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A glass-encapsulated calcium phosphate wasteform for the immobilization of actinide-, fluoride-, and chloride-containing radioactive wastes from the pyrochemical reprocessing of plutonium metal

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Abstract

Chloride-containing radioactive wastes are generated during the pyrochemical reprocessing of Pu metal. Immobilization of these wastes in borosilicate glass or Synroc-type ceramics is not feasible due to the very low solubility of chlorides in these hosts. Alternative candidates have therefore been sought including phosphate-based glasses, crystalline ceramics and hybrid glass/ceramic systems. These studies have shown that high losses of chloride or evolution of chlorine gas from the melt make vitrification an unacceptable solution unless suitable off-gas treatment facilities capable of dealing with these corrosive by-products are available. On the other hand, both sodium aluminosilicate and calcium phosphate ceramics are capable of retaining chloride in stable mineral phases, which include sodalite, $Na_8(AlSiO_4)_6Cl_2$, chlorapatite, $Ca_5(PO_4)_3Cl$, and spodiosite, $Ca_2(PO_4)Cl$. The immobilization process developed in this study involves a solid state process in which waste and precursor powders are mixed and reacted in air at temperatures in the range 700–800 °C. The ceramic products are non-hygroscopic free-flowing powders that only require encapsulation in a relatively low melting temperature phosphate-based glass to produce a monolithic wasteform suitable for storage and ultimate disposal.

1. Introduction

The immobilization of radioactive wastes in glass and ceramic hosts has been under investigation worldwide for over 40 years [1]. Most work in this area has been aimed at the development of candidates for the immobilization of high level waste, HLW, from the nuclear power and defence industries. Wastes from the reprocessing of spent nuclear fuel contain high concentrations of fission products, which make them highly radioactive, together with impurities from the fuel cladding, transuranic elements formed by neutron capture, and traces of unseparated Pu. Defence wastes, generated during

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the manufacture of Pu metal after separation of Pu from irradiated fuel, are less radioactive as they generally contain fewer fission products. This worldwide work culminated in the choice of borosilicate glass as the first generation wasteform for the immobilization of these wastes. As a result of this decision, many commercial waste vitrification plants are now in operation throughout the world, with major plants in the UK, France, USA, Russia, China, and India. Borosilicate glass was chosen as the first generation wasteform for many reasons. In particular, because it is already an established commercial material an extensive technological base exists on the manufacture and properties of this type of glass. It is also an excellent solvent for most HLW constituents; it is reasonably tolerant of variations in waste stream composition; it is relatively easy to manufacture; and it possesses acceptable thermal, mechanical, chemical and radiological characteristics.

In more recent years there has been an increased interest in the immobilization of special categories of waste arising, for example, from the pyrochemical reprocessing of plutonium metal [2–4]. These wastes differ significantly from those produced during the reprocessing of spent nuclear fuel and from most defence wastes in that not only do they contain significant quantities of actinides but, due to the nature of the processes, they also contain high concentrations of halides, in particular chlorides. Vitrification, employing alkali borosilicate glass as the host for these pyrochemical wastes, is not suitable due to the low solubilities of the actinide and chloride ions in these glasses. Alternative wasteform candidates must, therefore, be sought for this special type of waste.

2. Candidates for the immobilization of actinide- and chloride-containing wastes

2.1. Glasses

The solubility of actinides and chlorides in silicate-based glasses is relatively low, usually <5% for actinides and <1.5% for chlorides, and therefore these glasses are not generally suitable for the immobilization of waste streams containing significant quantities of these elements. Certain lanthanide borosilicate and alkali tin silicate-based glasses have, however, been proposed for immobilizing actinides, as these glasses do apparently exhibit a higher solubility for actinide elements [5]. Certain glass–ceramic hosts have also been proposed [6]. More recently, calcium aluminosilicate glasses have been suggested for treating chloride-containing incinerator wastes [7–9]. It was noted that, by melting under a reducing atmosphere, $CaCl_2$ could be incorporated at concentrations of approximately 10 mol%. The glasses obtained had unsuitable properties, however, because the glasses reacted not only with water and oxygen present in the atmosphere, but also with water present in the glass itself (and possibly by redox reactions directly between the chloride and oxide species present in the glass). These reactions could result in the evolution of chlorine and hydrogen chloride [10]. The unstable nature of these glasses renders them unsuitable for radioactive waste disposal, since the main goal of waste disposal is to control the release of radionuclides to the environment.

Phosphate-based glasses were originally investigated as potential hosts for spent nuclear fuel waste, but general interest declined because these early glasses had poor durability and the melts were generally highly corrosive. These unfavourable attributes outweighed their advantages of lower melt temperatures and lower viscosity relative to borosilicate glasses. Early work had shown, however, that aluminium phosphate glasses were durable [11], and in the former USSR sodium aluminium phosphate glasses were developed for immobilizing sulphate-containing wastes. It was noted that these glass compositions exhibited excellent durability, although their melts are still relatively corrosive to the melter refractory (e.g., [12]). More widespread interest in phosphate-based glasses was renewed with new compositions based on the lead iron phosphate system that offered improvements in durability and that resulted in melts with considerably less refractory corrosion [12–14]. More recently, glass compositions based on iron phosphate [15–17] have also been proposed as an alternative host to borosilicate glass for the vitrification of HLW which contains relatively high concentrations of actinide elements, the solubility of actinides in these glasses being higher than that of silicate-based glasses. It has been suggested that these glasses may also be suitable for immobilizing chloride-containing wastes [16].

In the case of halides, as an alternative approach to chemically immobilizing these anions in a primary host, treatments have been proposed that convert them into a non-radioactive volatile species, which can be driven off, collected, and disposed of separately. For example, it has been noted that lead silicate-based glasses may be suitable for treating wastes containing actinide chlorides, the chloride ions not being retained within the wasteform, but rather evolved from the melt as volatile lead chloride [18], as given by

$$3PbO + 2PuCl_3 \rightarrow 3PbCl_2\uparrow + Pu_2O_3 \tag{1}$$

It has also been noted that the metallic species of heavy metal chlorides can be converted into phosphate glasses or salts with ammonium dihydrogen phosphate as a precursor. In this method the chloride is volatilized off as ammonium chloride, leaving the heavy metals behind either as a vitrified wasteform or phosphate salts that can be incorporated into a silicate glass [19–21], according to the reaction

$$\begin{aligned}2NH_4H_2PO_4 + MCl_2 &\rightarrow MO\cdot P_2O_{5(\text{glass})}\\ &+ 2NH_4Cl\uparrow + 2H_2O\uparrow\end{aligned} \tag{2}$$

In Russia, phosphoric acid has also been proposed as a precursor for the treatment of chloride-containing wastes obtained from the pyrochemical reprocessing of spent reactor fuel [22]. The products include a metal phosphate glass, hydrogen chloride and water (where M is an alkali metal), as given by

$$MCl + H_3PO_4 \rightarrow MPO_3 + HCl\uparrow + H_2O\uparrow \tag{3}$$

A further method suggested for the treatment of pyrochemical salt wastes is oxidation of the chlorides by reaction at high temperature with steam. The chloride salts are converted to the metal oxide and hydrogen chloride [23], as given by

$$2MCl + H_2O \rightarrow M_2O + 2HCl\uparrow \tag{4}$$

The oxides are subsequently immobilized as a glass. It was noted that in order to achieve a practical conversion efficiency of chloride to oxide by this method temperatures in the range 900–1000 °C were necessary and it was essential to add B_2O_3 to the salt in order to increase the oxidation rate. The conversion of metal chlorides into oxides with B_2O_3 has also been investigated by Ikeda et al. [24] as a method for vitrifying radioactive salt wastes.

