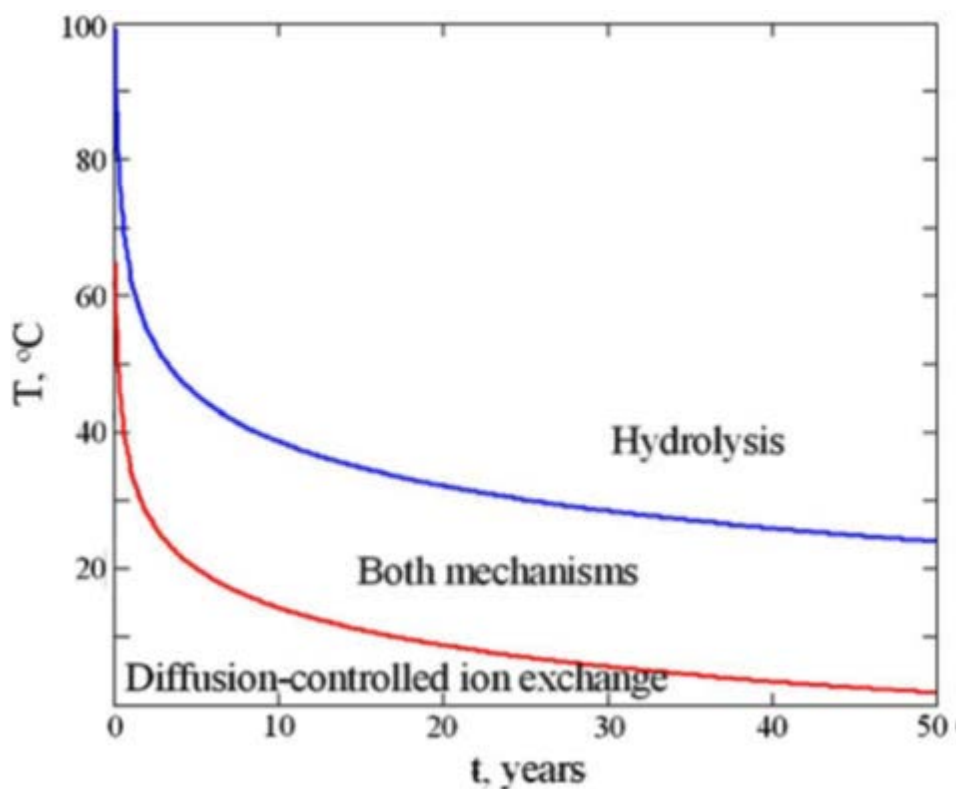


Figure 8. A temperature- time plot of the incongruent corrosion mechanisms exhibited by British Magnox-waste glass in deionized water showing that corrosion in deionized water at a constant temperature begins immediately with an instantaneous surface dissolution followed by a diffusion controlled ion exchange phase. As corrosion progresses the impact of hydrolysis becomes significant with comparable contributions from both ion exchange and hydrolytic reactions. Finally, glass corrosion in deionized water is fully controlled by hydrolysis.[36]



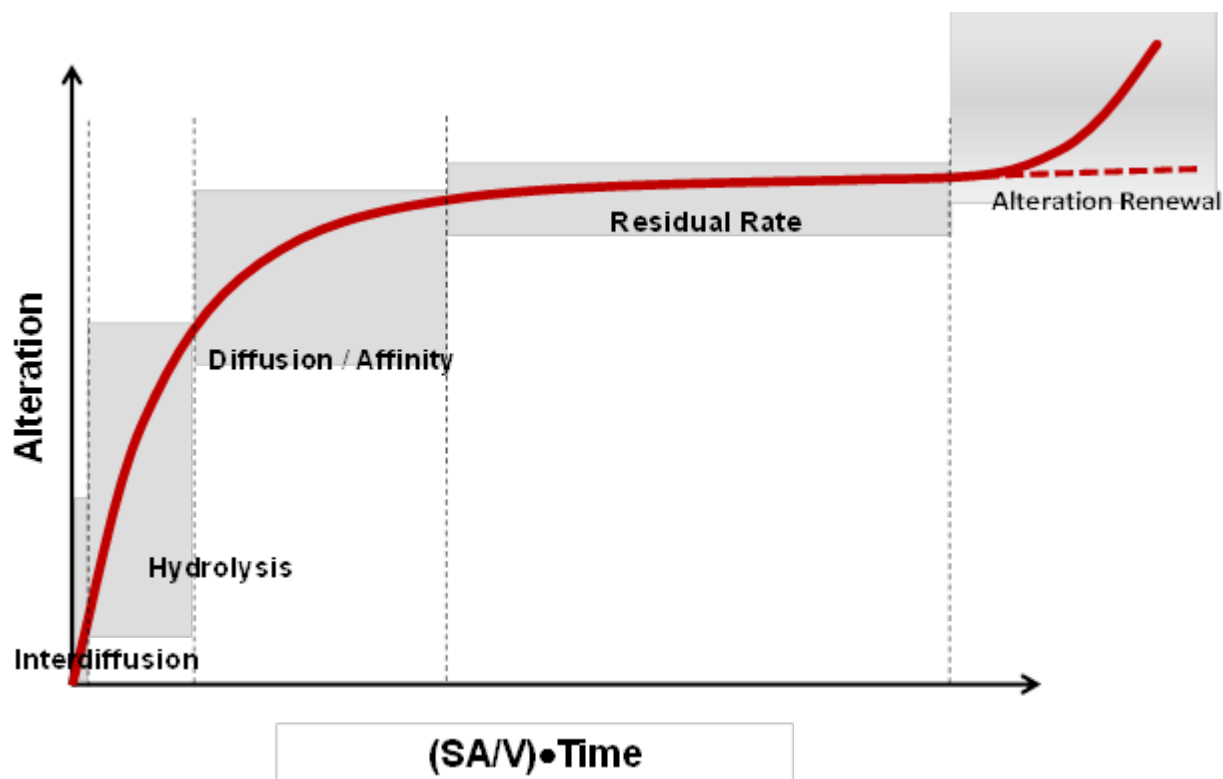


Figure 9. (a) Parabolic behavior of the diffusion profile of soluble species out of a waste glass through an increasingly thick surface layer.[159] Acceleration of glass durability tests using glass surface area (SA), leachant volume (V), and time. Acceleration appears to follow parabolic diffusion kinetics until  $SA/V$  is  $\sim 20,000\text{m}^{-1}$  when the glass dissolution mechanism appears to change reverting to a rate similar to the forward rate but likely controlled by precipitation of secondary phases.

## 7.11 References

---

1. L. P. Hatch, **"Ultimate Disposal of Radioactive Wastes,"** Am. Sci., 41, 410–21 (1953).
2. R. Roy, **"Ceramic Science of Nuclear Waste Fixation,"** Bull. Am. Ceram. Soc. 54, 459 (1975).
3. S.V. Stefanovsky, S. V. Yudintsev, R. Gieré, and G. R. Lumpkin, **"Nuclear Waste Forms,"** Geological Society of London Special Publications, v. 236, 37-63 (2004).
4. I.W. Donald, **"Waste Immobilization in Glass and Ceramic Based Hosts,"** John Wiley Ltd, West Sussex, UK, 507 pp. (2010).
5. M.I. Ojovan and W.E. Lee, **"New Developments in Glassy Nuclear Wasteforms,"** Nova Science Publishers, New York, 131 p. (2007).
6. M.I. Ojovan and W.E. Lee, **"An Introduction to Nuclear Waste Immobilization,"** Elsevier, Amsterdam, 315 p. (2005).
7. D. Caurant, P. Loiseau, and O. Majerus, V. Aubin-Chevaldonnet, I. Bardez, and A. Quintas, **"Glasses, Glass-Ceramics and Ceramics for Immobilization of Highly Radioactive Nuclear Wastes,"** Nova Science Publishers, Inc., New York, 359p. (2009).
8. I.W. Donald, B.L. Metcalfe, and R.N.J. Taylor, **"The Immobilization of High Level Radioactive Wastes Using Ceramics and Glasses,"** J. Materials Science, V. 32, 5851-5887 (1997).
9. Ewing, R. C. and W. J. Weber, **"Actinide Waste Forms and Radiation Effects, In: The Chemistry of the Actinides and Transactinide Elements,"** in vol. 6, Eds. L.R. Morss, N.M. Edelstein and J. Fuger (Springer, New York) 3813-3888 (2010).
10. M.I. Ojovan, **"Handbook of Advanced Radioactive Waste Conditioning Technologies,"** Woodhead Publishing Ltd, Oxford, 512 p. (2011).
11. National Research Council, **"Waste Forms Technology and Performance,"** National Academies Press, Washington, DC 294pp (2011).
12. International Atomic Energy Agency (IAEA), **"Radioactive Waste Management Glossary,"** IAEA, Vienna, Austria (2003).
13. International Atomic Energy Agency (IAEA), **"IAEA Safety Glossary-Version 2.0,"** IAEA, Vienna, Austria (2006).

14. C.M. Jantzen, **“Disposition of Tank 48H Organics by Fluidized Bed Steam Reforming (FBSR),”** U.S. DOE Report WSRC-TR-2003-00352 (September 18, 2003).
15. C.M. Jantzen, M.R. Williams, P.B. Burket, C.L. Crawford, and W.E. Daniel, **“Fluidized Bed Steam Reforming (FBSR) of High Level Waste (HLW) Organic and Nitrate Destruction Prior to Vitrification: Crucible Scale to Engineering Scale Demonstrations and Non-Radioactive to Radioactive Demonstration,”** WM09 (March 2009).
16. G.E. Brown, Jr., F. Farges and G. Calas, **“X-Ray Scattering and X-Ray Spectroscopy Studies of Silicate Melts,”** Structure, Dynamics and Properties of Silicate Melts, J.F. Stebbins, P.F. McMillan, and D.B. Dingwell (Eds.), Reviews in Mineralogy, V.32, 317-410 (1995).
17. C.M. Jantzen, **“Historical Development of Glass and Ceramic Waste Forms for High Level Radioactive Wastes,”** in Handbook of Advanced Radioactive Waste Conditioning Technologies, M. Ojovan (Ed.), Woodhead Publishing, Oxford, 159-172 (2011).
18. C.M. Jantzen, **“Development of Glass Matrices for HLW Radioactive Wastes,”** in Handbook of Advanced Radioactive Waste Conditioning Technologies, M. Ojovan (Ed.), Woodhead Publishing, Oxford, 230-292 (2011).
19. A.J.G. Ellison and A. Navrotsky, **“Thermochemistry and Structure of Model Waste Glass Compositions,”** Sci. Basis for Nuclear Waste Management, **XIII**, V.M. Oversby and P.W. Brown (Eds.) Materials Research Society, Pittsburgh, PA, 193-207 (1990).
20. H. Li, Y. Su, J.D. Vienna, and P. Hrma, **“Raman Spectroscopic Study - Effects of B<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and SiO<sub>2</sub> on Nepheline (NaAlSiO<sub>4</sub>) Crystallization in Simulated High Level Waste Glasses,”** Ceramic Trans. 107, 469-477 (2000).
21. W.B. White, **“Glass Structure and Glass Durability,”** in Materials Stability and Environmental Degradation, A. Barkatt, E.D. Vernik, and L.R. Smith (Eds.), MRS Symposium Proceedings V. 125, 109-114 (1988).
22. C.M. Jantzen, D.R. Clarke, P.E.D. Morgan, and A.B. Harker, **“Leaching of Polyphase Nuclear Waste Ceramics: Microstructural and Phase Characterization,”** J. Am. Ceram. Soc., 65 [6], 292-300 (1982).
23. I. Tovená, T. Advocat, D. Ghaleb, E. Vernaz, and F. Larche, **“Thermodynamic and Structural Models Compared with the Initial Dissolution Rate of SON Glass Samples,”** Sci. Basis for Nucl. Waste Mgt., **XVII**, A. Barkatt and R.A. VanKonynenburg (Eds.), Materials Research Society, Pittsburgh, PA, 595-602 (1994).

24. C.M. Jantzen, J.B. Pickett, K.G. Brown, T.B. Edwards and D.C. Beam, **“Process/Product Models for the Defense Waste Processing Facility (DWPF): Part I. Predicting Glass Durability from Composition Using a Thermodynamic Hydration Energy Reaction Model (THERMO™),”** US DOE Report WSRC-TR-93-0672, 464p. (September, 1995).
25. C.M. Jantzen, K.G. Brown, T.B. Edwards, and J.B. Pickett, U.S. Patent #5,846,278, **“Method of Determining Glass Durability (THERMO™)”** (December 8, 1998)
26. C.M. Jantzen, and K.G. Brown, **“Impact of Phase Separation on Waste Glass Durability,”** Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries, V, G. T. Chandler (Eds.), Ceramic Transactions, V. 107, 289-300 (2000).
27. C.M. Jantzen and D.F. Bickford, **“Leaching of Devitrified Glass Containing Simulated SRP Nuclear Waste,”** Sci. Basis for Nuclear Waste Management, VIII, C.M. Jantzen, J.A. Stone and R.C. Ewing (eds.), Materials Research Society, Pittsburgh, PA 135-146 (1985).
28. M.J.D. Rushton, R.W. Grimes, and S.L. Owens, **“Changes to Alkali Ion Content Adjacent to Crystal-Glass Interfaces,”** Sci. Basis for Nucl. Waste Mgt., XXXI, W.E. Lee, J.W. Roberts, N.C. Hyatt, and R.W. Grimes (Eds.), Materials Research Society, Pittsburgh, PA, 207-213 (2008).
29. M.I. Ojovan, and W.E. Lee, **“Topologically Disordered Systems at the Glass Transition,”** J. Phys.: Condens. Matter, 18, 11507-11520 (2006).
30. D.K. Peeler, **“Batch 1 Variability Study Using Twice Washed Tank 51 Sludge,”** U.S. DOE Report WSRC-RP-1045, Rev. 1 (January 1995).
31. D.K. Peeler, **“Batch 1 Variability Study Using Twice Washed Tank 51 Sludge and Frit 200,”** U.S. DOE Report WSRC-RP-96-20, Rev. 0 (1996).
32. J.R. Harbour, T.B. Edwards, and R.J. Workman, **“Summary of Results for Macrobatch 3 Variability Study,”** U.S. DOE Report WSRC-TR-2000-00351, Rev.0 (2000).
33. C.C. Herman, T.B. Edwards, and D.M. Marsh, **“Summary of Results for Expanded Macrobatch 3 Variability Study,”** U.S. DOE Report WSRC-TR-2001-00511, Rev. 0 (2001).
34. W.E. Lee, M.I. Ojovan, M.C. Stennett, and N.C. Hyatt, **“Immobilisation of Radioactive Waste in Glasses, Glass Composite Materials and Ceramics,”** Advances in Applied Ceramics, 105[1], 3-12 (2006).

