Journal of Alloys and Compounds 444–445 (2007) 424–428

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Development of a glass-encapsulated calcium phosphate wasteform for the immobilization of actinide and halide containing radioactive wastes from the pyrochemical reprocessing of plutonium metal

S.K. Fong *, I.W. Donald, B.L. Metcalfe

AWE, Aldermaston, Berkshire, UK

Received 30 June 2006; received in revised form 29 April 2007; accepted 30 April 2007
Available online 3 May 2007

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 viable due to the very low solubility of chlorides in these hosts. Alternative wasteforms, including zeolites and direct vitrification in phosphate glasses, were therefore studied. However, the preferred option was to immobilize the waste in calcium phosphate ceramics, forming a number of stable mineral phases including chlorapatite, chloride-substituted fluorapatite and spodiosite. The immobilization process developed in this study involves a solid state process in which waste and host powders are reacted in air at temperatures in the range of 700–800 °C. The ceramic products obtained by this process are non-hygroscopic free-flowing powders that require encapsulation in glass to produce a monolithic wasteform suitable for storage and ultimate disposal. A suitable relatively low melting temperature phosphate-based glass was identified. Durability trials of both the ceramic powder and sintered glass-ceramic hybrid wasteform indicate that both the halides and actinide surrogate ions are satisfactorily immobilized.

Keywords: Ceramics; Composite materials; Solid state reactions; Sintering

1. Introduction

Wastes arising from the pyrochemical reprocessing of plutonium metal [1] differ significantly from most defence and fuel reprocessing wastes in that they contain significant quantities of actinides and halides, in particular chlorides. Consequently, vitrification of these wastes in alkali borosilicate glass is not suitable due to the low solubilities of the actinide and chloride ions, both of which must be immobilized. For the same reason a number of ceramic systems, synroc (synthetic rock), zirconolite and zircon were not considered. Alternative wasteform candidates were therefore investigated for this special type of waste.

1.1. Ceramics

Both zeolites and calcium phosphate ceramics were initially investigated as hosts for actinide and chloride species. Although the chloride ions are not chemically bonded in zeolites, the structure can be transformed by heating to form the mineral phase sodalite, ideally $Na_8(AlSiO_4)_6Cl_2$. Previously work at AWE, using Zeolite (4A) as a source of reactive aluminosilicate, was carried out where calcination of the zeolite with simulant waste yielded a particulate product with good leach resistance.

However, the calcium phosphate/apatite system was the preferred option for a number of reasons. This system exhibited better leach resistance and studies of natural apatites have shown that this mineral phase is highly resistant to radiation-induced damage [2], which mitigates against release of radioactive nucleotides from the structure into the environment. This stability has also been confirmed in accelerated ageing studies, using the short lived ^{238}Pu isotope, where no radiation damage was detectable by XRD after the equivalent of 400 years ageing [3]. Also apatites are known to accommodate both a range of actinides [4] and non-stoichiometric compositions, which would allow the structure to cope with variations in the waste stream composition. It is suggested that various cations substitute for calcium into the apatite and whitlockite structures with the creation of cation vacancies to maintain charge balance.

---

* Corresponding author. Tel.: +44 118 982 6516.
E-mail address: shirley.fong@awe.co.uk (S.K. Fong).

0925-8388/$ – see front matter. Crown Copyright © 2007 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.04.305

However the exact substitution mechanism is not known and is currently the subject of extensive further study. The different waste streams were immobilized in calcium phosphate ceramics and characterized by XRD before leach trials were carried out to assess durability in water.

1.2. Glasses

Phosphate glasses were of interest for direct vitrification of the waste. Previous studies had indicated that these glasses may be able to immobilize chlorides [5] and high concentrations of actinide elements [5,6]. Consequently a number of compositions were studied to determine the maximum amount of chloride that could be incorporated into the glass by mixing the glass frit with calcium chloride powder and remelting. Also, to improve the thermal stability and resistance to crystallization, various additions were made, including $FePO_4$, ZnO and B_2O_3. Thermal characteristics of these glasses were then assessed by DSC.

1.3. Ceramic/glass composites

One disadvantage of the calcium phosphate ceramic system is that it yields particulate products. This property raises problems with the handling and storage of active fine powders as well as enhanced leach rates due to the large surface area. Additionally the high temperatures required to convert the powders into a monolithic form mean that the Cl would be likely to be lost due to volatilization. Instead a monolithic product can be obtained by sintering with a glass to bond together the ceramic particles, i.e. a suitable binder glass was required to be identified. Consequently, sintering trials of the ceramic powders with a number of phosphate glasses were carried out to assess the density and durability of the glass encapsulated wasteform.