All these methods suffer from the distinct disadvantage that, depending on the specific process, a volatile secondary waste is generated. This secondary waste, while potentially non-radioactive, does require further processing that adds to the overall cost of a waste processing facility. Because of the corrosive nature of these volatile chlorides, suitable off-gas treatment facilities are needed, and plenums must be made from materials compatible with chlorides at elevated temperatures. These also add significant cost to the facility. Therefore, a desirable wasteform characteristic is the immobilization of chloride directly.

It has also been proposed recently [25] that chloride wastes may be dissolved in aqueous solution and the Cl component precipitated out as AgCl which can be removed and treated separately. The remaining constituents of the waste may then be vitrified in a borosilicate glass.

2.2. Ceramics

It is well known that certain ceramic materials can be successfully employed to immobilize actinides, but fewer data are available on the immobilization of chloride-containing radioactive wastes. In the case of actinides, synroc (synthetic rock), zirconolite, zircon, gadolinium zirconate and rare earth silicate apatites have all been proposed for immobilizing high actinide wastes, and even surplus weapons-grade plutonium e.g., [26–28]. There are fewer crystalline mineral systems offering promise for the immobilization of chloride-containing wastes, although many minerals may contain Cl [25]. These include a variety of silicates, vanadates, selenates, tungstates, chromates and niobates. Of the minerals that incorporate Cl, potentially viable systems include zeolite-based and calcium phosphate-based phases. Zeolites have been extensively studied in the US as candidates for immobilizing chloride pyrochemical wastes generated during the reprocessing of fuel from experimental breeder reactor programmes [29,30]. These high level wastes contain a selection of fission products, including Cs, Sr and Ba, and actinides, including Pu, Am and Np. Although the chloride ions are not chemically bonded in zeolites and would be expected to be relatively easily ion exchanged or released by ion exchange, the zeolite structure can be transformed by heating to form the mineral phase sodalite, ideally $Na_8(AlSiO_4)_6Cl_2$, which exhibits a higher chloride retention [29,30]. As an alternative to zeolites, we have at AWE (Atomic Weapons Establishment), shown that calcium chloro-phosphates are excellent hosts for both actinide and chloride species [2,31–33].

2.3. Hybrid glass/ceramic systems

To be a viable wasteform, a monolithic form is usually required because the high surface area of a powder results in proportionately higher release rates if water comes in contact with the disposed wasteform. For actinide-bearing wasteforms, nuclear criticality, both as-produced and moderated with water, is important for worker and public safety. Therefore, it is highly desirable to have a monolithic wasteform that is passively safe, i.e., criticality safe when stacked in an infinite array and fully moderated with water. Because the decay of actinides (alpha decay) and the resulting recoiling atom causes extensive damage to atomic structures of a crystalline wasteform containing actinides [34], it is also desirable to have a wasteform whose chemical and physical properties do not degrade significantly with the in-growth of radiation-induced damage. Thus, significant demands are placed on the behaviour of a potential wasteform that will be used to immobilize any particular waste. Thus, where a ceramic or glass system separately is not a viable wasteform that meets all the necessary criteria, e.g., a monolith which is passively safe, chemically and radiologically stable, and with adequate durability, it may be possible to combine the two to form a useful final product. This has been shown possible in the cases of the zeolite [35–43] and calcium phosphate [44–49] hosts, that are produced as particulate products, and are subsequently encapsulated in a glassy matrix, which serves to bind the particles together and yield a viable monolithic wasteform. More recently, glass matrix composites have been proposed for actinide-containing wastes in which actinide-containing pyrochlore crystals are dispersed in a borosilicate glass matrix [50].

2.4. Cements

Conventional silicate-based cements are not generally considered suitable for immobilizing wastes containing substantial quantities of actinides or chlorides because cements typically have poor leach resistance and, because of the incorporated radionuclides and the hydrous nature of concrete, many radiolysis reactions can take place that either degrade the cement matrix or generate hydrogen. Chemically bonded phosphate-based cements ('ceramicrete'), originally proposed for immobilizing low level waste, LLW, [51] have recently been proposed for immobilizing TRU wastes that contain significant concentrations of actinides [52]. They have also been proposed as suitable hosts for immobilizing non-radioactive wastes and mixed wastes [53,54]. It has been noted that most of the combined water can be removed from this product, but radiolysis must still be regarded as an issue and, in our experience, the stability of the dehydrated wasteform is open to question.

2.5. Selection of suitable candidates

At AWE, we have studied the feasibility of employing zeolites, calcium phosphate ceramics, phosphate-based glasses, glass-encapsulated systems, and chemically bonded phosphates as immobilization hosts for a number of different wastes that are generated during the pyrochemical reprocessing of Pu metal and contain significant quantities of both actinide and chloride species. This work has culminated in the choice of glass-encapsulated calcium chloro-phosphate as the preferred candidate for immobilizing these special wastes. Details of waste compositions and the experimental programme to develop a suitable calcium phosphate-based system are outlined below.

3. Waste stream compositions

In the initial phases of this work, generic non-radioactive simulated waste compositions were employed to represent a number of specific radioactive waste streams generated during the pyrochemical reprocessing of plutonium metal. The first, designated Type I, was a simple waste stream consisting of a 4:1 blend (by mass) of calcium and samarium chlorides, the samarium chloride employed as a surrogate for plutonium and americium chlorides present in the actual waste, i.e., $PuCl_3$ (Pu^{3+}) and $AmCl_3$ (Am^{3+}). The additional waste streams, designated Types II, III and IV, are more complex, with the compositions given in Table 1. For these, HfO_2 was used as a surrogate for PuO_2 (Pu^{4+}) and Sm_2O_3 for Am_2O_3 (Am^{3+}).

4. Experimental

4.1. Preparation of samples

4.1.1. Calcium phosphate ceramics

The non-radioactive simulated Type I waste was incorporated into a calcium phosphate-based host

Table 1
Compositions of the non-radioactive simulated waste streams

Component (mass %)	Type I	Type II	Type III	Type IV
Oxides				
HfO_2 (as a surrogate for Pu^{4+})	–	20.7	62.2	11.4
Ga_2O_3	–	28.0	9.4	10.5
Al_2O_3	–	9.8	1.7	2.2
Sm_2O_3 (as a surrogate for Am^{3+})	–	4.6	11.7	1.0
MgO	–	6.3	–	10.1
FeO	–	1.3	–	0.7
Ta_2O_5	–	1.3	–	0.7
NiO	–	1.3	–	0.7
ZnO	–	–	–	35.7
SiO_2	–	–	–	0.8
B_2O_3	–	–	–	0.8
Halides				
$CaCl_2$	80.0	–	–	–
$SmCl_3$ (as a surrogate for Pu^{3+} and Am^{3+})	20.0	–	–	–
CaF_2	–	10.4	5.0	8.5
KCl	–	16.3	10.0	16.9

by reacting the simulant waste powders (Table 1) with $Ca_3(PO_4)_2$ at 750–800 °C in air. The product of this reaction is a free-flowing, non-hygroscopic powder with a particle size <10 μm, in which the waste constituents are chemically immobilized in a mixture of chlorapatite, $Ca_5(PO_4)_3Cl$, and spodiosite, $Ca_2(PO_4)Cl$, mineral phases. After preparation, the powders produced were washed in demineralized water to determine the washable chloride content (i.e., the amount of chloride that had not reacted and, therefore, had not been immobilized).

