



## Ageing of a phosphate ceramic used to immobilize chloride contaminated actinide waste

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### A B S T R A C T

A process for the immobilization of intermediate level waste containing a significant quantity of chloride using  $\text{Ca}_3(\text{PO}_4)_2$  as the host material has been developed. Waste ions are incorporated into two phosphate-based phases, chlorapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ ] and spodiosite [ $\text{Ca}_2(\text{PO}_4)\text{Cl}$ ]. Non-active trials performed using Sm as the actinide surrogate demonstrated the durability of these phases in aqueous solution. Trials of the process, in which actinide-doped materials were used, were performed at PNNL which confirmed the wastefrom resistant to aqueous leaching. Initial leach trials conducted on  $^{239}\text{Pu}/^{241}\text{Am}$  loaded ceramic at 313 K/28 days gave normalized mass losses of  $1.2 \times 10^{-5} \text{ g m}^{-2}$  and  $2.7 \times 10^{-3} \text{ g m}^{-2}$  for Pu and Cl, respectively. In order to assess the response of the phases to radiation-induced damage, accelerated ageing trials were performed on samples in which the  $^{239}\text{Pu}$  was replaced with  $^{238}\text{Pu}$ . No changes to the crystalline structure of the waste were detected in the XRD spectra after the samples had experienced an  $\alpha$  radiation fluence of  $4 \times 10^{18} \text{ g}^{-1}$ . Leach trials showed that there was an increase in the P and Ca release rates but no change in the Pu release rate.

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### 1. Introduction

The immobilization of an intermediate level legacy waste arising from the pyrochemical reprocessing of Pu metal, essentially a chloride-based waste, presents a particular problem. Neither the borosilicate glass vitrification process used to immobilize HLW waste arising from fuel element recycling nor the SYNROC process for immobilising Pu are suitable because of the presence of significant quantities of chloride ions present in the waste. At AWE the approach was to immobilize the chloride in a stable calcium phosphate host that was also capable of immobilizing the actinide cations. Apatite is a naturally occurring mineral of general formula,  $\text{A}_5(\text{BO}_4)_3(\text{OH,F,Cl})$ , where A can be a variety of 1–3 valent cations including Ca, Ba, Na, Pb, Sr, La or Ce and B is commonly P, V or As [1] although Terra et al. reports that tri- and tetra-valent cations require a coupled substitution ( $\text{Ca}_2\text{PO}_4 \leftrightarrow (\text{An,SiO}_4)$  [2]. They are highly non-stoichiometric, with vacancies, Ca deficiencies, excess of  $(\text{PO}_4)$ , etc. It was the ability to substitute such a wide range of ions into the structure and its aqueous durability [3,4] that made apatite attractive as the host material for immobilizing waste. In particular chlorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ , and spodiosite,  $\text{Ca}_2(\text{PO}_4)\text{Cl}$  appeared to be possible candidate phases as they contain 6.8 and 16.8 mass% of chlorine, respectively, a necessity to minimise the final waste volume. Initial research was performed at AWE using simulant waste

containing  $\text{Sm}^{3+}$  as the surrogate for the  $\text{Pu}^{3+}$  and  $\text{Am}^{3+}$  present in the legacy waste. This demonstrated that chlorapatite and spodiosite phases could easily be produced by calcining a mixture of finely ground waste and the host material  $\text{Ca}_3(\text{PO}_4)_2$  at 1023 K for 2 h [5]. The resulting product was a free-flowing, non hygroscopic powder with a particle size  $<10 \mu\text{m}$ . To confirm the process worked with actinides and carry out accelerated ageing trials, the process was transferred to PNNL where it was found that a more consistent product was achieved if the calcination time was increased to 4 h. Having confirmed the non-active process at PNNL, they then performed experiments there in which the  $\text{SmCl}_3$  was replaced by a mixture of  $\text{PuCl}_3$  and  $\text{AmCl}_3$ . In order to perform the accelerated ageing samples were made in which  $^{238}\text{Pu}$  replaced  $^{239}\text{Pu}$ , thereby accelerating the rate at which the waste underwent radiation damage by a factor of approximately 280. Here, the preparation of actinide-doped samples is described together with the effect of radiation-induced damage on the crystal structure and durability of the wastefrom.