35. M.T. Peters, R.C. Ewing, and C.I. Steefel, **“GNEP Waste Form Campaign Science & Technology and Modeling & Simulation Program: Roadmap With Rationale & Recommendations,”** U.S. DOE Report GNEP-M50-3040-303 (March 2008).
36. M.I. Ojovan, and W.E. Lee, **“Glassy Wasteforms for Nuclear Waste Immobilization,”** Metallurgical and Materials Transactions A, 42A, 837-851 (2011).
37. P. Loiseau, D. Caurant, O. Majerus, and N. Baffier, **“Crystallization study of (TiO<sub>2</sub>, ZrO<sub>2</sub>)-rich SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO glasses, Part I: Preparation and Characterization of Zirconolite-based Glass-ceramics, Part II: Surface and Internal Crystallization Processes Investigated by Differential Thermal Analysis (DTA),”** J. Mater. Sci., 38, 843–852 and 853–64 (2003).
38. A.R. Boccaccini, E. Bernardo, L. Blain, and D.N. Boccaccini, **“Borosilicate and Lead Silicate Glass Matrix Composites Containing Pyrochlore Phases for Nuclear Waste Encapsulation,”** J. Nucl. Mater., 327, 148-158 (2004).
39. J.M. Juoi, M.I. Ojovan, and W.E. Lee, **“Microstructure and Leaching Durability of Glass Composite Wasteforms for Spent Clinoptilolite Immobilisation,”** J. Nucl. Mater., 372, 358–66 (2008).
40. N. Henry, P. Deniard, S. Jobic, R. Brec, C. Fillet, F. Bart, A. Grandjean and O. Pinet, **“Heat Treatments Versus Microstructure in a Molybdenum-rich Borosilicate,”** J. Noncryst. Solids, 333, 199–205 (2004).
41. I.A. Sobolev, M.I. Ojovan, T.D. Scherbatova, and O.G. Batyukhnova, **“Glasses for Radioactive Waste,”** Energoatomizdat, Moscow, Russia, 1999.
42. I.A. Sobolev, S.A. Dmitriev, F.A. Lifanov, A.P. Kobelev, S.V. Stefanovsky, and M.I. Ojovan, **“Vitrification Processes for Low, Intermediate Radioactive and Mixed Wastes,”** Glass Tech., 46, 28–35 (2005).
43. D.S. Kim, J.D. Vienna, P.R. Hrma, M.J. Schweiger, J. Matyas, J.V. Crum, D.E. Smith, G.J. Sevigny, W.C. Buchmiller, J.S. Tixier, J.D. Yeager, K.B. Belew: **Development and Testing of ICV Glasses for Hanford LAW,”** US DOE Report PNNL-14351, Pacific Northwest National Laboratory, Richland, WA (2003).
44. M.J. Plodinec and J.R. Wiley, **“Evaluation of Glass as a Matrix for Solidifying Savannah River Plant Waste: Properties of Glasses Containing Li<sub>2</sub>O,”** U.S. DOE Report DP-1498, E.I. duPont de Nemours & Co., Savannah River Laboratory, Aiken, SC 29808 (February 1979).

45. A.K. De, B. Luckscheiter, W. Lutze, G. Malow, and E. Schiewer, **“Development of Glass Ceramics for the Incorporation of Fission Products,”** Ceramic Bulletin, 55, 500-503 (1976).
46. A.A. Minaev, S.N. Oziraner, and N.P. Prrochorova, **“The Use of Glass-Ceramic Materials for the Fixation of Radioactive Wastes,”** U.S. DOE Report CONF-790420, 229-232 (1979).
47. N. Ninomiya, T. Yamanaka, T. Sakane, M. Hora, S. Nakamura, and S. Kawamura, **“Diopside Glass-Ceramic Material for the Immobilization of Radioactive Wastes,”** in “Proc. Seminar on Chemistry and Process Engineering for High-Level Liquid Waste Solidification, R.Odoj and E. Merz (Eds), Julich Conference 42, vol 2, 675-693 (1981).
48. R.A. Speranzini and P.J. Hayward, **“Development of Sphene-Based Ceramics for Disposal of Some Canadian Wastes,”** Adv. Ceram. V. 8, 273-281 (1984).
49. W. Sinkler, T.P. O’Holleran, S.M. Frank, M.K. Richmann, S.G. Johnson, **“Characterization of A Glass-Bonded Ceramic Waste Form Loaded with U and Pu,”** Scientific Basis for Nuclear Waste Management, XXIII, R.W. Smith and D.W. Shoesmith (Eds.), Materials Research Society, Pittsburgh, PA, 423-429 (2000).
50. T. Moschetti, W. Sinkler, T. Disanto, M.H. Hois, A.R. Warren, D. Cummings, S.G. Johnson, K.M. Goff, K.J. Bateman, S.M. Frank, **“Characterization of a Ceramic Waste Form Encapsulating Radioactive Electrorefiner Salt,”** Scientific Basis for Nuclear Waste Management, XXIII, R.W. Smith and D.W. Shoesmith (Eds.), Materials Research Society, Pittsburgh, PA, 577-582 (2000).
51. L.R. Morss, M.L. Stanley, C.D. Tatko, W.L. Ebert, **“Corrosion of Glass Bonded Sodalite as a Function of pH and Temperature,”** Scientific Basis for Nuclear Waste Management, XXIII, R.W. Smith and D.W. Shoesmith (Eds.), Materials Research Society, Pittsburgh, PA, 733-738 (2000).
52. J.V. Crum, L.A. Turo, B.J. Riley, M. Tang, and A. Kossoy, **“Multi-Phase Glass-Ceramics as a Waste Form for Combined Fission Products: Alkalis, Alkaline Earths, Lanthanides, and Transition Metals.”** J. Am. Ceram.Soc. 95[4], 1297-303 (2012).
53. G.J. McCarthy, **“Quartz-Matrix Isolation of Radioactive Wastes,”** J. Mat. Sci. 8, 1358-59 (1973).
54. G.J. McCarthy and M.T. Davidson, **“Ceramic Nuclear Waste Forms: I. Crystal Chemistry and Phase Formation”** Bull. Am. Ceram. Soc. 54 782-786 (1975).
55. R. Roy, **“Rationale Molecular Engineering of Ceramic Materials,”** J. Am. Ceram. Soc. 60, 350-363 (1977).

56. R.O. Schoebel, "**Stabilization of High Level Waste in Ceramic Form,**" Bull. Am. Ceram. Soc, 54 [4], 459 (1975).
57. A.E. Ringwood, V.M. Oversby and S.E. Kesson, "**SYNROC: Leaching Performance and Process Technology,**" in "Proc. Seminar on Chemistry and Process Engineering for High-Level Liquid Waste Solidification, R.Odoj and E. Merz (Eds), Julich Conference 42, vol 1, 495-506 (1981).
58. A.E. Ringwood, "**Safe Disposal of High Level Nuclear Reactor Wastes: A New Strategy,**" Australian Nuclear University Press, Canberra, Australia, 1-64 (1978).
59. A.E. Ringwood, S.E. Kesson, N.G. Ware, W.O. Hibberson, and A. Major, "**The SYNROC Process: A Geochemical Approach to Nuclear Waste Immobilization,**" Geochemical Journal, 13, 141-165 (1979).
60. G.J. McCarthy, J.G. Pepin, D.E. Pfoertsch, and D.R. Clarke, "**Crystal Chemistry of the Synthetic Minerals in Current Supercalcine-Ceramics,**" U.S. DOE Report CONF-790420, 315-320 (1979).
61. W. Lutze and R.C. Ewing, "**Radioactive Waste Forms for the Future,**" North-Holland Publishers, Amsterdam, 778pp. (1988).
62. C.M. Jantzen, J. Flintoff, P.E.D. Morgan, A.B. Harker, and D.R. Clarke, "**Ceramic Nuclear Waste Forms,**" in "Proc. Seminar on Chemistry and Process Engineering for High-Level Liquid Waste Solidification, R.Odoj and E. Merz (Eds), Julich Conference 42, vol 2, 693-706 (1981).
63. P. E. Raison, R. G. Haire, T. Sato and T. Ogawa, "**Fundamental and Technological Aspects of Actinide Oxide Pyrochlores: Relevance for Immobilization Matrices,**" Sci. Basis for Nuclear Waste Mgt. XXII, Symp. Proc. Vol. 556, Materials Research Society, Warrendale, PA, 3-10 (1999).
64. D.R. Clarke, "**Preferential Dissolution of an Intergranular Amorphous Phase in a Nuclear Waste Ceramic,**" J. Am. Ceram. Soc., 64, C89-90 (1981).
65. J.A. Cooper, D.R. Cousens, J.A. Hanna, R.A. Lewis, S. Myhra, R.L. Segall, R.St.C. Smart, P.S. Turner, and T.J. White, "**Intergranular Films and Pore Surfaces in Synroc C: Structure, Composition, and Dissolution characteristics,**" J. Am. Ceram. Soc, 69 [4] (1986).
66. W.J. Buykx, K. Hawkins, D.M. Levins, H. Mitamura, R.St. C. Smart, G.T. Stevens, K.G. Watson, D. Weedon, and T.J. White, "**Titanate Ceramics for the Immobilization of Sodium-Bearing High-Level Nuclear Waste,**" J. Am. Ceram. Soc. 71 [8], 768-88 (1988).

67. F.J. Dickson, H. Mitamura, and T.J. White, **“Radiophase Development in Hot-Pressed Alkoxide-Derived Titanate Ceramics for Nuclear Waste Stabilization,”** J. Am. Ceram. Soc., 72 [6] 1055-1059 (1989).
68. W.J. Buykx, D.M. Levins, Roger St.C. Smart, K.L. Smith, G.T. Stevens, K.G. Watson, D. Weedon and T.J. White, **“Interdependence of Phase Chemistry, Microstructure, and Oxygen Fugacity in Titanate Nuclear Waste Ceramics,”** J. Am. Ceram. Soc. 73 [5], 1201-1207 (1990).
69. W.J. Buykx, D.M. Levins, Roger St.C. Smart, K.L. Smith, G.T. Stevens, K.G. Watson, and T.J. White, **“Processing Impurities as Phase Assemblage Modifiers in Titanate Nuclear Waste Ceramics,”** J. Am. Ceram. Soc. 73, 217-225 (1990).
70. H. Mitamura, S. Matsumoto, K.P. Hart, T. Miyazaki, E.R. Vance, Y. Tamura, Y. Togashi, and T.J. White, **“Aging Effects on Curium-Doped Titanate Ceramics Containing Sodium-Bearing High-Level Nuclear Waste,”** J. Am. Ceram. Soc., 75[2], 392-400 (1992).
71. Z. Zhang and M.L. Carter, **“An X-Ray Photoelectron Spectroscopy Investigation of Highly Soluble Grain-Boundary Impurity Films in Hollandite,”** J. Am. Ceram. Soc., 93[3] 894-899 (2010).
72. A.B. Harker, D.R. Clarke, C.M. Jantzen, and P.E.D. Morgan, **“The Effect of Interfacial Material on Tailored Ceramic Nuclear Waste Form Dissolution,”** Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems, J. Pask and A. Evans (eds.), Plenum Press, New York, Materials Sci. Res. Symp., 14, 207-216 (1981).
73. Roy, R., **“Hydroxylated Ceramic Waste Forms and the Absurdity of Leach Tests,”** Proc. Int. Sem. On Chem. and Process Eng. for High-Level Liquid Waste Solidification, Vol. 2, Julich, JUL-Conf-42, eds. R. Odoj and E. Merz, 576-602 (1981).
74. J.B. Mason, T.W. Oliver, M.P. Carson, and G.M. Hill, **“Studsвик Processing Facility Pyrolysis/Steam Reforming Technology for Volume and Weight Reduction and Stabilization of LLRW and Mixed Wastes,”** Waste Management 99 (1999).
75. J.B. Mason, J. McKibbin, K. Ryan, and D. Schmoker, **“Steam Reforming Technology for Denitration and Immobilization of DOE Tank Wastes,”** Waste Management 03 (2003).
76. C.M. Jantzen, T.H. Lorier, J.C. Marra, and J.M. Pareizs, **“Durability Testing of Fluidized Bed Steam Reforming (FBSR) Waste Forms”** WM06 Paper #6373 (February 2006).