2. Experimental

In the initial phases of this work, non-radioactive simulated waste compositions (Table 1) were used to simulate the waste streams generated during the pyrochemical reprocessing of plutonium metal. In Type I simulant waste, $SmCl_3$ was used as a surrogate for the $PuCl_3$ and $AmCl_3$, whereas in Types II, III and IV HfO_2 was used as a surrogate for PuO_2 (Pu^{4+}) and Sm_2O_3 for Am_2O_3 (Am^{3+}).

Type I waste (20 g) was reacted with 80 g $Ca_3(PO_4)_2$, while 20 g of Types II, III and IV wastes were reacted with 58.7, 40.4 and 46.4 g $CaHPO_4$, respectively. All four waste streams were calcined in air at 750 °C for 4 h, the target phases being spodiosite, cation substituted apatite and cation substituted whitlockite. After preparation, the powders produced were washed in demineralized water. X-ray diffraction patterns from both the powder ceramic and ceramic/glass composite samples were obtained on a Philips PW-1700 powder diffractometer using Cu Kα radiation.

Glasses were prepared by melting the appropriate constituents in alumina crucibles at 1250 °C in air, compositions are given in Table 2. The glasses were quenched in de-ionized water and the resulting frit dried and remelted in order to improve the homogeneity of the final product. Thermal characteristics were determined using a Netzsch differential scanning calorimeter (Model DSC 404S) at a standard heating rate of $10\,K\,min^{-1}$.

Chemical durability of the ceramic powders and glass-encapsulated samples was carried out using a modified MCC-1 test. The monolithic glass-encapsulated samples were ground down and the 0.6–1.0 mm particle size fraction used in the leach test. Approximately 1 g of sample was leached in 50 ml deionized water at 40 °C for 28 days in PFA Teflon vessels. At specified periods, 10 ml of leachate was removed and replaced with 10 ml deionized water. Leachants were analyzed for Hf, Ca, Ga and Sm by ICP-AAS (inductively coupled plasma atomic absorption spectroscopy) and anion concentrations measured using ion chromatography. The surface area values, measured by the BET method, were $3.297\,m^2\,g^{-1}$ for the waste ceramic powder and $0.05\,m^2\,g^{-1}$ for the ground glass encapsulated samples. Normalized elemental mass losses for each element, N_i, were then calculated from the expression below:

$$N_i = \frac{m_i}{Sf_i}$$

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

Sintering trials were conducted by the addition of between 10 and 35 mass% glass binder to the ceramic powder. 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 700–750 °C for 4 h.

Table 1
Compositions of the non-radioactive simulated waste streams

Component (mass%)	Waste stream type			
	I	II	III	IV
Oxides				
HfO_2	–	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	–	4.6	11.7	1.0
MgO	–	6.3	–	10.1
FeO	–	1.5	–	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	–	–	–
$SmCl_3$	20.0	–	–	–
CaF_2	–	10.4	5.0	8.5
KCl	–	16.3	10.0	16.9

3. Results

3.1. Calcium phosphate ceramics

Types I and III wastes yielded a mixture of chlorapatite ($Ca_5(PO_4)_3Cl$) and spodiosite, ($Ca_2(PO_4)Cl$). Types II and IV

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

Glass	Composition (mol%)				
	Na_2O	Al_2O_3	P_2O_5	Fe_2O_3	B_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-B1	40.6	19.3	39.6	–	0.5
NaAlP-B2	40.4	19.2	39.4	–	1.0
NaAlP-B4	40.0	19.0	30.0	–	2.0
NaAlP-B6	36.7	17.5	35.8	–	10.0

Table 3
Selected leaching data ($g\,m^{-2}$) for non-radioactive Types II, III and IV particulate ceramics

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

wastes 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 and $Ca_3(PO_4)_2$, respectively. Selected XRD patterns are shown in Fig. 1.

Leach trials of these ceramics that were calculated indicated low leach rates (Table 3) of both the actinide surrogate and halide ions, indicating that these ions had been effectively immobilized. These results were calculated using the value, surface area = $3.297\,m^{-2}\,g^{-1}$. Concentrations of Hf and Sm were both lower than the limit of detection and so are not shown in Table 3.

3.2. Phosphate glasses

Chloride retention of the glasses compositions studied (Table 4) was generally poor, the Fe-containing glasses appearing to lose most of the chloride by volatilization. However in the best candidate (NaAlP), of the 10 mass% chloride added, it was noted that approximately 70% was retained. Whilst this value was still too low for direct vitrification, the thermal properties (Table 4) suggested that it would be suitable to bond a ceramic powder. The addition of B_2O_3 to this NaAlP glass gave a further improvement by suppressing crystallization in the (Fig. 2) yielding a glass with low melting point, excellent thermal stability and resistance to crystallization.