Initially, Type II waste was reacted with $Ca_3(PO_4)_2$ together with additional P_2O_5 to provide sufficient phosphate ions for charge balance; however, as P_2O_5 is extremely hygroscopic, $CaHPO_4$ was substituted for both P_2O_5 and $Ca_3(PO_4)_2$. The standardized procedure for Type II, III and IV wastes was to react them with $CaHPO_4$ at 750 °C in air for 4 h. These more complex wastes tended to produce different mixtures of phases. Type II waste reacted to produce a phase indexed to a chloride substituted fluorapatite ($Ca_5(PO_4)_3F_{0.9}Cl_{0.1}$) in addition to β-$CaP_2O_7$. When P_2O_5 was used in the starter reagents, an additional phase was formed which was indexed to $Ca_{2.81}Mg_{0.19}(PO_4)_2$ but is likely be a substituted whitlockite, $Ca_3(PO_4)_2$. On calcination, Type III waste yielded chlorapatite and spodiosite, while Type IV waste gave phases which were indexed to a chloride substituted fluorapatite and $Ca_3(PO_4)_2$.

4.1.2. Phosphate-based glasses

Phosphate-based glasses were initially investigated to assess their suitability as either solvents for the chloride-containing wastes or as encapsulants for the calcium phosphate ceramic host. Glasses were prepared by melting the appropriate constituents in alumina crucibles at 1250 °C in air. The glasses were quenched into deionized water and the resulting frit dried and remelted in order to improve the homogeneity of the final product. Based on their thermal characteristics and durability in water, selected glasses were then subjected to more detailed examination. Of the many compositions investigated, the sodium aluminium phosphate glasses were selected for the most intense study. Some compositions were also examined from the strontium zinc phosphate and copper erbium phosphate systems (Table 2).

Table 2
Compositions of selected sodium aluminium phosphate-based glasses (nominal mol%)

Glass	Na_2O	Al_2O_3	P_2O_5	Fe_2O_3	ZnO	B_2O_3	SrO	CuO	Er_2O_3
NaAlP	40.8	19.4	39.8	–	–	–	–	–	–
NaAlP-Fe1	37.9	18.1	40.5	3.5	–	–	–	–	–
NaAlP-Fe2	36.4	17.4	40.9	5.3	–	–	–	–	–
NaAlP-Fe3	34.9	16.6	41.3	7.2	–	–	–	–	–
NaAlP-Fe4	33.2	15.9	41.7	9.2	–	–	–	–	–
NaAlP-FeB	29.7	14.2	37.3	8.2	–	10.6	–	–	–
NaAlP-Zn	23.3	11.1	33.5	–	32.1	–	–	–	–
NaAlP-B1	40.6	19.3	39.6	–	–	0.5	–	–	–
NaAlP-B2	40.4	19.2	39.4	–	–	1.0	–	–	–
NaAlP-B3	40.2	19.1	39.2	–	–	1.5	–	–	–
NaAlP-B4	40.0	19.0	39.0	–	–	2.0	–	–	–
NaAlP-B5	38.7	18.5	37.8	–	–	5.0	–	–	–
NaAlP-B6	36.7	17.5	35.8	–	–	10.0	–	–	–
SrZnP	–	–	50.0	–	25.0	–	25.0	–	–
CuErP	–	–	65.0	–	–	–	–	31.0	4.0

Experiments aimed at establishing the maximum amount of chloride that could be incorporated into some of these glasses were performed by mixing the glass frit with calcium chloride powder and melting in alumina crucibles. Melting schedules were adjusted according to the viscosity of the melt and the observed volatility.

4.1.3. Sintering trials

Sintering trials were conducted with ceramic powder both with and without the addition of a glass binder. Where glass binder was utilised, the amount of glass used ranged between 10 and 35 mass% and the particle size of glass encapsulant was varied from <45 μm to ≈150 μm. Cold pressed samples were prepared by adding 10 mass% water as a binder to the glass/ceramic powder mixture then pressing at 69 MPa. The resulting pellets were dried overnight at 40 °C and then sintered in air at temperatures in the range 650–850 °C. Samples were also produced by pressureless consolidation with loose glass/ceramic powder mixtures lightly tamped into cylindrical crucibles.

4.2. Characterization of samples

The thermal characteristics of the glasses were determined employing a Netzsch differential scanning calorimeter (Model DSC 404S) at a standard heating rate of 10 K min^{-1}. Identification of the crystalline phases present in the ceramic samples was performed with powder X-ray diffraction using a Philips PW-1700 powder diffractometer with Cu Kα radiation.

A qualitative assessment of the durability of the candidate glasses in deionized water at 70 °C for 28 days was made, for screening purposes, by monitoring the mass loss of crushed glass samples of particle size 600–1000 μm.

A quantitative assessment of the chemical durability in aqueous solution of waste loaded calcium phosphate samples and glass-encapsulated samples was carried out employing a test with powder rather than monolithic specimens. This type of test was used, rather than the traditional MCC-1 or PCT, because of the limited amount of sample, especially those containing ^{238}Pu, and to obtain multiple results from a single test specimen. In this test, a leachant-to-solids mass ratio of 100 was used. The powder samples (1 g) of known surface area were immersed in a known quantity (100 mL) of deionized water at 40 °C in a PFA Teflon vessel. At specified periods, 10 mL of leachate was removed from the vessel and replaced with 10 mL of fresh leachant. Each 10 mL aliquot and the final leachate were analyzed with inductively-coupled plasma – mass spectroscopy or optical emission spectroscopy, ICP/MS or ICP/OES. The chloride concentration was measured with a chloride-specific ion electrode. Powder surface areas were measured by the BET method. Normalized elemental mass losses for each element, N_i, were calculated from the expression

$$N_i = m_i/(Sf_i), \tag{5}$$

where m_i is the mass of element i in the leachant, S is the surface area of the sample, and f_i is the fraction of element i in the sample.

4.3. Radioactive studies

Samples containing radioactive simulated Type I and Type II wastes have also been prepared and characterized. In the case of the simple Type I waste, a mixture of $^{239}PuCl_3$ and $^{241}AmCl_3$ was substituted on a mass basis for some of the $SmCl_3$, whilst for the Type II waste PuO_2 was substituted, again on a mass basis, for the HfO_2 and Am_2O_3 and for the Sm_2O_3. Because of the strong gamma ray emission during the radioactive decay of ^{241}Am only a fraction of the $SmCl_3$ or Sm_2O_3 was replaced by the corresponding Am compound (to give 0.4 mass% Am in the test specimens, with the balance as Sm_2O_3). Type I waste samples were also prepared substituting the short lived ^{238}Pu isotope for ^{239}Pu in order to assess the influence of radiation-induced damage on the structure and properties of the calcium phosphate mineral phases. More recently, ^{238}Pu has also been substituted into the Type II waste loaded calcium phosphate and in the glass-encapsulated product. These specimens were just recently prepared and so are not discussed further in this article. Work with ^{238}Pu- and ^{239}Pu-bearing materials was carried out at the Pacific Northwest National Laboratory (PNNL, Richland, WA, USA). A Scintag PAD V X-ray diffractometer with Cu Kα radiation was used. The same dissolution test was employed to assess the durability of these products.