77. C.M. Jantzen, T.H. Lorier, J.M. Pareizs, and J.C. Marra, **“Fluidized Bed Steam Reformed (FBSR) Mineral Waste Forms: Characterization and Durability Testing,”** Scientific Basis for Nucl. Waste Management XXX, D. Dunn (Ed.), 379-386 (2007).
78. C.M. Jantzen, **“Mineralization of Radioactive Wastes By Fluidized Bed Steam Reforming (FBSR): Comparisons to Vitreous Waste Forms and Pertinent Durability Testing,,”** U.S. DOE Report WSRC-STI-2008-00268 (December 2008).
79. C.M. Jantzen, C.L. Crawford, P.B. Burket, W.G. Daniel, A.D. Cozzi and C.J. Bannochie, C.J. **“Radioactive Demonstrations of Fluidized Bed Steam Reforming (FBSR) as a Supplementary Treatment for Hanford’s Low Activity Waste (LAW) and Secondary Wastes (SW),”** Waste Management WM11, Paper #11593 (2011).
80. C.M. Jantzen, C.L. Crawford, P.R. Burket, C.J. Bannochie, W.G. Daniel, C.A. Nash, A.D. Cozzi and C.C. Herman, **“Radioactive Demonstrations of Fluidized Bed Steam Reforming (FBSR) with Actual Hanford Low Activity Wastes: Verifying FBSR as a Supplemental Treatment,”** WM12 Paper #12317 (February 2012).
81. C.M. Jantzen and F.P. Glasser, **“Crystallochemical Stabilization of Radwaste Elements in Portland Cement Clinker,”** Proceed. Intl. Symp. Ceramics in Nucl. Waste Mgt; CONF-790420, 342-348 (1979).
82. C.M. Jantzen and F.P. Glasser, **“Stabilization of Nuclear Waste Constituents in Portland Cement,”** Am. Ceram. Soc. Bull., 58[4], 459-66 (1979).
83. L. Bragg, G.F. Claringbull and W.H. Taylor, **“Crystal Structures of Minerals,”** G. Bell & Sons, London, 409pp (1965).
84. R.D. Shannon and C.T. Prewitt, **“Effective Ionic Radii in Oxides and Fluorides,”** Acta. Cryst., B25, 925-946 (1969).
85. R.D. Shannon and C.T. Prewitt, **“Revised Values of Effective Ionic Radii,”** Acta. Cryst., B26, 1046-1048 (1970).
86. R.D. Shannon, **“Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides,”** Acta. Cryst., A32, 751-767 (1976).
87. J. Felsche, **“Rare Earth Silicates with the Apatite Structure,”** J. Solid State Chem, 5[2], 266-275 (1972).
88. C.M. Jantzen, F.P. Glasser and E.E. Lachowsli, **“Radioactive Waste-Portland Cement Systems: I. Radionuclide Distribution,”** J. Am. Ceram. Soc., 67 [10], 668-673 (1984).

89. C.M. Jantzen, F.P. Glasser, and E.E. Lachowsli, **“Radioactive Waste-Portland Cement Systems: II. Leaching Characteristics,”** J. Am. Ceram. Soc., 67 [10], 674-678 (1984).
90. A.E. Ringwood and S.E. Kesson, **“Immobilization of High-Level Wastes in Synroc Titanate Ceramic,”** Proceed. Intl. Symp. Ceramics in Nucl. Waste Mgt; CONF-790420, 174-178 (1979).
91. J.A. Cooper, D.R. Cousens, R.A. Lewis, S. Myhra, R.L. Segall, R. St. C., Smart, P.S. Turner, and T.J. White, **“Microstructural Characterization of Synroc C and E by Electron Microscopy,”** J. Am. Ceram. Soc 68 [2] 64-70 (1985).
92. V. Aubin, D. Caurant, D. Gourier, N. Baffier, F. Advocat, F. Bart, G. Leturcq, and J.M. Costantini, **“Synthesis, Characterization and Study of the Radiation Effects on Hollandite Ceramics Developed for Cesium Immobilization,”** Mat. Res. Soc. Symp. Proc. V. 807, 315-320 (2004).
93. K.P. Hart, E.R. Vance, R.A. Day, B.D. Begg, and P.J. Angel, **“Immobilization of Separated Tc and Cs/Sr in SYNROC,”** Mat. Res. Soc. Symp. Proc. V. 412, 281-287 (1996).
94. S.M. McDeavitt, et al, **“Stainless Steel-Zirconium Alloy Waste Forms for Metallic Fission Products and Actinides Isolated During Treatment of Spent Nuclear Fuel”**, Spectrum '96 Conference, Seattle, WA, (August 1996).
95. K.M. Marsden, B.R. Wesphal, S.M. Frank, **“Production-Scale Metal Waste Process Qualification”**, Proc. 2006, Int. Pyrochemical Conf., Idaho Falls, ID, Aug. 2006. Materials Management, Charleston, SC, (September 2002).
96. J. V. Ryan, E. C. Buck, J. Chun, J. V. Crum, B. J. Riley, D. M. Strachan, S. K. Sundaram, L. A. Turo and J. D. Vienna, **“Alternate Waste Forms: Aqueous Processing,”** AFCI-WAST-PMO-MI-DV-2009-000360, Pacific Northwest National Laboratory, 40 p. (September 2009).
97. D. Cui, *et al.*, **“On Mo-Ru-Tc-Pd-Rh-Te alloy particles extracted from spent fuel and their leaching behavior under Ar and H-2 atmospheres”**, Radiochimica Acta **92**, 551-5 (2004).
98. D. Cui, *et al.*, **“On metal aggregates in spent fuel, synthesis and leaching of Mo-Ru-Pd-Rh alloy”**, Materials Research Society Symposium Proceedings **663**, 427-34 (2001).
99. D.L. Cocke, and M.Y.A. Molla, **“The Chemistry and Leaching Mechanisms of Hazardous Substances in Cementitious Solidification/Stabilization Systems,”** In Chemistry and Microstructure of Solidified Waste Forms (Spence R.D. (ed.)). Lewis, Boca Raton, 187-242 (1993).

100. M.D. L. Cougar, B.E. Scheetz, and D.M. Roy, **“Ettringite and C-S-H Portland Cement Phases for Waste Ion Immobilization,”** A Review. Waste Manag. **16**, 295-303 (1996).
101. F.P. Glasser, **“Fundamental aspects of cement solidification and stabilization,”** J. Haz. Mat., 52 [2-3], 151-170. (1997)
102. F.P. Glasser, **“Immobilization Potential of Cementitious Materials,”** Studies Env. Sci., 60, 77-86 (1994).
103. H.F.W. Taylor, (ed.). **“Cement Chemistry,”** 2nd edn., Thomas Telford, London, (1997).
104. C.M. Jantzen, A. Johnson, D. Read, and J.A. Stresemann, **“Cements in Waste Management,”** Advances in Cement Research, v. 22[4], 225-231. (2010).
105. D.E. McGhee and F.P. Glasser, **“Immobilization Science of Cement Systems,”** Materials Research Society Bulletin, 18, 66-71 (1993).
106. N. K. Ghetos, teal., **“Some Applications of Polymer Modified Cement for Nuclear Wastes,”** Spectrum '98, Denver, CO, 645, September 1998.
107. C. H. Mattes, **“Sulfur Polymer Cement for Macro Encapsulation of Mixed Waste Debris,”** Spectrum '98, Denver, CO, page 652 (1998).
108. R. Mars and M. Y. Khalid, **“Geopolymer and Cement Glass: Promising Fixation and Solidification Matrices for Nuclear and Hazardous Wastes,”** Spectrum '92, International Topical Meeting, Nuclear and Hazardous Waste Management, Vol. 2, Boise, ID, page 914, (1992).
109. Martin Marietta Energy Systems, Inc., EG&G Idaho, Inc., Westinghouse Hanford Company, and Westinghouse Savannah River Company), **“Radiological Performance Assessment for the Z-Area Saltstone Disposal Facility,”** WSRC-RP-92-1360, Westinghouse Savannah River Company, Aiken, South Carolina (1992).
110. N.E. Bibler, **“Radiolytic Gas Generation in Concrete Made With Incinerator Ash Containing Tran uranium Nuclides,”** Sci. Basis Nucl. Waste Manag. **2**, C.J.M. Northrup (ed.), Plenum Press, New York, 585-592 (1980).
111. N.E. Bibler, **“Radiolytic Gas Production from Concrete Containing Savannah River Plant Waste,”** U.S. DOE Report DP-1464, E.I. DuPont enamors (January 1978).
112. W. E. Tadlock and G.C. Asbell, **“Tritium Waste Controls,”** U.S.DOE Report MLM-2620, (1979).

113. N.E. Bibler and E.G. Orebaugh, **“Radiolytic Gas Production from Tritiated Waste Forms; Gamma and Alpha Radiolysis Studies”** U.S.DOE Report DP-1459, DuPont deNemors Co. (July 1977).
114. R.T. Pabalan,, F.P. Glasser, D.A. Pickett, G.R. Walter, S. Biswas, M.R. Juckett, L.M. Sabido, and J.L. Myers, **“Review of Literature and Assessment of Factors Relevant to Performance of Grouted Systems for Radioactive Waste Disposal,”** Center for Nuclear Waste Regulatory Analysis, San Antonio Texas Report # CNWRA 2009-001 (April 2009).
115. F.P. Glasser, **“Application of Inorganic Cements to the Conditioning and Immobilisation of Radioactive Wastes,”** in Handbook of Advanced Radioactive Waste Conditioning Technologies, M. Ojovan (Ed.), Woodhead Publishing, Oxford, 67-135 (2011).
116. D.M. Roy and C. A. Langton, **“Characterization of Cement-Based Ancient Building Materials in Support of Repository Seal Materials Studies,”** BMI/ONWI-523, The Pennsylvania State University, State College, Pennsylvania (1983).
117. C.A. Langton, and D. M. Roy. **"Longevity of Borehole and Shaft Sealing Materials: Characterization of Ancient Cement Based Building Materials."** pp. 543-549. In Scientific Basis for Nuclear Waste Management, VII. Ed. G. L. McVay, Materials Research Society Symposium Proceedings, North-Holland, New York, New York (1984).
118. D.M. Roy and C. A. Langton, **“Studies of Ancient Concrete as Analogs of Cementitious Sealing Materials for a Repository in Tuff,”** LA-11527-MS, Los Alamos National Laboratory, Los Alamos, New Mexico (1989).
119. J.A. Steadman, **"Archaeological Concretes as Analogues,"**Commission of the European Communities. Natural Analogue Working Group, Second Meeting, Interlaken, Switzerland, June 17-19, 1986, Eds. B. Cbme and N. A. Chapman, CEC Report No. EUR 10671, 165-171, Commission of the European Communities, Luxembourg. (1986).
120. W. Jiang and D. M. Roy. **"Ancient Analogues Concerning Stability and Durability of Cementitious Wasteform,"** Scientific Basis for Nuclear Waste Management XVII. Eds. A. Barkatt and R. A. Van Konynenburg, Materials Research Society Symposium Proceedings, Vol. 33, Pittsburgh, Pennsylvania, 335-340 (1994).
121. L.A. Kovach, and W. M. Murphy (eds.) **“Proceedings of the Workshop on the Role of Natural Analogs in Geologic Disposal of High-Level Nuclear Waste,”** NUREGICP-0 147 (CNWRA 93-020), Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas (1995).
122. W. Miller, R. Alexandeq, N. Chapman, I. McKinley, and J. Smellie, **“Natural Analogue Studies in the Geological Disposal of Radioactive Wastes,”** Studies in Environmental Science 57, Elsevier, New York, New York (1994).

123. K.M. Krupka and R.J. Serene, **“Effects on Radionuclide Concentrations by Interactions in Support of Performance Assessment of Low-Level Radioactive Waste Disposal Facilities,”** NUREG/CR-6377, PNNL -11408 (May 1998) 142pg.
124. M.W. Barsoum, A. Ganguley and G. Hug, **“Microstructural Evidence of Reconstituted Limestone Blocks in the Great Pyramids of Egypt,”** J. Amer. Ceram. Soc., 89[12], 3788-3796 (2006).
125. D. Jana, **“The Great Pyramid Debate: Evidence from Detailed Petrographic Examinations of Casing Stones from the Great Pyramid of Khufu, a Natural Limestone from Tura, and a Man-made (Geopolymeric) Limestone”** Proceedings of the Twenty-ninth Conference on Cement Microscopy, Quebec City, PQ Canada May 20-24, 207-266 (2007).
126. J. Davidovits, **“Geopolymers: Man-Made Rock Geosynthesis and the Resulting Development of Very Early High Strength Cement,”** J. of Materials Education, 16 [2-3], 91-137 (1994).
127. V.F.F. Barbosa, K.J.D. MacKenzie and C. Thaumaturgo, **“Synthesis and Characterisation of Materials Based on Inorganic Polymers of Alumina and Silica: Sodium Polysialate Polymers,”** Int. J. Inorganic Materials 2, 309-317 (2000).
128. W. M., Kriven, M., Gordon and J., Bell, **“Geopolymers: Nanoparticulate, Nanoporous Ceramics made under Ambient Conditions,”** Microscopy and Microanalysis ‘04, (Proc. 62<sup>nd</sup> Annual Meeting of Microscopy Society of America) vol. 10, 404-405 (2004).
129. L.M. Sheppard, **“Geopolymer Composites: A Ceramics Alternative to Polymer Matrices”** (<http://composite.about.com/library/weekly/aa030529.htm>) (April 2005).
130. T. Hanzlicek, M. Steinerova, P. Straka, **“Radioactive Metal Isotopes Stabilized in Geopolymer Matrix: Determination of a Leaching Extract by Radiotracer Method,”** J. Am. Ceram. Soc., 89[11], 3541-3543 (2006).
131. T. Hanzlicek and M. Steinerova-Bopndrakova, **“Immobilization of Toxic Metals in Solidified Systems of Siloxo-Sial Networks,”** J. Am. Ceram. Soc. 89[3] 968-970 (2006).
132. D.S. Perera, A. Zaynab, E.R. Vance, and M. Mizumo, **“Immobilization of Pb in a Geopolymer Matrix,”** J. of the Am. Ceram. Soc., 88 [9], 2586-88 (2005).
133. J. Davidovits, **“Recent Progresses in Concretes for Nuclear Waste and Uranium Waste Containment,”** Concrete International, 16, 53-58 (1995).