### 2. Experimental

Non-active studies had been performed using  $\text{Ca}_3(\text{PO}_4)_2$  as the host and a simulant waste (80mass%  $\text{CaCl}_2$  and 20mass%  $\text{SmCl}_3$ ). To the host was added 20mass% of the simulant waste and this was then calcined at 750 °C for 4 h. Trials performed at PNNL on Type I actinide-doped waste utilised a simulated waste consisting of 80mass%  $\text{Ca}_3(\text{PO}_4)_2$ , 16%  $\text{CaCl}_2$ , 3.8mass%  $\text{PuCl}_3$  and 0.2mass%

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AmCl<sub>3</sub>. Samples were prepared by adding the requisite amount of mixed <sup>241</sup>Am(III) and Pu(III) chlorides, prepared by the method of Harder et al. [6] and Christensen and Mullins [7], to the Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and CaCl<sub>2</sub> in an argon purged glove bag to prevent oxidation of the Pu(III). The powders were mixed in a polythene jar overnight using zirconia milling media after which the powder was transferred into an alumina crucible. This was placed in a quartz tube under flowing argon during calcination. When cool the tube was transferred into the glove bag and the powders removed and prepared for XRD. For the accelerated ageing trials, <sup>239</sup>Pu was replaced with <sup>238</sup>Pu which produced an  $\alpha$  fluence of approximately  $1.2 \times 10^{15} \text{ g}^{-1} \text{ d}^{-1}$ . The ageing trials continued for 1820 days during which time the samples experienced an  $\alpha$  radiation fluence of  $4 \times 10^{18} \text{ g}^{-1}$ .

Powder X-ray diffraction analyses were performed on samples using a Scintag PAD V powder diffractometer and CuK $\alpha$  radiation.

The chemical durability in aqueous solution was assessed employing a modified MCC-1 test protocol whereby 1 g powder samples were washed with 40 ml of deionised water to remove any unreacted chloride. Triplicate 1 g samples of the washed ceramic powder were leached with 100 ml of deionised water in stainless steel vessels at 313 K. At intervals over the 28 day test period 10 ml leachate aliquots were removed for chemical analysis and replaced with an equal quantity of fresh deionised water. Each aliquot was analysed by ICP-MS and ICP/OES, the chloride concentration measured using a chloride specific electrode and the pH measured with a combination pH probe. In order to compare data the elemental mass losses for each element were normalized and calculated according to Eq. (1):

$$N_i = \frac{m_i}{f_i \cdot s} \quad (1)$$

where  $m_i$  is the mass loss for element  $i$ ,  $f_i$  is the mass fraction of element  $i$  in the ceramic, and  $s$  is the specific surface area of the powder as measured by the BET method. In this case, because a powder specimen is used, the BET surface area was used rather than the geometric area. Different experimental runs produced a factor of three variations in powder surface area and so the lowest surface area was taken for all calculations.

### 3. Results and discussion

The XRD analysis revealed that the calcium phosphate precursor powder consisted primarily of the mineral phase whitlockite, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. After calcination the presence of chlorapatite and spodosite in the non-radioactive and radioactive materials was confirmed by XRD spectra (Fig. 1).

One of the expected signs of radiation-induced damage is a detectable change in the XRD peak width and lattice dimensions

of the phases. Visual examination of the diffraction traces obtained from <sup>238</sup>Pu loaded material at the start and end of the ageing trial (Fig. 2) showed no peak broadening. Lattice dimensions, calculated for chlorapatite and spodosite by Rietveld analysis using the free-ware profile fitting software package GSAS [8] are listed in Table 1 with the uncertainty in the last figure in parentheses. Included in the table are the lattice dimensions quoted in the JCPDS files 01-070-1454, chlorapatite and 00-019-0247, spodosite. Comparison of the JCPDS data and the nominally un-aged material suggests that substitution of Ca by Pu and Am at this concentration has little effect on lattice dimensions. When comparing the aged and un-aged data, there appears to be a small increase in all the lattice parameters of both phases but especially the spodosite. Increasing the lattice dimensions is normally associated with a decrease in durability.