5. Results and discussion

5.1. Calcium phosphate ceramics

Apatite belongs to the group of naturally occurring minerals of general formula, $M_{10}(XO_4)_6$-(O, OH, F, Cl)$_2$, where M may usually be a variety of 1–3 valent cations including Na, Ca, Ba, Pb, Sr, La, Ce etc., and X is commonly P, V or As [55]. Chlorapatite may be formed synthetically by reacting calcium phosphate with calcium chloride [56], according to the reaction

$$3Ca_3(PO_4)_2 + CaCl_2 \rightarrow 2Ca_5(PO_4)_3Cl \tag{6}$$

A maximum theoretical calcium chloride loading of ≈10.5 mass% (6.2% Cl) is possible. Additional calcium chloride, up to a total of ≈26 mass% (16.8% Cl), may be accommodated through further reaction of $CaCl_2$ with chlorapatite to form spodiosite, as given by

$$Ca_5(PO_4)_3Cl + CaCl_2 \rightarrow 3Ca_2(PO_4)Cl \tag{7}$$

For a loading of 20 mass% calcium chloride (taken as an arbitrary upper limit), a mixture of chlorapatite and spodiosite phases is expected, according to the reaction

$$3Ca_3(PO_4)_2 + 2CaCl_2 \rightarrow Ca_5(PO_4)_3Cl + 3Ca_2(PO_4)Cl \tag{8}$$

A micrograph of chlorapatite crystals formed by reaction of calcium phosphate with calcium chloride is shown in Fig. 1.

For the mixed Ca/Sm and Ca/Pu/Am chlorides (Type I waste), Sm, Pu and Am are accommodated within the crystalline lattice by substitution for Ca. As apatite mineral phases are notoriously non-stoichiometric, charge balance is most likely maintained through the generation of Ca vacancies. The X-ray analyses revealed that the calcium phosphate precursor powder consisted primarily of the mineral phase whitlockite, $Ca_3(PO_4)_2$. Reacted samples containing up to 11 mass% $CaCl_2$ were composed primarily of chlorapatite, whilst samples containing up to 26 mass% were a mixture of chlorapatite and spodiosite. The XRD traces shown in Figs. 2 and 3 for the Type I composition non-radioactive simulated 20 mass% waste loaded calcium phosphate and radioactive samples, respectively, confirm the presence of chlorapatite and spodiosite phases, although there appears to be more spodiosite in the Pu-containing samples.

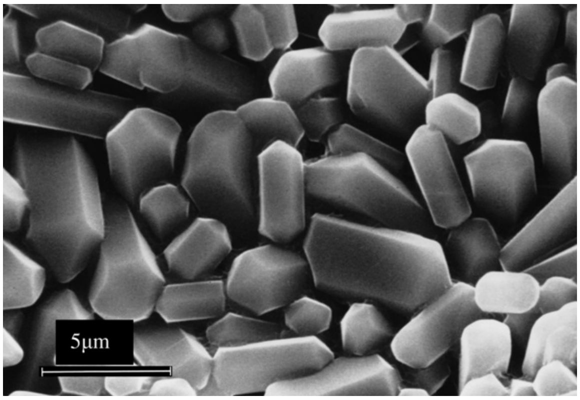

Fig. 1. Chlorapatite crystals showing the well-defined hexagonal pyramid terminators characteristic of this phase.

No significant effects of radiation-induced damage after 532 days (corresponding to approximately 400 years for the equivalent ^{239}Pu) on the resultant XRD patterns from the ^{238}Pu-bearing Type I waste-containing specimens (Fig. 4) are apparent, indicating no significant damage to the crystal structure.

For the more complex Types II, III and IV wastes, calcium phosphate has been confirmed as an excellent host for the constituents present in the non-radioactive samples and, more recently, confirmed for Type II radioactive samples, with the formation of a phase which was indexed to a chloride substituted fluorapatite ($Ca_5(PO_4)_3F_{0.9}Cl_{0.1}$) and not pure fluorapatite. The absence of a chlorapatite reflection at 31.227° indicates that chlorapatite is not formed. Peaks indexed to $Ca_2P_2O_7$ were also observed; however no other chloride-containing phases were identified. It is therefore suggested that a solid solution of chloride substituted fluorapatite is formed. It is known that much higher cation concentrations are possible in the F-containing phase [57], although we have observed that it is essential to incorporate sufficient phosphate ions in order to accommodate all the cations present in these wastes. Failure to do this results in excess free soluble chloride in the final product ($CaCl_2$ for the Type I wastes and KCl for the other wastes). Diffraction patterns for Type II waste samples are shown in Figs. 5 and 6 for non-radioactive and radioactive samples, respectively.

Chlorapatite is known to exhibit excellent durability in aqueous solution over a range of pH [58]. The particulate products obtained through the solid state reaction process reported here also offer excellent leach resistance in deionized water at 40 °C, as summarized for the radioactive Type I $PuCl_3$ and $AmCl_3$ containing ceramic in Table 3, and for the non-radioactive Type II, III and IV containing ceramics in Table 4. The data from the radioactive specimens may indicate that the primary release of Ca, P and Cl is from the dissolution of the chlorophosphate matrix and reprecipitation of alteration

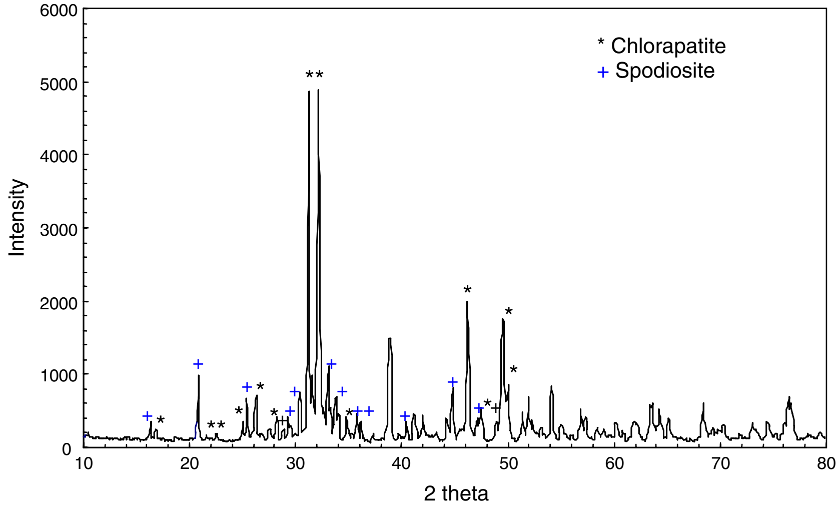

Fig. 2. X-ray diffraction pattern for non-radioactive simulated Type I waste-loaded calcium phosphate. Major phases present Chlorapatite (PDF No. 33-0271) and Spodiosite (PDF No. 19-0247).