134. J.G.S. van Jaarsveld, J.S.J. van Deventer, and L. Lorenzen, **“The Potential Use of Geopolymeric Materials to Immobilise Toxid Metals, Part I. Theory and Applications,”** Minerals Engineering, 10 [7], 659-669 (1996).
135. E. Hermann, C. Kunze, R. Gatzweiler, G. Kiebig, and J. Davidovits, **“Solidification of Various Radioactive Residues by Geopolymers with Special Emphasis on Long-Term Stability,”** Geopolymers 99 Proceedings (1999).
136. M. Y. Khalil and E. Merz, **“Immobilization of Intermediate-Level Wastes in Geopolymers,”** J. Nucl. Mater., 211, 141–8 (1994).
137. A. P. Zosin, T. I. Priimak, and K. B. Avsaragov, **“Geopolymer Materials Based on Magnesia-Iron Slags for Normalization and Storage of Radioactive Wastes,”** Atomic Energy, 85, 510–4 (1998).
138. C. M. Jantzen, P. R. Burket, A. R. Jurgensen, D. M. Missimer, and C. L. Crawford, **“Geopolymers: Low Temperature Waste Forms for Hazardous Wastes and Radioactive Thermal Treatment Residues,”** (in preparation for JACerS).
139. M. G. Blackford, J.V. Hanna, K. J. Pike, E. R. Vance, and Dan S. Perera, **“Transmission Electron Microscopy and Nuclear Magnetic Resonance Studies of Geopolymers for Radioactive Waste Immobilization,”** J. Am. Ceram. Soc., 90 [4] 1193–1199 (2007).
140. W. Gong, W. Lutze, I.L. Pegg, **“Low-Temperature Solidification of Radioactive and Hazardous Wastes,”** US Patent 2006/0211908A1 (2006).
141. R. L. Russell, M. J. Schweiger, J. H. Westsik, Jr., P. R. Hrma, D. E. Smith, A. B. Gallegos, M. R. Telander, S. G. Pitman, **“Low Temperature Waste Immobilization Testing,”** U.S. DOE Report PNNL-16052, Rev. 1, Pacific Northwest National Laboratory, Richland, WA (September 2006).
142. E.R. Vance and D.S. Perera, **“Development of Geopolymers for Nuclear Waste Immobilization,”** in Handbook of Advanced Radioactive Waste Conditioning Technologies, M. Ojovan (Ed.), Woodhead Publishing, Oxford, 207-229 (2011).
143. Y. Bao, S. Kwan, D. D. Siemer, and M.W. Grutzeck, **“Binders for Radioactive Waste Forms Made From Pretreated Calcined Sodium Bearing Waste,”** Journal of Materials Science, Vol. 39, 2004, pp. 481-488.
144. D.D. Siemer, **“Hydroceramics, a “new” Cementitious Waste Form Material for U.S. Defense-Type Reprocessing Waste,”** Mat Res Innovat, Vol. 6, 2002, pp. 96-104.
145. M.W. Grutzeck, **“Physical, Chemical, and Structural Evolution of Zeolite-Containing Waste Forms Produced from Metakaolinite and Calcined Sodium Bearing Waste**

- (HLW and/or LLW),” Final Report. September 15, 1998 to March 14, 2005,” U.S. DOE. EMSP, Project Number 81963, June 22. 2005.
146. B. E. Scheetz and J. Olanrewaju, **“Final Report Determination of the Rate of Formation of Hydroceramic Waste Forms made with INEEL Calcined Wastes”** U.S. DOE Report DOE/ID/13649, 281pp (2001).
147. A.S. Wagh, M.D. Maloney, G.H. Thomson, and A. Antink, **“Investigations in Ceramicrete Stabilization of Hanford Tank Wastes,”** WM’03 (2003).
148. A.S. Wagh and D. Singh. **“Method for Stabilizing Low-Level Mixed Wastes at Room Temperature.”** U. S. Patent 5,645,518 (1997).
149. G.G. Simon and W. Botzem, **“Volume Reduction and Solidification System for Radwaste,”** Nukem GmbH, Industriestrae 13, D-8755 (1984)
150. M.I. Ojovan, N.V. Ojovan, Z.I. Golubeva, I.V. Startceva and A.S. Barinov, **“Aging of the bitumen waste form in wet repository conditions.”** *Mat. Res. Soc. Symp. Proc.*, **713**, 713-718 (2002).
151. J.H. Westsik, **“Characterization of Cement and Bitumen Waste Forms Containing Simulated Low-level Waste Incinerator Ash,”** U.S. DOE Report PNL-5153, Pacific Northwest Laboratory, Richland, WA (1984).
152. R.C. Ewing, **“Novel Waste Forms,”** in *Radioactive Waste Forms for the Future*, W. Lutze and R. C. Ewing. Amsterdam, North-Holland, 589-633 (1988).
153. L.J. Jardine and M.J. Steindler, **“A Review of Metal-Matrix Encapsulation of Solidified Radioactive High Level Waste,”** U.S. DOE Report ANL 78-19, Argonne National Laboratory, Argonne, IL (1978)
154. R. L. Treat, **“Preliminary Evaluation of Alternative Waste Form Solidification Processes. Volume I. Identification of the Processes,”** U.S. DOE Report PNL-3244, Pacific Northwest Laboratory, Battelle, (1980).
155. J. M. Rusin, R. O. Lokken, J. M. Lukacs, K. R. Sump, M. F. Browning and G. J. McCarthy, **“Multibarrier Waste Forms, Part I. Development,”** Pacific Northwest Laboratory Report No. PNL-2668-1 (September 1978).
156. D. P. Stinton, P. Angelini, A.S. Caputo, W. J. Lackey, **“Coating of Crystalline Nuclear Waste Forms to Improve Inertness,”** *J. Am. Ceram. Soc.*, **65** [8] 394–98 (1982).
157. C.M. Jantzen **“Fluidized Bed Steam Reformer (FBSR) Product: Monolith Formation and Characterization,”** U.S. DOE Report WSRC-STI-2006-00033 (June 2006).

158. C.M. Jantzen, C.M. and C.L. Crawford, “**Mineralization of Radioactive Wastes by Fluidized Bed Steam Reforming (FBSR): Radionuclide Incorporation, Monolith Formation, and Durability Testing,**” WM10 Paper #10467 (2010).
159. P. VanIseghem, M. Aertsens, S. Gin, D. Deneele, B. Grambow, P. McGrail, D. Strachan, and G. Wicks, “**GLAMOR, A Critical Evaluation of the Dissolution Mechanisms of High Level Waste Glasses in Conditions of Relevance for Geological Disposal,**” EUR23097 (2007).
160. B. Grambow, “**Nuclear Waste Glasses – How Durable?,**” Elements, v.2, 357-364 (2006).
161. C.M. Jantzen, “**Lack of Slag Formation in the Scale Glass Melter,**” US DOE Report DPST-87-373, E.I. DuPont deNemours & Co., Savannah River Laboratory, Aiken, SC (April 1987).
162. N.R. Gribble, R. Short, E. Turner, and A.D. Riley, “**The Impact of Increased Waste Loading on Vitrified HLW Quality and Durability,**” Sci. Basis for Nuclear Waste Mgt, XXXIII, Materials Research Society, Pittsburgh, PA, 283-289 (2009).
163. A. Riley, S. Walker, N.R. Gribble, “**Composition Changes and Future Challenges for the Sellafield Waste Vitrification Plant,**” Sci. Basis for Nuclear Waste Mgt, XXXIII, Materials Research Society, Pittsburgh, PA, 267-273 (2009).
164. P. Hrma, P. Schill, and L. Nemec, “**Settling of Spinel in a High-Level Waste Glass Melter,**” Final Report, US DOE Contract DE-AC06-76RL01830, Project Number: 65422 (2001).
165. J.D. Vienna, T.B. Edwards, J.V. Crum, D.S. Kim, and D.K. Peeler, “**Liquidus Temperature and One Percent Crystal Content Models for Initial Hanford HLW Glasses,**” Ceramic Transactions, V. 168, 133-140 (2005).
166. W.J. Weber, R.C. Ewing, C.R.A. Catlow, T. Diaz de la Rubia, L.W. Hobbs, C. Kinoshita, H.J. Matzke, A.T. Motta, M. Nastasi, E.H.K. Salje, E.R. Vance and S.J. Zinkle, “**Radiation Defects in Crystalline Ceramics for the Immobilization of High-level Nuclear Waste and Plutonium,**” Journal of Materials Research, 13 (6), 1434-1484 (1998).
167. W.L. Ebert, “**Testing Protocols to Support Waste Form Development, Production, and Acceptance,**” U.S. DOE Report GNEP-WAST-WAST-AI-RT-2008-000302 (September 2008).
168. M.J. Plodinec and W.G. Ramsey, “**Glass Consistency and Glass Performance,**” Proceedings of Spectrum 94 Nuclear and Hazardous Waste Management International Topical Meeting, Am. Nuclear Soc., 1490-1495 (1994).



169. K.Chacey, J.M. Pope, M.J. Plodinec, P.S. Schaus, and E. Maestas, **“DOE-EM/Producers Strategy for Wasteform and Process Startup Acceptance,”** High-Level Radioactive Waste Management, V.2, American Nuclear Society, LaGrange IL, 785-789 (1990).
170. M.J. Plodinec, **“The DWPF Product, and its Qualification Program,”** High-Level Radioactive Waste Management, V.2, American Nuclear Society, LaGrange IL, 1124-1131 (1990).
171. W.T. Goldstone and M.J. Plodinec, **“The DWPF Strategy for Producing an Acceptable Product,”** Ceramic Transactions, V.23, American Ceramic Society, Westerville, OH, 443-452 (1991).
172. S.L. Marra and M.J. Plodinec, **“The DWPF Waste Form Qualification Program,”** Spectrum 94 (1994). Proceedings of Spectrum 94 Nuclear and Hazardous Waste Management International Topical Meeting, Am. Nuclear Soc.,1496-1501 (1994).
173. M.J. Plodinec and B.G. Kitchen, **“Establishing the Acceptability of Savannah River Site Waste Glass,”** Proceedings of Spectrum 90 Nuclear and Hazardous Waste Management International Topical Meeting, Am. Nuclear Soc.,Spectrum 90, 302-305 (1990)
174. J.L. Crandall, **“High Level Waste Immobilization,”** in **“The Treatment and Handling of Radioactive Wastes,”** by A.G. Blasewitz, John M. Davis, and Marilynne R. Smith, Battelle Press, and Springer Verlag, 178-183 (1983).
175. C.M. Jantzen, N.E. Bibler, D.C. Beam, and W.G. Ramsey, **“Development of an ASTM Standard Glass Durability Test, the Product Consistency Test (PCT), for High Level Radioactive Waste Glass,”** Proceedings of Spectrum 94 Nuclear and Hazardous Waste Management International Topical Meeting, Am. Nuclear Soc., 164-169 (1994).
176. C.M. Jantzen and N.E. Bibler, **“The Product Consistency Test (PCT): How and Why it Was Developed,”** Ceramic Transactions, V.207, 155-167 (2009).
177. C.M. Jantzen, N.E. Bibler, D.C. Beam, and M.A. Pickett, **“Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material,”** U.S. DOE Report WSRC-TR-92-346, Rev.1, 92p (February, 1993).
178. C.M. Jantzen, N.E. Bibler, D.C. Beam, and M.A. Pickett, **“Development and Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material,”** Environmental and Waste Management Issues in the Ceramic Industry, Ceramic Transactions, 39, American Ceramic Society, Westerville, OH, 313-322 (1994).
179. J.E. Mendel (Compiler), **Final Report of the Defense High-Level Waste Leaching Mechanisms Program**, US DOE Report PNL-5157, Battelle Pacific Northwest Laboratories, Richland WA (1984).
180. L.L. Hench and D.E. Clark, **“Physical Chemistry of Glass Surfaces,”** J. Non-Cryst.

- Solids, 28, 83-105 (1978).
181. L.L.Hench and D.E. Clark, **“Surface Properties and Performance Prediction of Alternative Waste Forms,”** NUREG/CR-3472, Vol. 2 (1986).
  182. G.G. Wicks, W.C. Mosley, P.G. Whitkop, and K.A. Saturday, **“Durability of Simulated Waste Glass-Effects of Pressure and Formation of Surface Layers,”** J. Non-Cryst. Solids, 49, 413-28 (1982).
  183. A.B. Woodland, J.K. Bates, T.J. Gerding, **“Parametric Effects on Glass Reaction in the Unsaturated Test Method,”** U.S. DOE Report ANL-91/36, 130pp (December, 1991).
  184. J.K. Bates, C.R. Bradley, E.C. Buck, J.C. Cunnane, N.L. Dietz, W.L. Ebert, J.W. Emery, R.C. Ewing, X. Feng, T.J. Gerding, M. Gong, W.-T Han, J.C. Hoh, J.J. Mazer, M. Tomozawa, L.-M. Wang, and D.J. Wronkiewicz, **“ANL Technical Support Program for DOE Environmental Restoration and Waste Management, Annual Report October 1990-September 1991,”** US DOE Report ANL-92/9, 149pp (March, 1992).
  185. X. Feng, J.C. Cunnane, and J.K. Bates, **“A Literature Review of Surface Alteration Layer Effects on Waste Glass Behavior,”** Ceramic Transactions, V. 39 , G.B. Mellinger (Ed.), American Ceramic Society, Westerville, OH, 341-352 (1994).
  186. A.K. Bandyopadhyai, R. Jabra, and J. Phalippou, **“Association of OH Groups with Boron and Silicon Atoms in SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> Glasses by Infrared Spectroscopy,”** J. Mat. Sci. Letters, 8[12], 1464-1467 (1989).
  187. C.M. Jantzen, K.G. Brown and J.B. Pickett, **“Durable Glass for Thousands of Years,”** International Journal of Applied Glass Science, 1 [1], 38-62 (2010).
  188. P. Frugier, S. Gin, Y. Minet, T. Chave, B. Bonin, N. Godon, J.-E. Lartigue, P. Jollivet, A. Ayrat, L. DeWindt, and G. Santarini, **“SON68 Nuclear Glass Dissolution Kinetics: Current State of Knowledge and Basis of the New GRAAL Model,”** Jour. Nucl. Materials, 380, 8-21 (2008).
  189. P. Frugier, T. Chave, S. Gin, and J.-E.Lartigue, **“Application of the GRAAL Model to Leaching Experiments with SON68 Nuclear Glass in Initially Pure Water,”** Jour. Nucl. Materials, 392, 552-567 (2009).
  190. C.M. Jantzen, D.I. Kaplan, N.E. Bibler, D.K. Peeler, and M.J. Plodinec, **“Performance of a Radioactive High Level Waste Glass After 24 Years Burial,”** Jour. Nucl. Materials, 378, 244-256 (2008).
  191. P. Van Iseghem and B. Grambow, **“The Long-Term Corrosion and Modeling of Two Simulated Belgian Reference High-Level Waste Glasses,”** Sci. Basis for Nuclear Waste