Release data for the anions and cations were calculated from their measured concentrations in the leachate adjusted for the dilution effect produced by the test protocol. This method assumes all dissolved ceramic is in solution and is not necessarily correct as insoluble by-products may be formed; however, as the main concern is the migration of soluble species into the biosphere, these are the important data. Although the un-aged leach data shown in Tables 2 and 3 indicate excellent behaviour with only very small releases as soluble species, some differences are noted between the various specimens.

In general the radioactive specimens exhibited higher releases in leach tests relative to the non-radioactive equivalent reported previously [9]. For example, releases of Cl after 28 days were  $2.7 \times 10^{-3} \text{ g m}^{-2}$  for the <sup>239</sup>Pu/<sup>241</sup>Am specimens and  $1.6 \times 10^{-3} \text{ g m}^{-2}$  for the non-radioactive specimens. Comparable release data for Ca were  $1.6 \times 10^{-3}$  and  $0.3 \times 10^{-3} \text{ g m}^{-2}$ , respectively. Release of Am from the mixed <sup>239</sup>Pu/<sup>241</sup>Am composition was exceptionally low at  $2.4 \times 10^{-7} \text{ g m}^{-2}$ . Comparison of the leach data for <sup>239</sup>Pu/<sup>241</sup>Am and <sup>238</sup>Pu/<sup>241</sup>Am loaded waste shows that Ca and P releases are an order of magnitude lower from the <sup>238</sup>Pu/<sup>241</sup>Am loaded waste simulant whereas Cl is an order of magnitude higher. The reason for this is not known. A comparison of the pH of the two solutions, Table 4, shows that the <sup>238</sup>Pu/<sup>241</sup>Am loaded waste generated a more acidic solution, probably as a result of radiolysis of the water.

Overall, the data suggest that the Cl, P and Ca present in the un-aged <sup>239</sup>Pu/<sup>241</sup>Am and aged <sup>238</sup>Pu/<sup>241</sup>Am (Table 5) ceramic dissolve congruently but this is not true of the <sup>238</sup>Pu/<sup>241</sup>Am-bearing waste (Table 3) which shows a decrease in the Ca and P release by one order of magnitude but an order of magnitude increase in the Cl release. These changes do not appear to have had a significant effect on the release of either Pu or Am. This is difficult to explain as any decreased durability of the matrix caused by radiation damage as suggested by the Ca and P releases should lead to an equally large

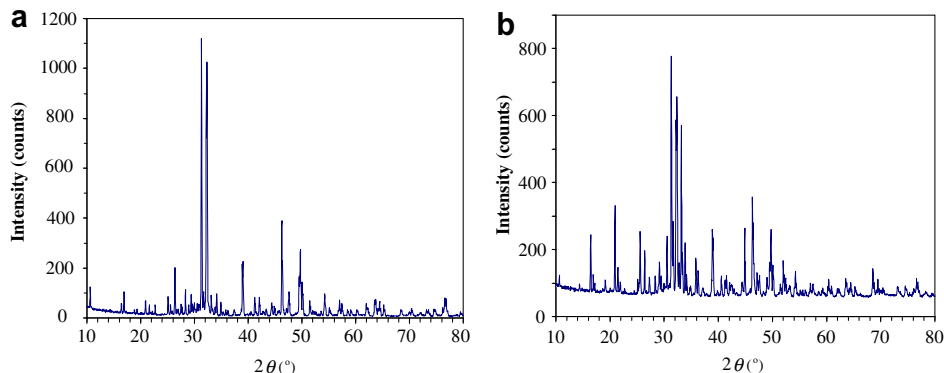


Fig. 1. XRD spectra of (a) surrogate containing waste and (b) Pu and Am containing waste.