3.3. Ceramic glass hybrids

Sintering the ceramic powders with either the ternary NaAlP glass or B_2O_3 modified NaAlP glass (1.5 mol% B_2O_3) yielded wasteforms of suitable density for all four waste streams. Selected densities are given in Table 5, theoretical densities were calculated from mass% of the glass and ceramic powders assuming no reaction between glass and ceramic. Samples are currently being tested to confirm that no significant losses of halide have taken place.

Leach trials of these ceramics indicated low leach rates (Table 6) of both the actinide surrogate and halide ions,

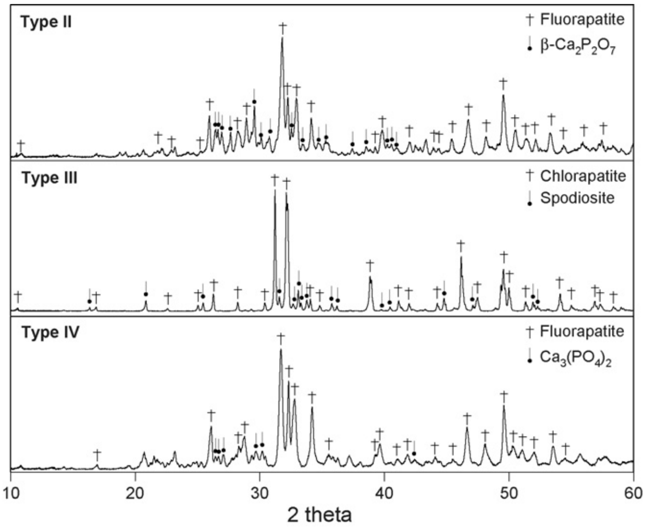

Fig. 1. XRD patterns of Types II–IV wastes after reaction with $CaHPO_4$.

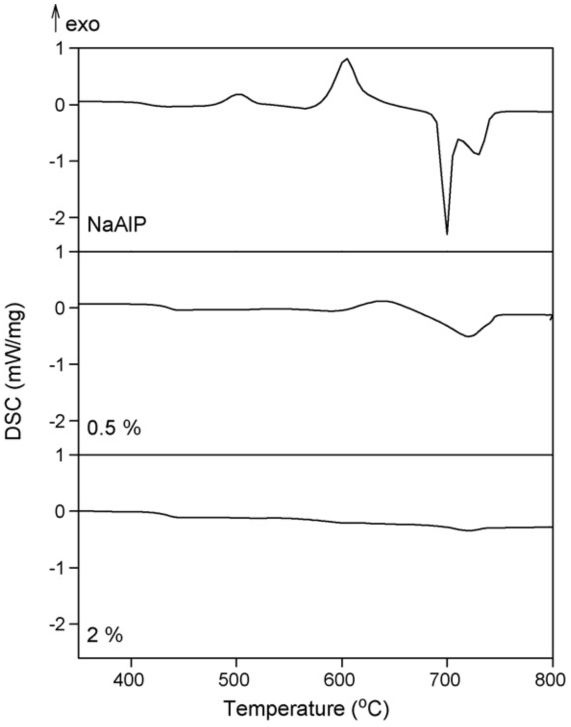

Fig. 2. DSC traces of selected glasses.

Table 4
Compositions and thermal properties of selected glasses

Glass	Composition (mass%)					Thermal properties					
	Na_2O	Al_2O_3	P_2O_5	Fe_2O_3	B_2O_3	T_g (°C)	T_{x1} (°C)	T_{x2} (°C)	H (J/g)	T_{liq} (°C)	T_g/T_{liq} (K/K)
NaAlP	40.8	19.4	39.8	–	–	405 ± 1	504 ± 1	607 ± 2	48; 176	741 ± 1	0.669
NaAlP-Fe1	37.9	18.1	40.5	3.5	–	437 ± 1	551 ± 7	601 ± 1	25; 125	777 ± 1	0.668
NaAlP-Fe2	36.4	17.4	40.9	5.3	–	442 ± 1	564 ± 2	593 ± 1	206[a]	782 ± 1	0.678
NaAlP-Fe3	34.9	16.6	41.3	7.2	–	443 ± 2	537 ± 1	563 ± 3	158[a]	830 ± 11	0.649
NaAlP-B1	40.6	19.3	39.6	–	0.5	427 ± 1	541 ± 4	640 ± 1	13; 58	747 ± 1	0.686
NaAlP-B2	40.4	19.2	39.4	–	1.0	428 ± 1	558 ± 2	663 ± 3	27; 52	740 ± 4	0.692
NaAlP-B4	40.0	19.0	30.0	–	2.0	427 ± 3	550 ± 8	No peak	≈9	742 ± 5	0.690
NaAlP-B6	36.7	17.5	35.8	–	10.0	441 ± 1	587 ± 2	No peak	≈6	746 ± 5	0.701

[a] Two superimposed peaks, T_g glass transition temperature, T_{x1}, T_{x2} first and second crystallization peak temperatures, respectively.