- Management XI, J.J. Apted and R.E. Westerman (Eds.), Materials Research Society, Pittsburgh, PA, (1987) 631-639.
192. K. Ferrand, A. Abdelouas, B. Grambow, **“Water Diffusion in the Simulated French Nuclear Waste Glass SON68 Contacting Silica Rich Solutions: Experimental and Modeling,”** J. Nuclear Materials, 355 [1-3] 54-67 (2006).
193. R.W. Douglas and T.M.M. El-Shamy, **“Reactions of Glasses with Aqueous Solutions,”** J. Am. Ceram. Soc., 50[1], 1-8 (1967)
194. C.M. Jantzen, **“Thermodynamic Approach to Glass Corrosion,”** Corrosion of Glass, Ceramics, and Ceramic Superconductors, D.E. Clark and B.K. Zoitos, Noyes Publications, Park Ridge, NJ (1992)153-215.
195. R.M. Wallace and G.G. Wicks, **“Leaching Chemistry of Defense Borosilicate Glass,”** Scientific Basis for Nuclear Waste Management, VI, D.G. Brookins (Ed.), Elsevier North Holland, New York, (1983) 23-28.
196. D. Cooke and A. Paul, **“Chemical Durability of Glass Enamels Containing B<sub>2</sub>O<sub>3</sub>: Part 1: Lead Borosilicates,”** J. Br. Ceram. Soc., 77, 104-116 (1978).
197. A. Gauthier, P. LeCoustumer, and J-H. Thomassin, **“Nature and Effect of the Alteration Layer During Nuclear Waste Glass Dissolution,”** Scientific Basis for Nuclear Waste Mgt. XXV, B.P. McGrail and G.A. Cragnoliono (Eds.), Materials Research Society, Pittsburgh, PA. (2002) 555-561.
198. M. Aertsens, **“The BRAG and GM2003 Models for Glass Dissolution,”** Sci. Basis for Nuclear Waste Management XXX, D. Dunn, C. Poinssot, and B. Begg (Eds.), Materials Research Society, Pittsburgh, PA, 117-122 (2007).
199. B. Grambow and R. Muller, **“First-order Dissolution Rate Law and the Role of Surface Layers in Glass Performance Assessment,”** J. of Nuclear Materials 298, 112-124 (2001).
200. Y. Inagaki, K. Idemitsu, T. Arima, T. Maeda, H. Ogawa, F. Itonaga, **“Alteration-Phase Formation and Associated Cesium Release During Alteration of R7T7 Waste Glass,”** Scientific Basis for Nuclear Waste Mgt. XXV, B.P. McGrail and G.A. Cragnoliono (Eds.), Materials Research Society, Pittsburgh, PA., 589-596 (2002).
201. T. A. Abrajano, J.K. Bates, and C.D. Byers, **“Aqueous Corrosion of Natural Nuclear Waste Glasses. I. Comparative Rates of Hydration in Liquid and Vapor Environments at Elevated Temperatures,”** J. Non-Cryst. Solids 84, 251-257 (1986).
202. I. S. Muller, S. Ribet, I.L. Pegg, S. Gin and P. Frugier **“Characterization of Alteration Phases on HLW Glasses After 15 Years of PCT Leaching,”** Ceramic Transactions, V.176, American Ceramic Society, Westerville, OH, 191-199 (2006).

203. J.V. Ryan, I.C. Bourg, G.A. Waychunas, W.L. Ebert, R.E. Williford, J.C. Marra, J.P. Icenhower, K.A. Murphy, J.D. Vienna, D.M. Strachan, E.M. Pierce, P. Zapol, C.I. Steefel, C.M. Jantzen, L.J. Criscenti, and D.K. Shuh, **“Technical Program Plan for the International Technical Evaluation of Alteration Mechanisms (I-TEAM)”** PNNL-21031 (2011).
204. G. Calas, M. Le Grand, L. Galois, D. Ghaleb, **“Structural Role of Molybdenum in Nuclear Glasses: an EXAFS Study,”** Journal of Nuclear Materials 322 (2003) 15–20.
205. W.G. Ramsey, N.E. Bibler, and T.F. Meaker, **“Compositions and Durabilities of Glasses for Immobilization of Plutonium and Uranium,”** Waste Management '95, Record 23828-23907, WM Symposia, Inc., Tucson, AZ (1995).
206. M. T. Harrison and C. R. Scales, **“Development of Borosilicate Glass Compositions for the Immobilization of the UK’s Separated Plutonium Stocks”**, Mater. Res. Soc. Symp. Proc. Vol. 1107, 405-412, Materials Research Society, Pittsburgh, PA (2008).
207. M. T. Harrison and C. R. Scales, **“Durability of Borosilicate Glass Compositions for the Immobilization of the UK’s Separated Plutonium Stocks”**, Mater. Res. Soc. Symp. Proc. Vol. 1107, 429-436, Materials Research Society, Pittsburgh, PA (2008).
208. J.C. Marra, D.K. Peeler, and C.M. Jantzen, C.M., **“Development of an Alternate Glass Formulation for Vitrification of Excess Plutonium,”** U.S. DOE Report WSRC-TR-2006-00031 (January 2006).
209. I. Bardez, D. Caurant, J. L. Dussossoy, P. Loiseau, C. Gervais, F. Ribot, D. R. Neuville, N. Baffier, and C. Fillet, **“Matrices Envisaged for the Immobilization of Concentrated Nuclear Waste Solutions,”** Nuclear Science and Engineering 153, 272–284 (2006).
210. G.N. Greaves, **“EXAFS and the Structure of Glass,”** J. Non-Crystalline Solids, 71, 203-217 (1985).
211. G.N. Greaves, N.T. Barrett, G.M. Antonini, F.R. Thornley, B.T.M. Willis, and A. Steel, **“Glancing-Angle X-ray Absorption Spectroscopy of Corroded Borosilicate Glass Surfaces Containing Uranium,”** J. Am. Chem. Soc. 111, 4313-4324 (1989).
212. D. Gombert, **“Global Nuclear Energy Partnership Integrated Waste Management Strategy Waste Treatment Baseline Study,”** U.S. DOE Report GNEP-WAST-WAST-AI-RT-2007-000324, Idaho National Laboratory, Idaho Falls, ID, 69p. (2007).
213. R.C. Ewing and L.M. Wang, **“Phosphates as Nuclear Waste Forms”** in: Reviews in Mineralogy & Geochemistry, vol. 48, M.J. Kohn, J. Rakovan and J.M. Hughes (Editors), 673-699 (2002).

214. K. J. Schneider, Editor, **"Waste Solidification Program, Vol. 1, Process Technology – Pot Spray, and Phosphate Glass Solidification Processes,"** BNWL-1073, Battelle Memorial Institute, Pacific Northwest Laboratories, Richland WA, (August, 1969).
215. L. P. Hatch, G. G. Neth, and E. J. Tuthill, **"Ultimate Disposal of High Level Radioactive Wastes - Fixation in Phosphate Glass with Emphasis on the Continuous Mode of Plant Operation,"** U.S. DOE Report BNL-6321. Brookhaven National Laboratory, Upton, New York, October 1962.
216. B. C. Sales and L. A. Boatner, **"Lead-Iron Phosphate Glass: A Stable Storage Medium for High-Level Nuclear Waste,"** Science, Vol. 226, No. 4670, 45-48, (Oct. 5, 1984).
217. C.M. Jantzen, **"Investigation of Lead-Iron-Phosphate Glass for SRP Waste,"** U.S. DOE Report DP-1729, E.I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC, 66 p. (October, 1986).
218. G.K. Marasinghe, M. Karabulut, X. Fang, C.S. Ray, D.E. Day, **"Vitrified Iron Phosphate Nuclear Waste Forms Containing Multiple Waste Components,"** Ceramic Transactions, Vol. 107, pp.115-122. American Ceramic Society, Westerville, Ohio (2000).
219. C.M. Jantzen, **"Investigation of Lead-Iron-Phosphate Glass for SRP Waste,"** Advances in Ceramics, 20, D.E. Clark, W.B. White and A.J. Machiels (Eds.), American Ceramic Society, Westerville, OH, 157-165 (1986).
220. L.A. Chick, L.R. Bunnell, D.M. Strachan, H.E. Kissinger, and F.N. Hodges, **"Evaluation of Lead-Iron-Phosphate Glass as a High Level Waste Form,"** Advances in Ceramics, 20, D.E. Clark, W.B. White and A.J. Machiels (Eds.), American Ceramic Society, Westerville, OH, 149-156 (1986).
221. L. Kahl, **"Hydrolytic Durability of Lead-Iron-Phosphate Glasses,"** Advances in Ceramics, 20, D.E. Clark, W.B. White and A.J. Machiels (Eds.), American Ceramic Society, Westerville, OH, 141-148 (1986).
222. Lawrence Livermore National Laboratory (LLNL). **"Fissile Material Disposition Program – Screening of Alternate Immobilization Candidates for Disposition of Surplus Fissile Materials,"** UCRL-ID-118819, L-20790-1, LLNL, Livermore, California (1996).
223. G.N. Greaves, **"EXAFS, Glass Structure and Diffusion,"** Phil. Mag. B, 60[6] 793-800 (1989).

224. X. Yu and D.E. Day, **“Effect of Raw Materials on the Redox State of Iron and Properties of Iron Phosphate Glasses,”** Proceedings of the 17th International Congress on Glass, Vol. 2, pp. 45-51. International Academic Publishers, Beijing, The Peoples Republic of China (1995).
225. A. Mogus-Milankovic, M. Fajic, A. Drasner, R. Tojiko, and D.E. Day **“Crystallization of Iron Phosphate Glasses,”** Physics and Chemistry of Glasses, 39(2), 70-75 (1998).
226. D.E. Day, Z. Wu, C.S. Ray, and P.R. Hrma, **“Chemically Durable Iron Phosphate Glass Wasteforms,”** Journal of Non-Crystalline Solids 241(1), 1-12 (1998)
227. M. Mesko, D.E. Day, and B.C. Bunker, **“Immobilization of High-Level Radioactive Sludges in Iron Phosphates Glasses,”** In Science and Technology for Disposal of Radioactive Tank Waste, eds. W.W. Schulz and N.J. Lombardo, pp. 379-390. Plenum Publishing Corp., New York (1998).
228. F. Chen and D.E. Day, **“Corrosion of Selected Refractories by Iron Phosphate Melts”** Ceramic Transactions, Vol. 93, 213-220. The American Ceramic Society, Westerville, Ohio (1999).
229. C.R. Ray, X. Fang, M. Karabulut, G.K. Marasinghe, and D.E. Day, **“Iron Redox and Crystallization of Iron Phosphate Glass,”** Ceramic Transactions, Vol. 43, 187-194. American Ceramic Society, Westerville, Ohio (1999).
230. M. Mesko, and D.E. Day, **“Immobilization of Spent Nuclear Fuel in Iron Phosphate Glass,”** Journal of Nuclear Materials, 273(1), 27-36 (1999).
231. Y. Badyal, M. Karabulut, G.K. Marasinghe, M.L. Saboungi, D. Haeffner, S. Shastri, D.E. Day, and C.S. Ray, **"The Effects of Uranium Oxide High-Level Waste on the Structure of Iron Phosphate Glasses,"** Scientific Basis for Nuclear Waste Management XXII, Vol. 556, pp. 297-303. Materials Research Society, Pittsburgh, Pennsylvania (1999).
232. G.K. Marasinghe, M. Karabulut, X. Fang, C.S. Ray, and D.E. Day, **“Iron Phosphate Glasses: An Alternative to Borosilicate Glasses for Immobilizing Certain Nuclear Wastes,”** Environmental Issues and Waste Management Technologies VI; Ceramic Transactions v. 119, 361-368 (2001).
233. G.K. Marasinghe, M. Karabulut, C.S. Ray, D.E. Day, M.G. Shumsky, W.B. Yelon, C.H. Booth, P.G. Allen, and D.K. Shuh, **"Structural Features of Iron Phosphates Glasses,"** J. Non-Crystalline Solids, 222, 144-152 (1997).
234. G.K. Marasinghe, M. Karabulut, C.S. Ray, D.E. Day, C.H. Booth, P.G. Allen, and D.K. Shuh, **"Redox Characteristics and Structural Properties of Iron Phosphate Glasses: A**

- Potential Host Matrix for Vitrifying High Level Nuclear Waste,"** Ceramic Transactions, Vol. 87, 261-270, American Ceramic Society, Westerville, Ohio (1998).
235. G.K. Marasinghe, M. Karabulut, C.S. Ray, D.E. Day, P.G. Allen, J.J. Bucher, D.K. Shuh, Y. Bagyal, M.L. Saboungi, M. Grimsditch, S. Shastri, and D. Heaffner, **"Effects of Nuclear Waste Composition on Redox Equilibria, Structural Features, and Crystallization Characteristics of Iron Phosphate Glasses,"** Ceramic Transactions, Vol. 93, 195-202. American Ceramic Society, Westerville, Ohio (1999).
236. D. E. Day, C. S. Ray, and C.-W. Kim, **"Iron Phosphate Glasses: An Alternative for Vitrifying Certain Nuclear Wastes,"** Final Report for DE-FG07-96ER45618 (For the period September 15, 2000 to September 30, 2004) Project Number: 73976 (December 28, 2004).
237. D.-S. Kim, W. C. Buchmiller, M. J. Schweiger, J. D. Vienna, D. E. Day, C. W. Kim, D. Zhu, T. E. Day, T. Neidt, D. K. Peeler, T. B. Edwards, I. A. Reamer, and R. J. Workman, **"Iron Phosphate Glass as an Alternative Waste-Form for Hanford LAW,"** U.S. DOE Report PNNL-14251, Pacific Northwest National Laboratory Richland, WA, 59 p. (February 2003).
238. D.E. Day, X. Yu, G.J. Long, and R.K. Brow, **"Properties and Structure of Sodium-Iron Phosphate Glasses,"** J.Non-Crystalline Solids, 215(1), 21-31 (1997).
239. M. Mesko, D.E. Day, and B.C. Bunker, **"Immobilization of CsCl and SrF<sub>2</sub> in Iron Phosphate Glass,"** WasteManagement, 20(4), 271-278 (2000).
240. G.K. Marasinghe, M. Karabulut, X. Fang, C.S. Ray, D.E. Day, **"Vitrified Iron Phosphate Nuclear Waste Forms Containing Multiple Waste Components,"** Ceramic Transactions, Vol. 107 115-122. American Ceramic Society, Westerville, Ohio (2000).
241. M. Karabulut, G.K. Marasinghe, C.S. Ray, D.E. Day, O. Ozturk, and G.D. Waddill, **"X-ray Photoelectron and Mossbauer Spectroscopic Studies of Iron Phosphate Glasses Containing U, Cs, and Bi,"** J. Non-Crystalline Solids, 249(2-3): 106-116 (1999).
242. D.E. Day and C.W. Kim, **"Reaction of Inconel 690 and 693 in Iron Phosphate Melts: Alternative Glasses for Waste Vitrification,"** Final Report for Contract DE-FG02-04ER63831 Project 0010255 (2005).
243. X. Yu, D.E. Day, G.J. Long, R.K. Brow, **" Properties and Structure of Sodium-Iron Phosphate Glasses,"** J. Non-Cryst. Solids, 215, 21-31 (1997).
244. A.C. Wright, R.N. Sinclair, J.L. Shaw, R. Haworth, G. Kanishka Marasinghe, D.E. Day, P.A. Bingham, S.D. Forder, G.J. Cuello, and H.E. Fischer, **"The Atomic and Magnetic**