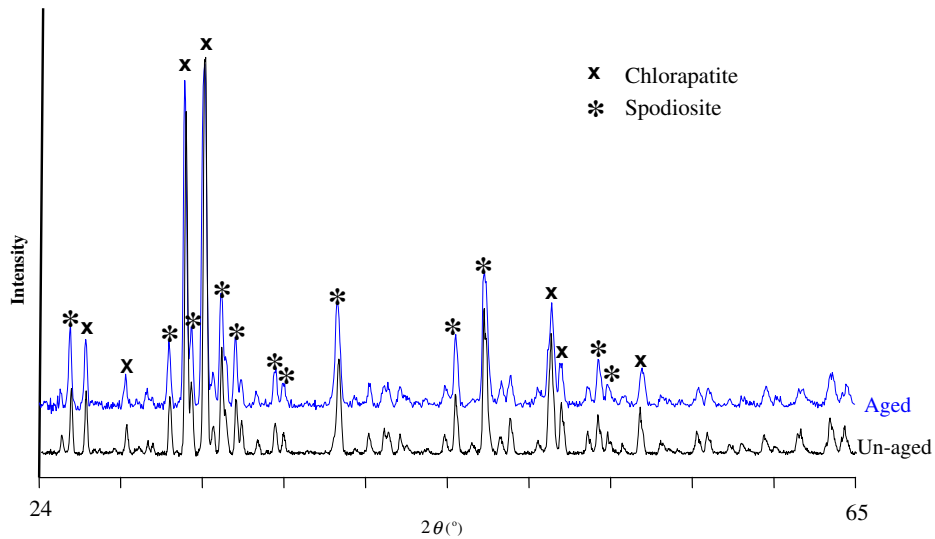


Fig. 2. XRD spectra of aged and un-aged <sup>238</sup>Pu/<sup>241</sup>Am loaded simulant waste.

Table 1  
Calculated lattice dimensions of the chlorapatite and spodiosite.

	Chlorapatite			Spodiosite		
	a <sub>0</sub> (nm)	b <sub>0</sub> (nm)	c <sub>0</sub> (nm)	a <sub>0</sub> (nm)	b <sub>0</sub> (nm)	c <sub>0</sub> (nm)
JCPDS	0.9628(5)	1.9256(10)	0.6764(5)	0.6185(2)	0.6983(2)	0.10816(4)
Pu/Am un-aged	0.9622(3)	1.9234(4)	0.6765(1)	0.6189(1)	0.6973(1)	0.10818(1)
Pu/Am aged	0.9637(1)	1.9281(2)	0.6788(1)	0.6213(1)	0.6989(1)	0.10850(1)

Table 2  
Normalized elemental mass loss from un-aged <sup>239</sup>Pu/<sup>241</sup>Am-loaded waste simulant.

Time (d)	Normalized elemental mass loss (g m <sup>-2</sup> )				
	Ca	P	Cl	Pu	Am
1	1.1 × 10 <sup>-3</sup>	1.4 × 10 <sup>-3</sup>	1.9 × 10 <sup>-3</sup>	0.9 × 10 <sup>-5</sup>	2.0 × 10 <sup>-7</sup>
3	1.3 × 10 <sup>-3</sup>	1.7 × 10 <sup>-3</sup>	1.3 × 10 <sup>-3</sup>	1.0 × 10 <sup>-5</sup>	1.3 × 10 <sup>-7</sup>
9	1.5 × 10 <sup>-3</sup>	2.1 × 10 <sup>-3</sup>	2.6 × 10 <sup>-3</sup>	1.1 × 10 <sup>-5</sup>	1.5 × 10 <sup>-7</sup>
14	1.5 × 10 <sup>-3</sup>	2.1 × 10 <sup>-3</sup>	3.4 × 10 <sup>-3</sup>	1.0 × 10 <sup>-5</sup>	2.7 × 10 <sup>-7</sup>
28	1.6 × 10 <sup>-3</sup>	2.3 × 10 <sup>-3</sup>	2.7 × 10 <sup>-3</sup>	1.2 × 10 <sup>-5</sup>	2.4 × 10 <sup>-7</sup>

Table 3  
Normalized elemental mass loss from un-aged <sup>238</sup>Pu/<sup>241</sup>Am loaded waste simulant.

Time (d)	Normalized elemental mass loss (g m <sup>-2</sup> )				
	Ca	P	Cl	Pu	Am
1	1.6 × 10 <sup>-4</sup>	9.3 × 10 <sup>-5</sup>	4.4 × 10 <sup>-2</sup>	1.6 × 10 <sup>-5</sup>	<(6.0 × 10 <sup>-7</sup> )
3	1.3 × 10 <sup>-4</sup>	4.9 × 10 <sup>-5</sup>	2.5 × 10 <sup>-2</sup>	1.4 × 10 <sup>-5</sup>	<(5.0 × 10 <sup>-7</sup> )
9	1.6 × 10 <sup>-4</sup>	5.8 × 10 <sup>-5</sup>	3.2 × 10 <sup>-2</sup>	1.6 × 10 <sup>-5</sup>	<(7.0 × 10 <sup>-7</sup> )
14	1.7 × 10 <sup>-4</sup>	5.5 × 10 <sup>-5</sup>	2.8 × 10 <sup>-2</sup>	1.8 × 10 <sup>-5</sup>	<(7.0 × 10 <sup>-7</sup> )
28	1.6 × 10 <sup>-4</sup>	5.4 × 10 <sup>-5</sup>	2.0 × 10 <sup>-2</sup>	1.6 × 10 <sup>-5</sup>	<(8.0 × 10 <sup>-7</sup> )