Table 5
Sintering behaviour of selected glass/ceramic mixtures

Waste type	Glass	Glass content (%)	Glass particle size (μm)	Sintering temperature (°C)	%Theoretical density
I	NaAlP	40	<150	700	92
II	NaAlP	25	<45	750	83
II	NaAlP-B3	25	<45	750	80–81
II	NaAlP-B3	30	<45	750	78
III	NaAlP	20	<45	750	80
III	NaAlP-B3	20	<45	750	81
III	NaAlP-B3	30	<45	750	79
IV	NaAlP-B3	25	<45	750	83
IV	NaAlP-B3	30	<45	750	82

Table 6
Leaching data ($g\,m^{-2}$) for non-radioactive Type II, III and IV glass/ceramic wasteforms

Types	Time (days)	Normalized elemental mass loss (g/m^2)			
		Ca	Ga	Cl	PO_4
II	1	1.12×10^{-3}	3.96×10^{-2}	<LOD	2.26×10^{-2}
	7	6.75×10^{-3}	1.68×10^{-1}	1.26×10^{-2}	6.50×10^{-2}
	28	1.57×10^{-2}	2.23×10^{-1}	3.87×10^{-2}	1.08×10^{-1}
III	1	<LOD	<LOD	2.60×10^{-3}	9.36×10^{-3}
	7	3.81×10^{-3}	8.12×10^{-2}	<LOD	5.65×10^{-2}
	28	8.89×10^{-3}	2.67×10^{-1}	1.60×10^{-2}	9.60×10^{-2}
IV	1	2.43×10^{-3}	9.06×10^{-2}	3.38×10^{-2}	3.89×10^{-2}
	7	1.22×10^{-3}	2.49×10^{-1}	9.81×10^{-2}	1.02×10^{-1}
	28	4.86×10^{-3}	6.11×10^{-1}	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).

indicating that these ions had been effectively immobilized. These results were calculated using the value, surface area = $0.05\,m^{-2}\,g^{-1}$. Concentrations of Hf and Sm were again both lower than the limit of detection indicating that these ions have precipitated out as insoluble species and so are not shown in Table 6.

4. Conclusions

Calcium phosphate has been shown to be a viable starting material for the immobilization of a variety of actinide, and halide-containing wastes, forming durable apatite, spodiosite, whitlockite and related mineral phases. However the ceramic products require further processing to yield a monolithic wasteform suitable for storage. The phosphate glasses studied did not have sufficiently high chloride retention for direct vitrification of the waste but a ternary NaAlP glass was identified as a possible sintering aid for the particulate ceramic products. Sintering trials of the calcium phosphate ceramics with the NaAlP and B_2O_3 modified ternary yielded monolithic wasteforms of suitable durability and density, i.e. above 80% theoretical density.

References

[1] I.W. Donald, B.L. Metcalfe, R.N.J. Taylor, J. Mater. Sci. 32 (1997) 5851.

[2] S. Utsunomiya, S. Yudintsev, et al., J. Nucl. Mater. 322 (2003) 180–188.

[3] B.L. Metcalfe, I.W. Donald, R.D. Scheele, D.M. Strachan, in: J.M. Hanchar, S. Stroes-Gascoyne, L. Browning (Eds.), Mat. Res. Soc. Symp. Proc., vol. 824, Warrendale, PA, 2004, pp. 255–260.

[4] E.R. Vance, C.J. Ball, et al., J. Am. Ceram. Soc. 86 (2003) 1223–1225.

[5] D.E. Day, C.S. Ray, G.K. Marasinghe, M. Karabulut, X. Fang, EMSP Project Summaries, Project ID No. 55110, June 1998, http://www.energy.gov.

[6] G.K. Marasinghe, M. Karabulut, C.S. Ray, D.E. Day, D.K. Shuh, P.G. Allen, M.L. Saboungi, M. Grimsditch, D. Haeffner, J. Non-Cryst. Solids 253–254 (2000) 146.