

Progress in the Assessment of Wasteforms for the Immobilisation of UK Civil Plutonium - 8241

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ABSTRACT

The alternatives for the disposition of the UK's civil plutonium stocks are currently being investigated by Nexia Solutions Ltd. on behalf of the Nuclear Decommissioning Authority (NDA). A number of scenarios are currently being considered depending on the strategic requirements of the UK. The two main disposition options are: re-use as MOX (Mixed Oxide) fuel in reactors, or immobilisation in the event of any material being declared surplus to requirements. The amount of Pu which will require immobilisation will depend on future UK nuclear strategy, along with the extent of any stocks deemed unsuitable for re-use. However, it is likely that some portion will have to be immobilised and therefore three credible wasteforms are under consideration; ceramic, glass and 'immobilisation' MOX¹. These are currently being developed and assessed in a systematic programme that involves periodic evaluation against a range of criteria. In this way, by down-selecting on the basis of robust and technical review, the most appropriate option for immobilising surplus civil plutonium in the UK can be recommended.

The latest results from the immobilisation experimental programme are presented following the de-selection of the least favourable glass and ceramic candidates. The main criteria for this decision were waste loading, durability, processability, criticality and proliferation resistance. In addition, the durability of unirradiated MOX fuel is being examined to determine its potential as a wasteform for Pu, and recent leach test data is discussed. The current evaluation comprises not only a comparison of the relevant physical properties of the various wasteforms, but also key processing parameters, e.g. glass viscosity and melter technology, ceramic fabrication routes, and criticality issues. Other important aspects of the long-term behaviour of the wasteforms under consideration in a potential repository environment, such as radiation damage, criticality control and the properties of any neutron poisons present, are also included.

INTRODUCTION

The options for disposition of the UK's separated civil plutonium stocks are currently being assessed by the NDA. Nexia Solutions Ltd is carrying out a package of work on behalf of the NDA considering technical aspects of both the options of re-use as fuel and immobilisation as waste [1]. This will allow robust decisions to be made on future management options for UK separated civil plutonium. The majority of the Pu-inventory could be used in the manufacture of MOX fuel in potential power generation scenarios, but immobilisation is being investigated for any surplus or unsuitable material. Immobilisation would be achieved by assimilation of the

¹ 'Immobilisation' MOX would comprise MOX fuel pellets manufactured 'as normal', with the exception that the dimensional tolerances required of reactor operations could be relaxed.

plutonium into a durable host matrix followed by long term storage and subsequent final repository disposal.

The immobilisation component of the Civil Plutonium Disposition Project is intended to develop and subsequently recommend to the NDA a technically underpinned option or options for the immobilisation of any, or all, of the UK plutonium stockpile. This will entail the evaluation of a range of candidate wastefoms using a variety of criteria and will result in a fully qualified wasteform. These evaluation criteria include:

- waste loading,
- durability,
- criticality protection,
- proliferation resistance,
- radiation damage tolerance,
- processability, and
- chemical flexibility to accommodate impurities.

It is important that the UK programme on plutonium disposition is targeted at UK needs and requirements while taking account of the technical efforts that have been carried out elsewhere [2]. To that end, ceramic, vitreous, and 'immobilisation' MOX wastefoms along with the possibility of cementation have been identified as the most appropriate for study as plutonium host matrices.

For the vitrification option, following an initial set of trials [3], three borosilicate glasses were selected for inclusion in a more detailed experimental programme: *lanthanide borosilicate (LaBS)*, *alkali tin silicate (ATS)* and high-lanthanide alkali borosilicate, or '*modified-MW*' (*MMW*).² The minimum acceptable waste loading of 10 wt% Pu was applied, and the temperature dependence of the solubility of inactive surrogates in these leading candidate glass hosts was studied. The durability of the glasses was also investigated in detail, and powder-based static leach test data is now available for a range of waste loadings at different pHs. Similar data is being generated through the systematic examination of a number of ceramic host phases based on *zirconolites*, *pyrochlores* and related phases where the capability of including neutron poisons alongside plutonium while maintaining durability and tolerance of radiation damage is being explored [4]. In addition to vitreous and tailored ceramic hosts, the suitability of unirradiated MOX fuel pellets as a potential wasteform for plutonium is being investigated via a series of durability tests. These are being carried out at the Institute for Transuranium Elements (ITU), Karlsruhe, Germany, and preliminary data from short-term leaching is presented below.

WORK TO DATE

Ceramic Wastefoms

A systematic study of ceramic phases suitable for plutonium immobilisation has been performed in collaboration with the Immobilisation Science Laboratory (ISL), Sheffield, UK. Cerium was

² MW is the glass used for the immobilisation of UK high-level radioactive waste, and has a composition (in wt%) 62 SiO₂, 22 B₂O₃, 11 Na₂O and 5 Li₂O.

used as the surrogate for plutonium in the initial work on the examination of phase development and waste loading. This has now been extended to the use of uranium. Several ceramic phases have been investigated and a number of these have been confirmed as having adequate capacity to accommodate PuO₂ and neutron poisons such as Gd and Hf. Surrogate loading levels of over 10 wt% have been shown to be possible, and work is being carried out to evaluate higher incorporation rates. The availability of the glove box at the ISL has allowed an investigation of the capacity of these phases to accommodate uranium, which is known to be a better surrogate for plutonium and unlike cerium has no tendency to auto-reduce to the 3+ state. This work has established that while some phases can accommodate over 10 w% Pu surrogate in the oxidised state, a very different result is seen with the reduced species.