- Structure and Dynamics of Iron Phosphate Glasses,”** 8th Intl. Otto Schott Colloquium, Jena (2006).
245. A.C. Wright, R.N. Sinclair, J.L. Shaw, R. Haworth, G.K. Marasinghe & D.E. Day, “**A Neutron Diffraction Study of the Structure of Iron Phosphate Glasses,”** Physics & Chemistry of Glasses: European Journal of Glass Science & Tech. Part B, 49 (1) 1-7 (2008).
246. J. S. Sanghera, J. Heo, and J. D. Mackenzie, “**Chalcohalide Glasses,”** *J. Non-Cryst. Solids*, **103**, 155 (1988).
247. J. V. Crum, B. J. Riley, S. K. Sundaram, S. A. Arreguin, J. Matyas, M. J. Schweiger, B. T. Rieck, and J.D. Vienna, “**Alternative Waste Forms for Electro-Chemical Salt Waste,”** AFCI-WAST-PMO-MI-DV-2009-000293, Pacific Northwest National Laboratory, 22 p. (October 28, 2009).
248. A.K. Varshneya, “**Fundamentals of Inorganic Glasses,”** Academic Press, Inc. San Diego, CA, 570pp. (1994).
249. D.F. Bickford and C.M. Jantzen, “**Devitrification of SRL Defense Waste Glass**”, Sci. Basis for Nuclear Waste Management, VII, G.L. McVay (ed). Elsevier Publ., New York 557-565 (1984).
250. C.M. Jantzen, D.F. Bickford, D.G. Karraker, and G.G. Wicks, G.G., “**Time-Temperature-Transformation Kinetics in SRL Waste Glass,**” Advances in Ceramics, 8, American Ceramic Society, Westerville, OH, 30-38 (1984).
251. C.A. Cicero, S.L. Marra, and M.K. Andrews, “**Phase Stability Determinations of DWPF Waste Glasses,”** U.S. DOE Report WSRC-TR-93-227, Rev. 0, Westinghouse Savannah River Company, Aiken, SC 74pp., (May 1993).
252. P.R. Hrma, G.F. Peipel, M.J. Schweiger, D.E. Smith, D.S. Kim, P.E. Redgate, J.D. Vienna, C.A. LoPresti, D.B. Simpson, D.K. Peeler, M.H. Langowski, “**Property/Composition Relationships for Hanford High-Level Waste Glasses Melting at 1150°C, Vols. 1 and 2,”** U.S. DOE Report PNL-10359, Battelle Memorial Institute, Pacific Northwest Laboratory, Richland, WA (December, 1994).
253. W.L. Ebert, “**Testing to Evaluate the Suitability of Waste Forms Developed for Electrometallurgically Treated Spent Sodium-Bonded Nuclear Fuel for Disposal in the Yucca Mountain Repository,”** U.S. DOE Report ANL 05/43 (September 2005).
254. W. Lutze, J. Borchardt and A. K. De’, “**Characterization of Glass and Glass Ceramic Nuclear Waste Forms,”** in Scientific Basis for Nuclear Waste Management’, Vol. 1, G. J. McCarthy (Ed.), Plenum Press, New York, 69—81 (1979).



255. M. Ninomiya, T. Yamanaka, T. Sakane, M. Hora, S. Nakamura, S. Kawamura, “**Diopside Glass-Ceramic Material for the Immobilization of Radioactive Wastes,**” Proceedings of the International Seminar on Chemistry and Process Engineering for High-Level Liquid Waste Solidification, Julich, R. Odoj and E. Merz (Eds), 675-692 (1981).
256. P.J. Hayward, “**Glass-Ceramics**” in W. Lutze & R.C. Ewing (eds) Radioactive Waste Forms for the Future. Elsevier Science Publishers B.V., Amsterdam, 427-494 (1988).
257. E.R. Vance, R.A. Day, Z. Zhang, B.D. Begg, C.J. Ball, and M.G. Blackford, “**Charge Compensation in Gd-doped CaTiO<sub>3</sub>,**” Journal of Solid State Chemistry, 124, 77-82 (1996).
258. E.R. Vance, R.A. Day, M.L. Carter and A. Jostons, “**A Melting Route to Synroc for Hanford HLW Immobilization,**” Materials Research Society Symposium Proceedings V. 412, 289-295 (1996).
259. T.P. O'Holleran, S.G. Johnson, S.M. Frank, M.K. Meyer, M. Noy, E.L. Wood, D.A. Knecht, K. Vinjamuri, and B.A. Staples, “**Glass-ceramic Waste Forms for Immobilizing Plutonium,**” Materials Research Society Symposium Proceedings, 465, 1251-1258 (1997).
260. T. Advocat, C. Fillet, J. Marillet, G. Leturcq, J.M. Boubais, and A. BoOnnetier, “**Nd-doped Zirconolite Ceramic and Glass-ceramic Synthesized by Melting and Controlled Cooling**” Materials Research Society Symposium Proceedings, 506, 55 -62 (1998).
261. T.N. Lashtchenova and S.V. Stefanovsky, “**Titanium-silicate Based Glass-crystalline Wasteforms,**” In: M.K. Choudhary, N.Y. Huff and C.H. Drummond III (eds) Proceedings of the XVIII International Congress on Glass. San-Francisco, CD-ROM (1998).
262. T.N. Lashtchenova and S.V. Stefanovsky, “**Immobilization of Incinerator Ash in Synroc-glass Material,**” In: Proceedings of the IT3 International Conference on Incineration & Thermal Treatment Technologies, Salt Lake City, 603-607 (1998).
263. P. Loiseau, D. Caurant, N. Baffler, L. Mazerolles and C. Fillet, “**Development of Zirconolite-Based Glass-ceramics for the Conditioning of Actinides,**” Materials Research Society Symposium Proceedings, 663, 179-187 (2001).
264. P.J. McGlinn, T. Advocat, E. LoI, G. Leturcq and J.P. Mestre, “**Nd- and Ce-doped ceramic Glass Composites: Chemical Durability Under Aqueous Conditions and Surface Alteration in a Moist Clay Medium at 90°C,**” Materials Research Society Symposium Proceedings, 663, 249-258 (2001).

265. C. Martin, I. Bibet, and T. Advocat, **“Alteration of a Zirconolite Glass-ceramic Matrix under Hydrothermal Conditions,”** Materials Research Society Symposium Proceedings, 713, 405-411 (2002).
266. K. Vinjamuri, **“Candidate Glass-Ceramic Waste Forms for Immobilization of the Calcines Stored at the Idaho Chemical Processing Plant,”** Ceramic Transactions, V.61, 439-446 (1995).
267. J. Saidl and J. Ralkova, **“Radioactive Waste Solidification by Means of Melting with Basalt,”** Atomic Energy, 10, 285-289 (in Russian) (1966).
268. O.V. Tolstova, T.N. Lashtchenova, and S.V. Stefanovsky, **“Glassy Materials From Basalt for Intermediate-Level Waste Immobilization,”** Glass and Ceramic, 6, 28-31 (in Russian) (2002).
269. D.L. Wronkiewicz, S.F. Wolf, T.S. Disanto, **“Apatite- and Monazite-bearing Glass-crystal Composites for the Immobilization of Low-level Nuclear and Hazardous Wastes,”** Materials Research Society Symposium Proceedings, 412, 345-352 (1996).
270. D. Zhao, L. Li, L.L. Davis, W.J. Weber and R.C. Ewing, **“Gadolinium Borosilicate Glass-bonded Gd-silicate Apatite: A Glass-ceramic Nuclear Waste Form for Actinides,”** Materials Research Society Symposium Proceedings, 663, 199-206 (2001).
271. D.A. Knecht and J. R. Berreth, **“Immobilization of Idaho Chemical Processing Plant High Level Wastes,”** Proceedings of the International Seminar on Chemistry and Process Engineering for High-Level Liquid Waste Solidification, Julich, R. Odoj and E. Merz (Eds), 252-276 (1981).
272. C. Poinssot, C. Ferry, M. Kelm, M., B. Grambow, A. Martinez-Esparza, L. Johnson, Z. Andriambololona, J. Bruno, C. Cachoir, J.M. Cavedon, H. Christensen, C. Corbel, C. Jegou, K. Lemmens, A. Loida, P. Lovera, F. Miserque, F., J. de Pablo, A. Poulesquen, J. Quiñones, , V. Rondinella, K. Spahiu, and D. Wegen, **“Final Report of the European Project: Spent Fuel Stability under Repository Conditions,”** (2005).
273. M. Burghatz, H. Matzke, C. Leger, G.Vambenepe, and M. Rome, **“Inert Matrices for the Transmutation of Actinides; Fabrication, Thermal Properties and Radiation Stability of Ceramic Materials,”** Journal of Nuclear Materials, 271, 544-548 (1998).
274. K.E. Sickafus, R.J. Hanrahan, K.J. McClellan, J.N. Mitchell, C.J. Wetteland, D.P. Butt, P. Chodak, K.B. Ramsey, T.H. Blair, K. Chidester, H. Matzke, K. Yasuda, R.A Verrall, and N. Yu, **“Burn and Bury Option for Plutonium,”** American Ceramic Society Bulletin **78** (1), 69-74 (1999).
275. W.L. Gong, W. Lutze, W. and R.C. Ewing, **“Zirconia Ceramics for Excess Weapons Plutonium Waste,”** Journal of Nuclear Materials, **277**(2-3), 239-49 (2000).

276. B.C. Chakoumakos, **“Systematics of the Pyrochlore Structure Type, Ideal  $A_2B_2X_6Y$ ,”** Journal of Solid State Chemistry, 53 120-129 (1984).
277. B. C. Chakoumakos and R.C. Ewing, **“Crystal Chemical Constraints on the Formation of Actinide Pyrochlores,”** in Materials Research Society Symposium Proceedings, Vol. 44, “Scientific basis for nuclear waste management, edited by C. M. Jantzen, J. A. Stone and R. C. Ewing (Materials Research Society, Pittsburgh, PA, 1985) pp. 641-646 (1985)
278. N.P. Laverov, S.V. Yudintsev, T.S. Livshits, S.V. Stefanovsky, A.N. Lukinykh, and R.C. Ewing, **“Synthetic Minerals with the Pyrochlore and Garnet Structures for Immobilization of Actinide-Containing Wastes,”** Geochemistry International, 48, 1-14 (2010).
279. R.C. Ewing, W.J. Weber and J. Lian, **“Pyrochlore ( $A_2B_2O_7$ ): A Nuclear Waste Form for the Immobilization of Plutonium and “Minor” Actinides,”** (Focus Review) Journal of Applied Physics, vol. 95, 5949-5971 (2004).
280. P.E.D. Morgan and F.J. Ryerson, **“A new “Cubic” Crystal Compound,”** J. Mater. Sci. Lett, 1, 351-352 (1982).
281. I.A. Sobolev, S.V. Stefanovsky, S.V. Ioudintsev, B.S. Nikonov, B.I. Omelianenko, and A.V. Mokhov, **“Study of Melted Synroc Doped with Simulated High-level Waste,”** Materials Research Society Symposium Proceedings, 465, 363-370 (1997).
282. I.A. Sobolev, S.V. Stefanovsky, B.I. Omelianenko, S.V. Ioudintsev, E.R. Vance, and A. Jostsons, **“Comparative Study of Synroc-C Ceramics Produced by Hotpressing and Inductive Melting,”** Materials Research Society Symposium Proceedings, 465, 371-378 (1997).
283. I. Lian, S.V. Yudintsev, S.V. Stefanovsky, O.I. Kirjanova and R.C. Ewing, **“Ion Induced Amorphization of Murataite,”** Materials Research Society Symposium Proceedings, 713, 455 -460 (2002).
284. V.S. Urusov, N.I. Organova, O.V. Karimova, S.V. Yudintsev, and S.V. Stefanovsky, **“Synthetic “Murataits” as Modular Members of Pyrochlore-Murataite Polysomatic Series,”** Doklady Earth Sciences, **401**(2), 319-25 (2005).
285. S.V. Stefanovsky, S.V. Yudintsev, B.S. Nikonov, O.I. Stefanovsky, **“Rare Earth-Bearing Murataite Ceramics,”** Mater. Res. Soc. Symp. Proc. Vol. 985, Materials Research Society, 175-180 (2007).
286. S.V. Stefanovsky, A.G. Ptashkin, O.A. Knyazev, S.A. Dimitriev, S.V. Yudintsev, and B.S. Nikonov, **“Inductive Cold Crucible Melting of Actinide-bearing Murataite-based Ceramics,”** Journal of Alloys and Compounds, 444, 438-442 (2007).