() Values calculated from the detection limit.

Table 4  
pH values of leachate from un-aged samples (powder).

Time (d)	1	3	9	14	28
pH ( <sup>239</sup> Pu/ <sup>241</sup> Am)	6.83	6.65	6.62	6.89	6.64
pH ( <sup>238</sup> Pu/ <sup>241</sup> Am)	6.72	6.76	6.30	5.93	5.97

increase in the Cl releases but this is not supported by the data. The release of Am has also been increased by some two orders of magnitude but this still remains at a very low level.

Table 5  
Normalized elemental mass loss from aged <sup>238</sup>Pu/<sup>241</sup>Am-bearing waste simulant.

Time (d)	Normalized elemental mass loss (g m <sup>-2</sup> )				
	Ca	P	Cl	Pu	Am
1	2.4 × 10 <sup>-2</sup>	1.8 × 10 <sup>-2</sup>	8.4 × 10 <sup>-2</sup>	1.6 × 10 <sup>-3</sup>	6.8 × 10 <sup>-5</sup>
3	2.2 × 10 <sup>-2</sup>	1.8 × 10 <sup>-2</sup>	8.0 × 10 <sup>-2</sup>	1.8 × 10 <sup>-3</sup>	6.5 × 10 <sup>-5</sup>
9	2.3 × 10 <sup>-2</sup>	1.9 × 10 <sup>-2</sup>	8.9 × 10 <sup>-2</sup>	1.6 × 10 <sup>-3</sup>	5.4 × 10 <sup>-5</sup>
14	2.0 × 10 <sup>-2</sup>	1.8 × 10 <sup>-2</sup>	9.4 × 10 <sup>-2</sup>	1.5 × 10 <sup>-3</sup>	5.0 × 10 <sup>-5</sup>
28	1.9 × 10 <sup>-2</sup>	1.7 × 10 <sup>-2</sup>	8.8 × 10 <sup>-2</sup>	1.4 × 10 <sup>-3</sup>	4.7 × 10 <sup>-5</sup>

Table 6  
pH values of leachate from aged <sup>238</sup>Pu/<sup>241</sup>Am samples.

Time (d)	1	3	9	14	28
pH	6.66	6.80	6.68	6.44	6.83

Table 6 shows the pH values of the leachate at various times during the leaching of aged samples. These values do not show the increasing acidification of the water observed in the un-aged <sup>238</sup>Pu/<sup>241</sup>Am waste.

#### 4. Conclusions

Chloride-containing simulated actinide waste has been reacted with calcium phosphate to produce a ceramic in which the majority of the chloride and actinide constituents are immobilized in chlorapatite and spodiosite mineral phases. The durability of the <sup>239</sup>Pu/<sup>241</sup>Am and <sup>238</sup>Pu/<sup>241</sup>Am loaded ceramic measured at the start of the ageing trial was encouraging although slightly lower than the non-active surrogate loaded ceramic. Normalized leach data for Ca, P and Cl are indicative of congruent dissolution of the ceramic with

subsequent formation of an insoluble calcium phosphate phase. The very low normalized concentrations of Pu and Am in the leachant solution suggest that these cations form insoluble phases as by-products of the dissolution process. Durability data from the aged samples shows an increase of two orders of magnitude in the release of the Ca and P but this is not matched by a comparable increase in the Cl release and therefore dissolution is no longer congruent.

Although visual comparison of the XRD traces obtained from original and aged samples showed no significant change in peak shape or position, Rietveld refinement of the structure suggests a slight increase in the lattice parameters for chlorapatite and slightly larger increase for spodosite.

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