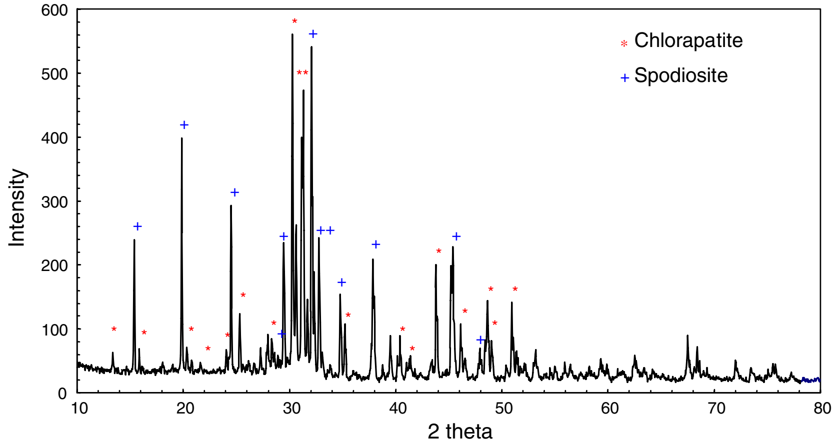

Fig. 3. X-ray diffraction pattern for $PuCl_3$ and $AmCl_3$ containing Type I waste-loaded calcium phosphate. Major phases present Chlorapatite (PDF No. 33-0271) and Spodiosite (PDF No. 19-0247).

products. The Am and Pu, however, appear to precipitate as very insoluble alteration products, possibly a monazite-type phase. Further work is in progress in an attempt to confirm this. In the case of the non-radioactive specimens, the case is not so clear; the Ca, Ga, F and Cl are inconsistent with uniform dissolution of the constituent phases. It is clear that the Hf and Sm precipitated. Hafnium oxide is very insoluble [59] and Sm might also precipitate as a monazite-like phase.

Because of their dispersible nature, the particulate products obtained by reaction of these wastes with calcium phosphate are not, of course, suitable for long-term storage or disposal. It is therefore necessary to process further in order to obtain a dense monolithic wasteform. Attempts to sinter the calcium phosphate ceramic to form a dense monolithic product were unsuccessful; each attempt resulted in porous materials with densities <60% theoretical when cold pressed and sintered at temperatures up to 900 °C. Higher sintering temperatures could not be used due to the thermal instability of the spodiosite and chlorapatite mineral phases. It is known [56], for example, that spodiosite decomposes at temperatures around 945 °C to yield chlorapatite and calcium chloride, according to

$$3Ca_2(PO_4)Cl \rightarrow Ca_5(PO_4)_3Cl + CaCl_2 \quad (9)$$

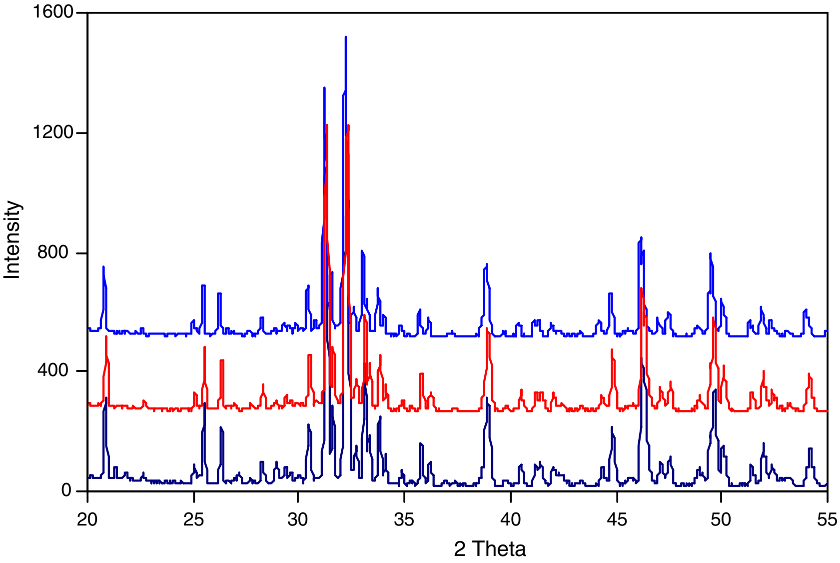

Fig. 4. X-ray diffraction patterns for ^{238}Pu Type I waste-loaded calcium phosphate after 8 days (bottom pattern), 77 days (middle pattern) and 532 days (top pattern).

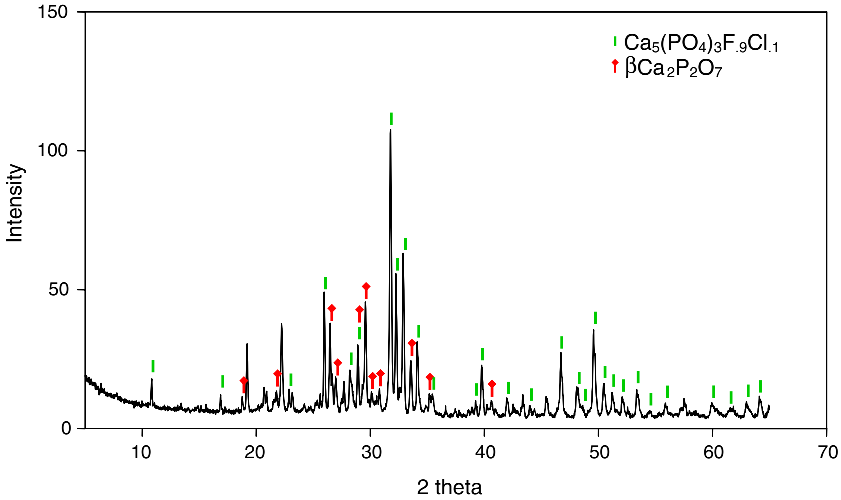

Fig. 5. X-ray diffraction pattern for non-radioactive simulated Type II waste-loaded calcium phosphate. The two Major phases shown are Chlor-substituted Fluorapatite (PDF No. 84-1997) and Beta-calcium phosphate (PDF No. 09-0346).

Chlorapatite itself decomposes in air at around 980 °C to give chloroxyapatite and gaseous chlorine

$$Ca_5(PO_4)_3Cl + x/2O_2 \rightarrow Ca_5(PO_4)_3O_xCl_y + (1-y)Cl\uparrow \quad (x \leqslant 1/2; y \leqslant 1) \tag{10}$$

In view of the inability to sinter the calcium phosphate-based product by itself, it is necessary to consolidate the ceramic powder with a suitable binder, with glass providing a practical medium.

5.2. Phosphate-based glasses

As noted in Section 4.1.2, a range of phosphate-based glasses were prepared and assessed for their effectiveness as either a solvent for chlorides or as an encapsulating phase for the calcium phosphate-based host. The thermal properties of the glass compositions given in Table 2 are summarized in Table 5.

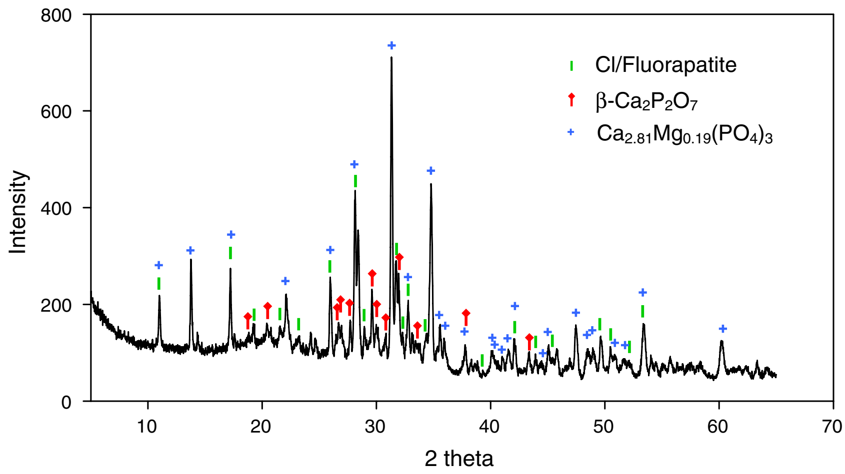

Fig. 6. X-ray diffraction pattern for radioactive ^{239}Pu Type II waste-loaded calcium phosphate. Three major phases shown are Cl/Fluorapatite (PDF No. 84-1997), Beta-calcium phosphate (09-0346) and a Mg-substituted whitlockite (PDF No. 77-0692).