287. S.V. Stefanovsky, S.V. Yudintsev, S.A. Perevalov, I.V. Startseva, G.A. Varlakova, **“Leach Resistance of Murataite-based Ceramics Containing Actinides,”** Journal of Alloys and Compounds, 444, 618-620 (2007).
288. S.V. Krivovichev, S.V. Yudintsev, S.V. Stefanovsky, N.I. Organova, O.V. Karimova, V. S. Urusov, **“Murataite–Pyrochlore Series: A Family of Complex Oxides with Nanoscale Pyrochlore Clusters,”** Angewandte Chemie International Edition, 49 [51], 9982-9984 (2010).
289. F.W. Clinard Jr., L.W. Hobbs, C.C. Land, D.E. Peterson, D.L. Rohr, R.B. Roof, **“Alpha Decay Self-irradiation Damage in <sup>238</sup>Pu-substituted Zirconolite,”** J. Nucl. Materials, 105, 248-256 (1982).
290. F.W. Clinard Jr., D.E. Peterson, D.L. Rohr, L.W. Hobbs, **“Self-irradiation Effects in <sup>238</sup>Pu-substituted Zirconolite: I. Temperature Dependence of Damage,”** J. Nucl. Mater., 126, 245-254 (1984).
291. K. A. Boulton, J. T. Dalton, J. P. Evans, A. R. Hall, A. J. Inn, J. A. C. Marples and E. L. Paige, **“The Preparation of Fully-active Synroc and its Radiation Stability,”** Report No. AERE-R 13 318 (1987).
292. E.R. Vance, C.J. Ball, R.A. Day, K.L. Smith, M.G. Blackford, B.D. Begg and P.J. Angel, **“Actinide and Rare Earth Incorporation in Zirconolite,”** J. Alloys and Compounds, 213/214, 406-9 (1994).
293. E.R. Vance, P.J. Angel, B.D. Begg and R.A. Day, **“Zirconolite-Rich Titanate Ceramics for High-Level Actinide Wastes,”** in Scientific Basis for Nuclear Waste Management XVII, Eds. R. Van Konynenburg and A.A. Barkatt, Materials Research Society, PA, pp. 293-8 (1994).
294. Y. Zhang, M.W.A. Stewart, H. Li, M.L. Carter, E.R. Vance, S. Moricca, **“Zirconolite-rich Titanate Ceramics for Immobilization of Actinides – Waste form/HIP Can Interactions and Chemical Durability,”** Journal of Nuclear Materials, 395, 69-74 (2009).
295. E.R. Vance, M.L. Carter, Z. Zhang, K.S. Finnie, S.J. Thomson and B.D. Begg, **“Uranium valences in perovskite, CaTiO<sub>3</sub>,”** Environmental Issues and Waste Management Technologies in the Ceramic & Nuclear Industries IX. Ceramic Transactions, pages 3-10 (2004).
296. J.F.W. Bowles, R.A. Howie, D.J. Vaughan, and J. Zussman, **“Rock-Forming Minerals, V5A: Non-Silicates: Oxides, Hydroxides and Sulphides,”** The Geological Society, London, 920pp. (2011).

297. M.L. Carter, E.R. Vance, H. Li, **“Hollandite-rich Ceramic Melts for the Immobilization of Cs,”** Materials Research Society Proceedings, 807, 249-254 (2004).
298. M.L. Carter, E.R. Vance, D.R.G. Mitchell, J.V. Hanna, Z. Zhang, and E. Loi, **“Fabrication, Characterization, and Leach Testing of Hollandite, (Ba,Cs)(Al,Ti)<sub>2</sub>Ti<sub>6</sub>O<sub>16</sub>,”** Journal of Materials Research, 17, 2578-2589 (2002).
299. A.S. Utsonomiya, L.M. Wang, S.V. Yudintsev and R.C. Ewing, **“Ion Irradiation Effects in Synthetic Garnets Incorporating Actinides,”** *Materials Research Society Symposium Proceedings*, 713, 495 -500 (2002).
300. S.V. Yudintsev, **“A Structural-chemical Approach to Selecting Crystalline Matrices for Actinide Immobilization,”** *Geology of Ore Deposits*, 45, 151-165 (2003).
301. S.V. Yudintsev, **“Incorporation of U, Th, Zr, and Gd into the Garnet-structured Host,”** In: Proceedings of the 8th International Conference on Radioactive Waste Management and Environmental Remediation, The American Society of Mechanical Engineers, New York, CD-ROM. (2001).
302. S.V. Yudintsev, M.I. Lapina, A.G. Ptashkin, T.S. Ioudintseva, S. Utsonomiya, M.L. Wang and R.C. Ewing, **“Accommodation of Uranium into the Garnet Structure,”** *Materials Research Society Symposium Proceedings*, 713, 477-480 (2002).
303. W.L. Gong, R.C. Ewing, L.M. Wang and H.S. Xie, **“Crichtonite Structure Type (AM<sub>21</sub>O<sub>38</sub> and A<sub>2</sub>M<sub>19</sub>O<sub>36</sub>) as a Host Phase in Crystalline Waste Form Ceramics,”** *Scientific Basis for Nuclear Waste Management XVIII*, T. Murakami and R.C. Ewing, Eds., Proceedings of the Materials Research Society, vol. 353, 807-815 (1995).
304. I.E. Grey, D.J. Lloyd, J.S. White, Jr., **“The Structure of Crichtonite and its Relationship to Senaite,”** *Am. Mineralogist*, 61, 1203-1212 (1976).
305. E.R. Vance, P.J. Angel, D.J. Cassidy, M.W.A. Stewart, M.G. Blackford and P.A. McGlinn, **“Freudenbergite: A Possible Synroc Phase for Sodium-Bearing High-Level Waste,”** *J. Amer. Ceram. Soc.*, 77, 1576-80 (1994).
306. T. Ishiguro, K. Tanaka, F. Marumo, M.G.M.U. Ismail, S. Hirano, and S. Somiya, **“Freudenbergite,”** *Acta Cryst. B*34, 255-256 (1978).
307. R.C. Ewing, W. Lutze and W.J. Weber, **“Zircon: A host-phase for the disposal of weapons plutonium,”** *Journal of Materials Research*, 10 (2), 243-246 (1995).
308. A. Meldrum, L.A. Boatner and R.C. Ewing, **“A comparison of radiation effects in crystalline ABO<sub>4</sub>-type phosphates and silicates,”** *Mineralogical Magazine*, 64, 185-194 (2000).

309. T.J. Park, S. Li, and A. Navrotsky, **“Thermochemistry of glass forming Y-substituted Sr-analogues of titanite (SrTiSiO<sub>5</sub>),”** Journal of Materials Research, 24, 3380-3386 (2009).
310. Fahey, J.A., Weber, W.J. and Rotella, F.J., **“An X-ray and Neutron Powder Diffraction Study of the Ca<sub>2+x</sub>Nd<sub>8-x</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2-0.5x</sub> System,”** J. Solid State Chem. 60, 145-158 (1985).
311. S. Utsunomiya, S. Yudintsev, L.M. Wang, and R.C. Ewing, **“Ion-beam and Electron-beam Irradiation of Synthetic Britholite,”** Journal of Nuclear Materials, 322, 180-188 (2003).
312. W.J. Weber, **“Alpha-decay-induced Amorphization in Complex Silicate Structures,”** Journal of the American Ceramic Society, 76(7), 1729-38 (1993).
313. W.J. Weber, **“Radiation-induced Swelling and Amorphization in Ca<sub>2</sub>Nd<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>,”** Radiation Effects and Defects in Solids, 77, 295-308 (1983).
314. L. Leo’n-Reina, E.R. Losilla, M. Martı’nez-Lara, S. Bruque, A. Llobet, D.V. Sheptyakov and M. A. G. Aranda, **“Interstitial Oxygen in Oxygen-stoichiometric Apatites,”** J. Mater. Chem., 15, 2489–2498 (2005).
315. A.F. Cronstedt, **“Observation and Description of an Unknown Kind of Rock to be Named Zeolites,”** Kong Vetenskaps Acad. Handl. Stockholm, 12, 120-123 (1756 in Swedish).
316. J.V. Smith, **“Structural Classification of Zeolites,”** Mineral. Soc. Am. Spec. Pap. 1963, 1, 281pp (1963).
317. J.V. Smith, **“Origin and Structure of Zeolites,”** in Zeolite Chemistry and Catalysis (Edited by J. A. Rabo), Vol. 171, A.C.S. Series (1976).
318. D.W. Breck, **“Zeolite Molecular Sieves: Structure, Chemistry and Use,”** John Wiley & Sons, 1974
319. F.M. Higgins, N.H. de Leeuw, and S.C. Parker, **“Modelling the Effect of Water on Cation Exchange in Zeolite A,”** J. Materials Chemistry 12, 124-131 (2002)
320. K.P. Chapman, P. Chupas, and T.M. Nenoff, **“Radioactive Iodine Capture in Silver Loaded Zeolites Through Nanoscale Silver Iodide Formation,”** J. Am. Chem. Soc., 132 [26], 8897-8899 (2010).
321. R.M. Barrer, **“Hydrothermal Chemistry of Zeolites,”** Academic Press, New York, 360pp (1982): see references by St. J. Thugutt, Z. Anorg. Chem, 2, 65 (1892) and E. Flint, W.

- Clarke, E.S. Newman, L. Shartsis, D. Bishop and L.S. Wells, J. Res. Natl. Bur. Stds, 36, 63 (1945).
322. S. A. Gallagher and G. J. McCarthy, **“Preparation and X-ray Characterization of Pollucite ( $\text{CsAlSi}_2\text{O}_6$ )”**, Inorg. Nucl. Chem., 43, 1773–77 (1981).
323. D.M.Strachan and W.W. Schulz, **“Characterization of Pollucite as a Material for Long-Term Storage of Cesium-137,”** Am. Ceram. Soc. Bull., v58 [9], 865-871 (1979).
324. K. Yanagisawa, M. Nishioka, and N. Yamasaki, **“Immobilization of Cesium into Pollucite Structure by Hydrothermal Hot-Pressing”** J. Nucl. Sci. Technol., 24 [1] 51–60 (1987).
325. S. Komameni and W. B. White, **“Stability of Pollucite in Hydrothermal Fluids,”** Sci. Basis Nucl. Waste Management, 3, 387–96 (1981).
326. H. Mimura, M. Shibata, and K. Akiba, **“Surface Alteration of Pollucite Under Hydrothermal Conditions,”** J. Nucl. Sci. Technol., 27, 835–43 (1990).
327. M.D. Kaminski, C.J. Mertz, M. Ferrandon, N.L. Dietz, G. Sandi, **“Physical properties of an Alumino-silicate Waste Form for Cesium and Strontium”** J. Nuclear Materials, 392, 510-518 (2009).
328. D. E. McCready, M. L. Balmer, and K. D. Keefer, **“Experimental and Calculated X-ray Diffraction Data for Cesium Titanium Silicate,  $\text{CsTiSi}_2\text{O}_{6.5}$ : A New Zeolite,”** Powder Diffr., 12 [1] 40–46 (1997).
329. H. Xu, A. Navrotsky, M. L. Balmer, Y. Su, and E. R. Bitten, **“Energetics of Substituted Pollucites Along the  $\text{CsAlSi}_2\text{O}_6$ - $\text{CsTiSi}_2\text{O}_{6.5}$  Join: A High-Temperature Calorimetric Study,”** J. Am. Ceram. Soc., 84 [3] 555–60 (2001).
330. R. G. Anthony, C. V. Phillip, and R. G. Dosch, **“Selective Adsorption and Ion Exchange of Metal Cations and Anions with Silico-Titanates and Layered Titanates,”** Waste Manage., 13, 503–12 (1993).
331. H. Xu, A. Navrotsky, M. D. Nyman, and T. M. Nenoff, **“Thermochemistry of Microporous Silicotitanate Phases in the  $\text{Na}_2\text{O}$ - $\text{Cs}_2\text{O}$ - $\text{SiO}_2$ - $\text{TiO}_2$ - $\text{H}_2\text{O}$  System,”** J. Mater. Res., 15, 815–23 (2000).
332. Y. Su, M. L. Balmer, and B. C. Bunker, **“Evaluation of Cesium Silicotitanates as an Alternate Waste Form,”** Mater. Res. Soc. Symp. Proc., 465, 457–64 (1996).

333. Y. Su, M. L. Balmer, L. Wang, B. C. Bunker, M. Nyman, T. Nenoff, and A. Navrotsky, **“Evaluation of Thermally Converted Silicotitanate Waste Forms,”** Mater. Res. Soc. Symp. Proc., 556, 77–84 (1999).
334. M.L. Balmer and B.C. Bunker, **“Inorganic Ion Exchange Evaluation and Design-Silicotitanate Ion Exchange Waste Conversion”** PNL-10460, Pacific Northwest Laboratory, (1995).
335. T.G. Garino, T.M. Nenoff, T.J. Park, and A. Navrotsky, **“The Crystallization of Ba-Substituted  $\text{CsTiSi}_2\text{O}_{6.5}$  Pollucite using  $\text{CsTiSi}_2\text{O}_{6.5}$  Seed Crystals,”** J. Amer. Cer. Soc., 92(9), 2144-2146 (2009).
336. T-J. Park, T.J. Garino, T.M. Nenoff, D. Rademacher, and A. Navrotsky, **“The Effect of Vacancy and Ba-Substitution on the Stability of the  $\text{CsTiSi}_2\text{O}_{6.5}$  Pollucite,”** J. Amer. Ceram. Soc. 2011, 94(9), 3053-3059.
337. T.J. Garino, D.X. Rademacher, M. Rodriguez, and T.M. Nenoff, **“The Synthesis and Characterization of Ba and Fe Substituted  $\text{CsAlSi}_2\text{O}_6$  Pollucites,”** J. Am. Ceram. Soc, in preparation (2012).
338. W. A. Deer, R. A. Howie, and J. Zussman, **“Rock-Forming Minerals, Vol IV,”** John Wiley & Sons, Inc., New York, 435pp. (1963).
339. L.G. Berry and B. Mason, **“Mineralogy Concepts, Descriptions, Determinations,”** W.H. Freeman & Co., San Francisco, CA, 630pp (1959).
340. R. Klingenberg and J. Felsche, **“Interstitial Cristobalite-type Compounds  $(\text{Na}_2\text{O})_{0.33}\text{Na}[\text{AlSiO}_4]$ ,”** J. Solid State Chemistry, 61, 40-46 (1986).
341. American Mineralogist Crystal Structure Database:  
<http://rruff.geo.arizona.edu/AMS/result.php?mineral=Nepheline>
342. C.M. Jantzen, **“Mineralization of Radioactive Wastes by Fluidized Bed Steam Reforming (FBSR): Comparison to Vitreous Waste Forms, And Pertinent Durability Testing,”** WSRC-STI-2008-00268, Savannah River National Laboratory (2008).
343. J.G. Kim, J.H. Lee, I.T. Kim, and E.H. Kim, **“Fabrication of a Glass-Bonded Zeolite Waste Form for Waste  $\text{LiCl}$  Salt,”** J. Ind. Eng. Chem., Vol. 13, No. 2, 292-298 (2007).
344. D.G. Brookins, **“Geochemical Aspects of Radioactive Waste Disposal,”** Springer-Verlag, New York, 347pp. (1984).
345. J.Ch. Buhl, G. Englehardt, and J. Felsche, **“Synthesis, X-ray Diffraction, and MAS n.m.r. Characteristics of Tetrahydroxoborate Sodalite,”** Zeolites, 9, 40-44 (1989).