Table 3
Dissolution test results for PNNL-prepared Pu/Am Type I particulate ceramic

Time (days)	Normalized elemental mass loss (g/m^2)				
(Type I)	Ca	Pu	Am	P	Cl
1	1.1×10^{-3}	8.5×10^{-6}	2.0×10^{-7}	1.4×10^{-3}	1.9×10^{-3}
3	1.3×10^{-3}	10.3×10^{-6}	1.3×10^{-7}	1.7×10^{-3}	1.3×10^{-3}
9	1.5×10^{-3}	10.9×10^{-6}	1.5×10^{-7}	2.1×10^{-3}	2.6×10^{-3}
14	1.5×10^{-3}	9.9×10^{-6}	2.7×10^{-7}	2.1×10^{-3}	3.4×10^{-3}
28	1.6×10^{-3}	11.9×10^{-6}	2.4×10^{-7}	2.3×10^{-3}	2.7×10^{-3}

Table 4
Dissolution test results for non-radioactive Type II, III and IV particulate ceramics

Time (days)	Normalized elemental mass loss (g/m^2)				
	Ca	Hf	Sm	Ga	F	Cl
(Type II)						
1	1.69×10^{-4}	<LOD	<LOD	4.16×10^{-3}	<LOD	2.41×10^{-4}
7	1.30×10^{-5}	<LOD	<LOD	5.48×10^{-3}	<LOD	9.30×10^{-5}
28	<LOD	<LOD	<LOD	7.19×10^{-3}	2.27×10^{-4}	2.41×10^{-4}
(Type III)						
1	1.08×10^{-4}	<LOD	<LOD	1.85×10^{-3}	<LOD	1.87×10^{-3}
7	5.40×10^{-5}	<LOD	<LOD	3.58×10^{-3}	<LOD	2.05×10^{-3}
28	4.05×10^{-5}	<LOD	<LOD	5.93×10^{-3}	<LOD	2.75×10^{-3}
(Type IV)						
1	1.10×10^{-4}	<LOD	<LOD	4.49×10^{-3}	<LOD	<LOD
7	2.75×10^{-5}	<LOD	<LOD	1.24×10^{-2}	<LOD	7.54×10^{-5}
28	4.13×10^{-5}	<LOD	<LOD	1.62×10^{-2}	2.34×10^{-4}	7.54×10^{-5}

LOD – limit of detection (Ca < 0.1 ppm; Hf < 0.3 ppm; Sm < 0.3 ppm; F < 0.2 ppm; Cl < 0.2 ppm).

In this table, T_g is the glass transition temperature (extrapolated start), T_x is the peak crystallization temperature; ΔH_x is the crystallization enthalpy; T_{liq} is the end of melting range; and T_g/T_{liq}, is the reduced glass temperature, which is related to the critical cooling rate for glass formation and is therefore a measure of the glass-forming ability of a system.

Table 5
Thermal properties of selected glasses

Glass	T_g (°C)	T_{x1} (°C)	T_{x2} (°C)	ΔH (J/g)	T_{liq} (°C)	T_g/T_{liq} (K/K)
NaAlP	405 ± 1	504 ± 1	607 ± 2	48; 176	741 ± 1	0.669
NaAlP-Fe1	437 ± 1	551 ± 7	601 ± 1	25; 125	777 ± 1	0.668
NaAlP-Fe2	442 ± 1	564 ± 2	593 ± 1	206[a]	782 ± 1	0.678
NaAlP-Fe3	443 ± 2	537 ± 1	563 ± 3	158[a]	830 ± 11	0.649
NaAlP-Fe4	445 ± 3	539 ± 2	No peak	172	860 ± 4	0.634
NaAlP-FeB	462 ± 1	589 ± 2	No peak	166	817 ± 1	0.674
NaAlP-Zn	409 ± 1	495 ± 1	No peak	91	968 ± 1	0.550
NaAlP-B1	427 ± 1	541 ± 4	640 ± 1	13; 58	747 ± 1	0.686
NaAlP-B2	428 ± 1	558 ± 2	663 ± 3	27; 52	740 ± 4	0.692
NaAlP-B3	428 ± 1	551 ± 2	663 ± 5	11; 24	742 ± 2	0.691
NaAlP-B4	427 ± 3	550 ± 8	No peak	≈9	742 ± 5	0.690
NaalP-B5	433 ± 2	573 ± 3	No peak	≈6	734 ± 3	0.707
NaAlP-B6	441 ± 1	587 ± 2	No peak	≈6	746 ± 5	0.701
SrZnP	500	680	No peak	–	976	0.618
CuErP	490	No peak	–	–	890	0.656

T_g is the glass transition temperature (extrapolated start), T_x is the peak crystallization temperature; ΔH_x is the crystallization enthalpy; T_{liq} is the end of melting range; and T_g/T_{liq}, is the reduced glass temperature, which is related to the critical cooling rate for glass formation and is therefore a measure of the glass-forming ability of a system.

[a] Two superimposed peaks.

In general, all the glasses investigated underwent some degree of crystallization. This is not necessarily detrimental to the properties of the final wasteform, unless crystalline products are formed that are less durable than the glass matrix or the formation of these phases degrades the durability of the surrounding glass matrix. In an attempt to improve the thermal stability and resistance to crystallization of the NaAlP glass, various additions were made, including $FePO_4$ (as a source of Fe_2O_3), ZnO and B_2O_3 [60–64]. As noted from the DSC enthalpy of crystallization values given in Table 5 and the DSC traces shown in Fig. 7, the addition of B_2O_3 was particularly effective at suppressing crystallization in the NaAlP glass.

The effectiveness of these glasses in immobilizing chlorides, added as $CaCl_2$, was poor. At one extreme, the ternary NaAlP glass was noted on analysis to have retained approximately 7 mass% of chloride compared to the 10 mass% added, whilst the Fe-containing glasses appeared to lose most of the chloride by volatilization, possibly through formation of $FeCl_3$ and/or gaseous chlorine. The ability of these phosphate glasses to incorporate appreciable quantities of chloride ions is therefore poor. Overall, the levels of chloride solubility are

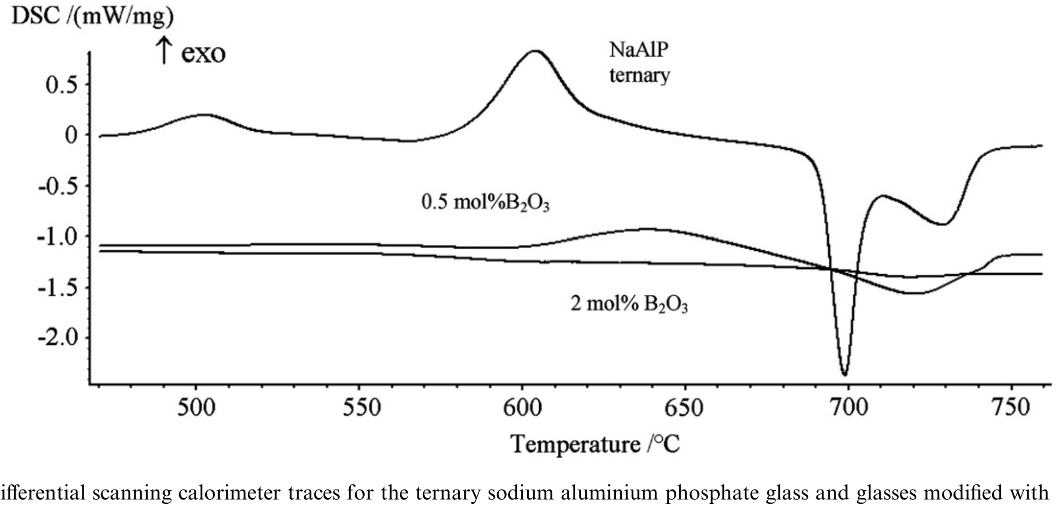

Fig. 7. Differential scanning calorimeter traces for the ternary sodium aluminium phosphate glass and glasses modified with 0.5%, 2.0% and 10 mol% B_2O_3 addition.

too low for these glasses to be used for direct vitrification of the waste and/or the durability of the product is unacceptably low. Their thermal properties do suggest, however, that they could be suitable as an encapsulating phase (binder) for the manufacture of monolithic wasteforms based on the calcium phosphate ceramic, due to their relatively low melting temperatures and, in the case of the B_2O_3 modified sodium aluminium phosphate glasses, excellent thermal stability and resistance to crystallization.

5.3. Glass-encapsulated calcium phosphate ceramic hybrid

Trials to identify a glass suitable as an encapsulating phase for the calcium phosphate host were conducted using glass/ceramic mixtures that were consolidated either by cold pressing and sintering or pressureless consolidation. Results for selected non-radioactive samples are summarized in Table 6. A satisfactory product was arbitrarily defined as a robust monolith with a theoretical density ⩾80% and with only desirable reaction products present.

Alternative glass compositions based on silver phosphate and copper phosphate were also tested as it was believed that any reaction between the glass constituents and chloride ions would not be detrimental and would lead to the formation of an insoluble chloride compound; however, no dense samples could be made using these glasses. In addition, the silver glass contained a colloidal dispersion of metallic silver.

Table 6
Sintering behaviour of glass/ceramic mixtures

Glass	Glass content (%)	Glass particle size (μm)	Cold pressed	Sintering schedule (°C/h)	%TD[a]	Comments
Type I waste						
NaAlP	40	<150	No	625/4	83	Trace of halite formed
NaAlP	20	<150	No	800/4	93	Halite formed
NaAlP	40	<150	Yes	700/4	92	Halite free
NaAlP[b]	40	<150	No	650/4	88	Halite free
SrZnP	40	<150	Yes	800/4	57	Zinc chloride formed
CuErP	50	<150	Yes	800/4	60	Porous product
Type II waste						
NaAlP	25	<150	Yes	750/4	79–81	Satisfactory product
NaAlP	25	<150	No	750/4	79	Low density
NaAlP	25	<45	Yes	750/4	83	Satisfactory product
NaAlP	25	<45	No	750/4	85	Satisfactory product
NaAlP-B3	25	<45	Yes	750/4	80–81	Satisfactory product
NaAlP-B3	25	<45	No	750/4	83	Satisfactory product
NaAlP-B3	30	<45	Yes	750/4	78	Satisfactory product
NaAlP-B3	30	<45	No	750/4	80	Satisfactory product
Type III waste						
NaAlP	20	<150	Yes	750/4	70	Low density
NaAlP	20	<150	No	750/4	51	Porous product
NaAlP	20	<45	Yes	750/4	80	Satisfactory product
NaAlP	20	<45	No	750/4	81	Satisfactory product
NaAlP	30	<45	Yes	750/4	79	Satisfactory product
NaAlP	30	<45	No	750/4	79	Satisfactory product
NaAlP-B3	20	<45	Yes	750/4	81	Satisfactory product
NaAlP-B3	20	<45	No	750/4	80	Satisfactory product
NaAlP-B3	30	<45	Yes	750/4	79	Satisfactory product
NaAlP-B3	30	<45	No	750/4	80	Satisfactory product
Type IV waste						
NaAlP-B3	25	<45	Yes	750/4	83	Satisfactory product
NaAlP-B3	25	<45	No	750/4	81	Satisfactory product
NaAlP-B3	30	<45	Yes	750/4	82	Satisfactory product
NaAlP-B3	30	<45	No	750/4	82	Satisfactory product

[a] TD = theoretical density.

[b] Loaded with 11 mass% calcium chloride, all other Type I samples are loaded with 20 mass% calcium chloride.

In the case of samples containing Type I waste, it was noted that a small proportion of halite crystals often formed in the sintered product, as noted in Fig. 8. It was found that halite formation can be avoided, however, by keeping the waste loading in the calcium phosphate-based host to <11 mass% calcium chloride, suggesting that it is the spodiosite phase that reacts with Na present in the glass to form NaCl. The possible reaction sequence is given by

$$Na_2O + Ca_6(PO_4)_3Cl_3 \rightarrow 2NaCl + Ca_5(PO_4)_3Cl + CaO \quad (11)$$

For Type I waste-containing samples prepared with <11 mass% calcium chloride and for Types II, III and IV samples, formation of halite is avoided. A typical fracture surface for a Type I sample is shown in Fig. 9. In the case of the Types II, III and IV waste-containing samples, and which contain a mixture of oxides, chloride and fluoride, there is no reaction to form halite. This results in a waste loading limit in the calcium phosphate of around 26 mass%. This is because the concentration of chloride in these particular wastes is lower than in the Type I waste (which is entirely composed of chlorides), and this results in a lower concentration or even an absence of the apparently less stable spodiosite phase in the ceramic host.

As noted from the results given in Table 6, it was observed that the sintered density of the glass/ceramic products prepared using the pressureless consolidation route could be improved significantly by decreasing the initial particle size of the glass. An increase in sintered density was also noted on increasing the glass volume fraction, with maximum densities occurring around 20–30 mass% glass depending on the waste type. Although higher density is obtained at these higher glass concentrations, this also decreases the storage density of the Am, Pu and Cl. Graphical data for selected samples are summarized in Fig. 10.

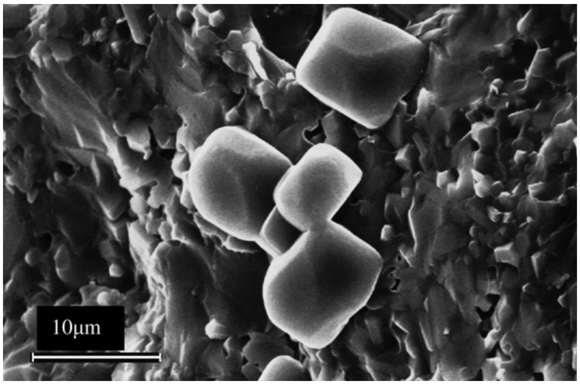

Fig. 8. Micrograph of a fracture surface in a glass-encapsulated Type I non- radioactive simulated wasteform showing the presence of halite crystals.