346. M.E. Fleet, **“Structures of Sodium Alumino-Germanate Sodalites,”** Acta Cryst., C45, 843-847 (1989).
347. S.V. Mattigod, B.P. McGrail, D.E. McCready, L.Wang, K.E. Parker and J.S. Young, **“Synthesis and Structure of Perrhenate Sodalite,”** J. Microporous & Mesoporous Materials, 91 (1-3), 139-144 (2006).
348. Zeolite structural information from the International Zeolite Association (IZA) website <http://www.iza-structure.org/databases/see> : sodalite (SOD)
349. H.F. McFarlane, K.M. Goff, F.S. Felicione, C.C. Dwight, and D.B. Barber, **“Hot Demonstrations of Nuclear-Waste Processing Technologies”**, JOM, 49(7), p. 14-21, 83 (1997).
350. A.L. Olson, N.R. Soelberg, D.W. Marshal, and G.L. Anderson, **“Fluidized Bed Steam Reforming of INEEL SBW Using THOR Mineralizing Technology”**, INEEL/EXT-04-02564, Idaho National Laboratory (2004).
351. T. Nakazawa, H. Kato, K. Okada, S. Ueta, and M. Mihara, **“Iodine Immobilization by Sodalite Waste Form,”** Materials Research Society Symposium Proceedings, 663, 51-57 (2001).
352. W.A. Deer, R.A. Howie, W.S. Wise, and J. Zussman, **“Rock-Forming Minerals, Vol. 4B, Framework Silicates: Silica Minerals, Feldspathoids and the Zeolites,”** The Geological Society, London, UK, 982pp (2004).
353. Zeolite structural information from the International Zeolite Association (IZA) website <http://www.iza-structure.org/databases/> see: Cancrinite (CAN)
354. R.G. Anthony, C.V. Philip and R.G. Dosch, **“Selective Adsorption and Ion Exchange of Metal Cations and Anions with Silico-titanates and Layered Titanates”** Waste Management, 13, 503-512 (1993).
355. J.E. Miller, and N.E. Brown, **“Development and Properties of Crystalline Silicotitanate (CST) Ion Exchangers for Radioactive Waste Applications”** Sandia National Laboratories, SAND97-0771 (1997).
356. M.K. Andrews, and J. Harbour, **“Glass Formulation Requirements for Hanford Coupled Operations Using Crystalline Silicotitanates (CST)”** WSRC-RP-97-0265 (1997).
357. M.D. Nyman, T.M. Nenoff, and T.J. Headley, **“Characterization of UOP IONSIV IE-911”**. Sandia National Laboratories, SAND2001-0999 (2001).

358. B. Yu, J. Chen, and C. Song, **“Crystalline Silicotitanate: A New Type of Ion Exchanger for Cs Removal from Liquid Waste”**, J. Mater. Sci. Technol., 18(3), 206-210 (2002)
359. A. Tripathi, D.G. Medvedev, M. Nyman, and A. Clearfield, **“Selectivity for Cs and Sr in Nb-Substituted Titanosilicate with Sitinakite Topology,”** J. Solid State Chem., 175, 72-83 (2003).
360. H. Keppler, **“Ion Exchange Reactions Between Dehydroxylated Micas and Salt Melts and the Crystal Chemistry of the Interlayer Cation in Micas,”** Am. Min. V. 75, 529-538 (1990).
361. C.M. Jantzen, M.R. Williams, N.E. Bibler, C.L. Crawford, and A.R. Jurgensen, **“Fluidized Bed Steam Reformed (FBSR) Mineral Waste Forms: Application to Cs-137/Sr-90 Wastes for the Global Nuclear Energy Partnership (GNEP),”** U.S. DOE Report WSRC-MS-2008-00013 (March 2008).
362. C.M. Jantzen and M.R. Williams, **“Fluidized Bed Steam Reforming (FBSR) Mineralization for High Organic and Nitrate Waste Streams for the Global Nuclear Energy Partnership (GNEP),”** WM08, Paper #8314 (2008).
363. M.E. Fleet, **“Rock-Forming Minerals: Sheet Silicates: Micas,”** V. 3A, The Geological Society, London, 758pp. (2003).
364. L.A. Boatner and B.C. Sales, **“Monazite,”** In Radiation Waste Forms for the Future, Eds. W. Lutze and R.C. Ewing, Amsterdam, Holland, North-Holland Press, 495-564 (1988).
365. J.M. Montel, B. Glorieux, A.M. Seydoux-Guillaume, and R. Wirth, **“Synthesis and Sintering of a Monazite-brabantite Solid Solution Ceramic for Nuclear Waste Storage,”** Journal of Physics and Chemistry of Solids, 67, 2489-2500 (2006).
366. B. Glorieux, J.M. Montel and M. Matecki, **“Synthesis and Sintering of a Monazite-brabantite Solid Solution Ceramics Using Metaphosphate,”** Journal of the European Ceramic Society, 29, 1679-1686 (2009).
367. Y.J. Zhang and E.R. Vance, **“Plutonium in Monazite and Brabantite: Diffuse Reflectance Spectroscopy Study,”** Journal of Nuclear Materials, 375, 311-314 (2008).
368. R.C. Ewing, W.J. Weber, and W. Lutze, **“Crystalline Ceramics: Waste Forms for the Disposal of Weapons Plutonium,”** in Disposal of Ex-weapons Plutonium as Waste,” E.R. Merz and C.E. Walter (Eds.), NATIO ASI Series, Kluwer Academic Publishers, Dordrecht, The Netherlands, 65-83 (1996).

369. L.L. Y. Chang, R.A. Howie, J. Zussman, **“Rock Forming Minerals, V.5B NonSilicates: Sulphates, Carbonates, Phosphates, Halides,”** The Geological Society, London, 383pp. (1998)
370. J.Y. Kim, Z.L. Dong, and T.J. White, **“Model Apatite Systems for the Stabilization of Toxic Metals: II, Cation and Metalloid Substitutions in Chlorapatites,”** Journal of the American Ceramic Society, 88, 1253-1260 (2005).
371. H.S. Park, I.T. Kim, H.Y. Kim, K.S. Lee, S.K. Ryu, and J.H. Kim **“Application of Apatite Waste Form for the Treatment of Water-soluble Wastes Containing Radioactive Elements. Part 1: Investigation on the Possibility,”** Journal of Industrial and Engineering Chemistry, 8, 318-327 (2002).
372. W.J. Weber, R.C. Ewing and A. Meldrum, **“The Kinetics of Alpha-decay-induced Amorphization in Zircon and Apatite Containing Weapons-grade Plutonium or Other Actinides,”** Journal of Nuclear Materials 250(2-3), 147-55 (1997).
373. J. Carpena, and J.L. Lacout, **“Calcium Phosphate Nuclear Materials: Apatitic Ceramics for Separated Wastes,”** Actualite Chimique, pages 66-71 (2005).
374. J. Carpena, B. Donazzon, E. Ceraulo, and S. Prene, **“Composite Apatitic Cement as a Material to Retain Cesium and Iodine,”** Comptes Rendus de L Academie Des Sciences Serie II Fascicule C-Chimie, 4, 301-308 (2001).
375. F.J. Audubert, J.L. Lacout, and F. Tetard, **“Elaboration of an Iodine-Bearing Apatite Iodine Diffusion into a  $Pb_3(VO_4)_2$  Matrix,”** Solid State Ionics, 95 [1-2], 113-119 (1997).
376. W.J. Weber, **“Radiation Damage in Rare-earth Silicate with the Apatite Structure,”** J. Am. Ceram. Soc., 65, 544-548 (1982).
377. W.J. Weber, R.P. Turcotte, L.R. Bunnell, F.P. Roberts, and J.H. Westsik, Jr., **“Radiation Effects in Vitreous and Devitrified Simulated Waste Glass (Contains Apatite),”** Proceedings International Symposium on Ceramics in Nuclear Waste Management; CONF-790420, U.S. DOE, Cincinnati, Ohio, 294-299 (1979).
378. L. Boyer, J. Carpena, and J.L. Lacout, **“Synthesis of Phosphate-Silicate Apatites at Atmospheric Pressure,”** Solid State Ionics, 95 [1-2], 121-129 (1997).
379. R. Bros, J. Carpens, V. Sere, and A. Beltritti, **“Occurrence of Plutonium and Fissiogenic REE in Hydrothermal Apatites from the Nuclear Reactor 16 at Oklo (Gabon),”** Radiochimica Acta, 74, 277-282 (1996).
380. J.C. Elliott, R.M. Wilson and S.E.P. Dowker, **“Apatite Structures,”** Advances in X-ray Analysis, 45, 172-181 (2002).

381. B.E. Scheetz and R. Roy, **"Novel Waste Forms,"** In Radioactive Waste Forms for the Future. W. Lutze and R. C. Ewing. Amsterdam, North-Holland, 596-9 (1988).
382. A.I. Orlova, Y.F. Volkov, R.F. Melkaya, L.Y. Masterova, I.A. Kulikov, and V.A. Alferov, **"Synthesis and Radiation Stability of NZP Phosphates Containing F-elements,"** Radiochemistry 36(4), 322-5(1994).
383. B.E. Scheetz, D.K. Agrawal, E. Breval and R. Roy, **"Sodium Zirconium-phosphate (NZP) as a Host Structure for Nuclear Waste Immobilization – A Review,"** Waste Management, 14, 489-505 (1994).
384. H.T. Hawkins, B.E. Scheetz, and G.D. Guthrie, Jr., **"Preparation of Monophasic [NZP] Radiophases: Potential Host Matrices for the Immobilization of Reprocessed Commercial High-Level Wastes,"** Material Research Society Symposium Proceeding 465, Pittsburgh, PA, Scientific Basis for Nuclear Waste Management. XX, 387-394 (1997).
385. R. Roy, E.R. Vance and J. Alamo, **"[NZP], A New Radiophase for Ceramic Nuclear Waste Forms"**, Mater. Res. Bull., 17, 585-9 (1982).
386. V. N. Zyryanov and E. R. Vance, **"Comparison of Sodium Zirconium Phosphate-Structured HLW forms and Synroc for High-Level Nuclear Waste Immobilization"**, Scientific Basis for Nuclear Waste Management XX, Ed. W. J. Gray and I.R. Triay, Materials Research Society, PA., pp. 409-16 (1997).
387. E. Pichot, N. Dacheux, V. Brandel, M. Genet, **"Investigation of Cs-137(+), Sr-85(2+) and Am-241(3+) Ion Exchange on Thorium Phosphate Hydrogenphosphate and their Immobilization in the Thorium Phosphate Diphosphate,"** New Journal of Chemistry, 24, 1017-1023 (2000).
388. N. Dacheux, R. Podor, V. Brandel, and M. Genet, **"Investigations of systems ThO<sub>2</sub>-MO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> (M=U, Ce, Zr, Pu). Solid Solutions of Thorium-Uranium(IV) and Thorium-Plutonium(IV) Phosphate-diphosphates,"** Journal of Nuclear Materials 252(3), 179-86 (1998).
389. N. Dacheux, R. Podor, B. Chassigneux, V. Brandel, and M. Genet, **"Actinides Immobilization in New Matrices Based on Solid Solutions: Th<sub>4-x</sub>M<sub>x</sub><sup>IV</sup>(PO<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, (M-IV = U-238, Pu-239),"** Journal of Alloys and Compounds 271, 236-9 (1998).
390. P. Bénard, V. Brandel, N. Dacheux, S. Jaulmes, S. Launay, C. Lindecker, M. Genet, D. Louër, M. Quarton, **"Th<sub>4</sub>(PO<sub>4</sub>)<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, a New Thorium Phosphate: Synthesis, Characterization, and Structure Determination,"** Chem. Mater. 8 [1], 181-188 (1996).
391. P.E.D. Morgan, D.R. Clarke, C.M. Jantzen and A.B. Harker, A.B., **"High Alumina Tailored Nuclear Waste Ceramics,"** J. Am. Ceram. Soc., 64[5], 249-258 (1981).

- 392. A.B. Harker, C.M. Jantzen, D.R. Clarke and P.E.D. Morgan, "**Tailored Ceramic Nuclear Waste Forms: Preparation and Characterization,**" Sci. Basis for Nuclear Waste Management, III, J.G. Moore (ed.), Plenum Press, New York, 139-146 (1981).
- 393. P.E.D. Morgan and E.H. Cirlin, "**The Magnetoplumbite Crystal Structure as a Radwaste Host,**" J. Am. Ceram. Soc., 65 [7], C114-C115 (1982).
- 394. W.D. Townes, J.H. Fang and A.J. Perrotta, A.J., "**The Crystal Structure and Refinement of Ferromagnetic Barium Ferrite,  $\text{BaFe}_{12}\text{O}_{19}$ ,**" Z. Kristallogr. 125, 437-49 (1967).
- 395. R.E. Grim, "**Clay Mineralogy,**" Science, 135, #3507, 890-898 (1962).
- 396. R.E. Grim, **Clay Mineralogy,** McGraw Hill Book Company, Inc., 384 (1953).
- 397. C.M. Jantzen and W.G. Ramsey, "**Prediction of Radioactive Waste glass Durability by the Hydration Thermodynamic Model: Application to Saturated Repository Environments,**" Scientific Basis for Nuclear Waste Management, XIII, V.M. Oversby and P.W. Brown (Eds.), Materials Research Society, Pittsburgh, PA, 217-228 (1990).