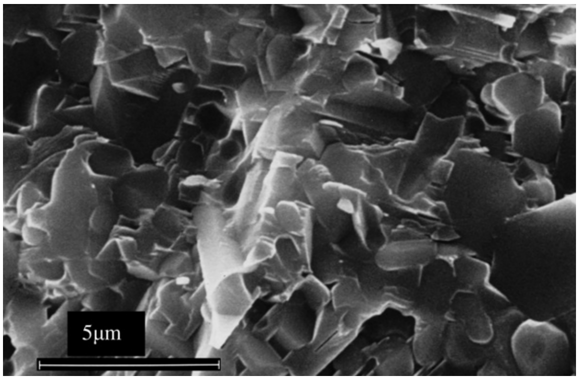

Fig. 9. Micrograph of a typical fracture surface in a glass-encapsulated Type I non- radioactive simulated wasteform with an absence of halite crystals.

Initial results from short-term durability studies of the glass-encapsulated Types II, III and IV bearing non-radioactive ceramic wasteforms are very good, as summarized in Table 7 for 75:25 ceramic/glass mixtures. Data are given for samples cold pressed at 69 MPa and then sintered at 750 °C and also for samples prepared by pressureless consolidation (i.e., unpressed samples sintered at 750 °C). Very little difference between the pressed and unpressed samples is noted.

These results indicate that calcium phosphate is an excellent host for immobilizing complex actinide- and halide-containing waste streams and that a satisfactory monolithic product can be manufactured by pressureless consolidation employing a phosphate glass as an encapsulating phase. Before this material is selected for use in an actual process to immobilize Am-, Pu, and Cl-bearing waste at AWE, however, more testing is required. In particular, the dissolution testing performed in this study needs to be augmented with more comprehensive testing of the durability. This will include single-pass flow-through tests, and will be carried out especially on radioactive samples. These results will be reported at a later date. In the meantime, trials are also continuing at PNNL to assess the long-term effects of radiation-induced damage on Types I and Type II wasteforms containing ^{238}Pu.

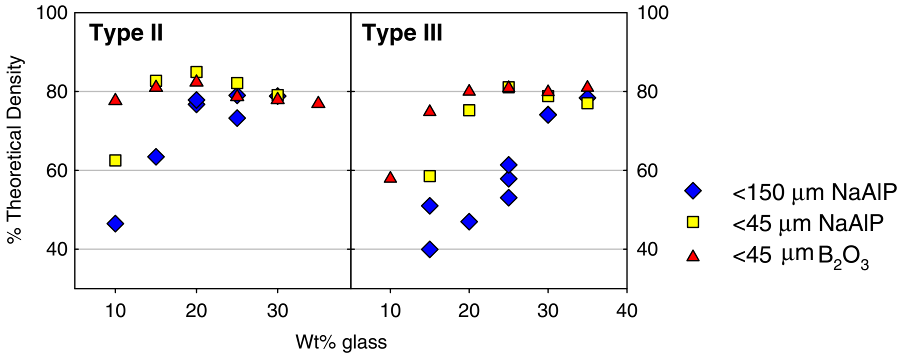

Fig. 10. Density of pressed and unpressed wasteforms for Types II and III non-radioactive waste sintered at 750 °C.

Table 7
Dissolution test results for non-radioactive Type II glass/ceramic wasteform

Time (days)	Normalized elemental mass loss (g/m^2)						
	Ca	Hf	Sm	Ga	F	Cl	PO_4
(Type II)							
Pressed							
1	1.12×10^{-3}	<LOD	<LOD	3.96×10^{-2}	<LOD	<LOD	1.64×10^{-2}
3	5.62×10^{-3}	<LOD	<LOD	1.19×10^{-1}	<LOD	<LOD	3.00×10^{-2}
7	6.75×10^{-3}	<LOD	<LOD	1.68×10^{-1}	<LOD	1.26×10^{-2}	4.73×10^{-2}
14	1.12×10^{-2}	<LOD	<LOD	1.98×10^{-1}	<LOD	2.21×10^{-2}	7.84×10^{-2}
28	1.57×10^{-2}	<LOD	<LOD	2.23×10^{-1}	<LOD	3.87×10^{-2}	8.65×10^{-2}
Unpressed							
1	1.12×10^{-3}	<LOD	<LOD	3.46×10^{-2}	<LOD	<LOD	1.42×10^{-2}
3	4.49×10^{-3}	<LOD	<LOD	7.91×10^{-2}	<LOD	<LOD	2.46×10^{-2}
7	5.62×10^{-3}	<LOD	<LOD	1.14×10^{-1}	<LOD	6.86×10^{-3}	4.06×10^{-2}
14	1.24×10^{-2}	<LOD	<LOD	1.73×10^{-1}	<LOD	1.98×10^{-2}	6.24×10^{-2}
28	1.24×10^{-2}	<LOD	<LOD	2.18×10^{-1}	<LOD	3.34×10^{-2}	8.08×10^{-2}
(Type III)							
Pressed							
1	<LOD	<LOD	<LOD	<LOD	<LOD	2.60×10^{-3}	6.56×10^{-3}
3	<LOD	<LOD	<LOD	2.32×10^{-2}	<LOD	5.59×10^{-2}	1.95×10^{-2}
7	3.81×10^{-3}	<LOD	<LOD	8.12×10^{-2}	<LOD	<LOD	3.96×10^{-2}
14	5.08×10^{-3}	<LOD	<LOD	2.09×10^{-1}	<LOD	<LOD	6.74×10^{-2}
28	8.89×10^{-3}	<LOD	<LOD	2.67×10^{-1}	<LOD	1.60×10^{-2}	1.60×10^{-2}
Unpressed							
1	3.73×10^{-3}	<LOD	<LOD	<LOD	<LOD	< LOD	7.12×10^{-3}
3	<LOD	<LOD	<LOD	1.14×10^{-1}	<LOD	< LOD	2.19×10^{-2}
7	3.73×10^{-3}	<LOD	<LOD	1.25×10^{-1}	<LOD	<LOD	4.22×10^{-2}
14	7.45×10^{-3}	<LOD	<LOD	2.16×10^{-1}	<LOD	<LOD	6.51×10^{-2}
28	8.69×10^{-3}	<LOD	<LOD	2.38×10^{-1}	<LOD	1.06×10^{-2}	9.74×10^{-2}
(Type IV)							
Pressed							
1	2.43×10^{-3}	<LOD	<LOD	9.06×10^{-2}	<LOD	3.38×10^{-2}	2.76×10^{-2}
3	<LOD	<LOD	<LOD	1.58×10^{-1}	<LOD	3.48×10^{-2}	4.56×10^{-2}
7	1.22×10^{-3}	<LOD	<LOD	2.49×10^{-1}	<LOD	9.81×10^{-2}	7.26×10^{-2}
14	3.65×10^{-3}	<LOD	<LOD	4.41×10^{-1}	<LOD	1.48×10^{-1}	1.10×10^{-1}
28	4.86×10^{-3}	<LOD	<LOD	6.11×10^{-1}	<LOD	2.22×10^{-1}	1.54×10^{-1}

LOD – limit of detection (Ca < 0.1 ppm; Hf < 0.3 ppm; Sm < 0.3 ppm; F < 0.2 ppm; Cl < 0.2 ppm).

6. Conclusions

Initial test results indicate that calcium phosphate appears to be a viable starting material for the immobilization of a variety of actinide-, fluoride- and chloride-containing wastes, with the waste constituents chemically immobilized within durable chlorapatite, spodiosite, and related mineral phases. The ceramic products do, however, require further processing to yield a monolithic wasteform suitable for storage, and this can readily be accomplished by encapsulation of the particulate ceramic product in a B_2O_3 modified sodium aluminium phosphate glass.

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