Table I summarises the ceramic phases currently under investigation along with a synopsis of some of their properties.

Table I. Synopsis of the properties of the ceramic phases currently under consideration for the immobilisation of the UK's surplus civil plutonium.

Phase	Structure	Loading (wt%)		Neutron Poisons	Spatial Density ^a (10 wt% Pu) (kg m ⁻³)	Sinter Temp (°C)	% Theoretical Density by CPS ^b
		Ce	U				
Zirconolite $Ca(Zr_{1-x}M_x)Ti_2O_7$	2M	<14	<13	Hf & Gd	530	1450	98
	4M	<33	tbd			1450	98
Zirconolite with Ca substitution $(Ca_{1-x}M_x)Zr(Ti_{2-x}Mg_x)O_7$	2M	<26	<24	Hf & Gd	700	1450	98
	3O	<43	tbd			1450	98
Zirconate Pyrochlore $Gd_2(Zr_{2-x}M_x)O_7$	Pyrochlore	<19	tbd	Hf & Gd	780	1650	94
	Fluorite	<54	tbd			1650	94
Britholite $(Ca_{2-x}Y_{8-2x}M_x)(SiO_4)_6$	Apatite	<67	<14	Gd only	480	1400	93
Kosnarite $Na(Zr_{2-x}M_x)(PO_4)_3$		<9	<18	Hf (part Gd)	350	1350	91

^a Spatial density is the Pu waste loading (wt%) × wastefrom density in kg m⁻³.

^b CPS is Cold Press and Sinter

Of the phases shown in

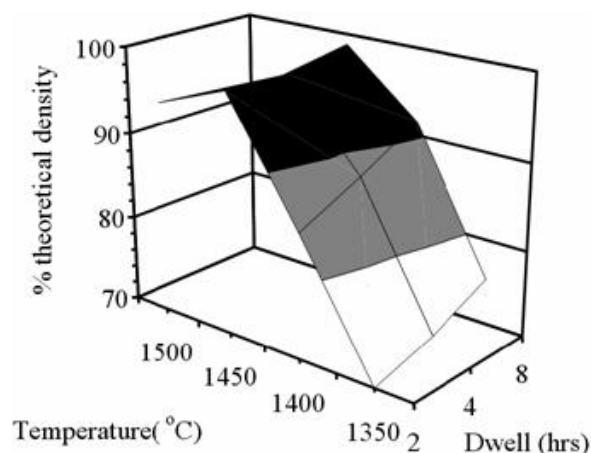
Table I, *kosnarite* has now been discarded as an option on the grounds of difficulty of fabrication and low waste loading. Previously, *murataite* A_2O_3 - MO - TiO_2 (A = Gd, Y; M = Zn, Mn) phases were also rejected and deemed unsuitable as plutonium wastefroms, again due to the difficulty of fabrication [1]. Phases being taken forward include those based on zirconia and titania as well as britholite, a silica based phase, although the latter has problems with the incorporation of a 4+ ion (Hf) as a neutron poison.

Cubic zirconia ($Zr_{0.85}Y_{0.15}O_{1.93}$) has also been added to the list for evaluation, and is expected to behave similarly to zirconate pyrochlore. Cubic zirconia is known to have high capacity for Gd_2O_3 , HfO_2 and PuO_2 . For example, $(Zr_{0.85}Y_{0.15}O_{1.93})_{0.95}(PuO_2)_{0.05}$ has been shown to be a solid solution [5], which is equivalent to $x = 0.2$ in zirconolite or pyrochlore. This gives a PuO_2 spatial density $\sim 650 \text{ kg m}^{-3}$, and more extensive solid solutions are probable.

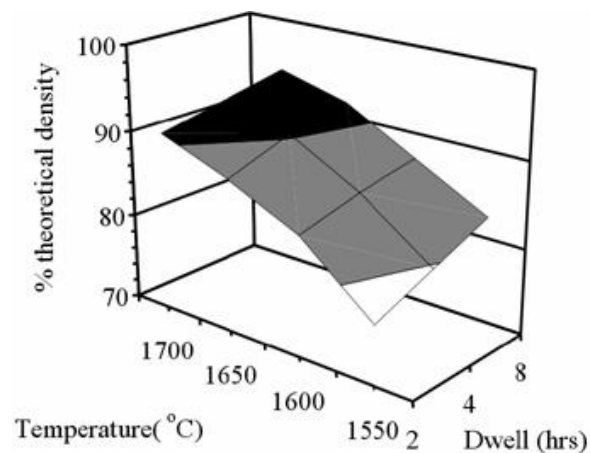
As part of the wastefrom development programme at the ISL, fabrication temperatures have been established for each ceramic candidate phase using simple cold press and sinter (CPS) techniques [4].

Fig. 1 shows the % theoretical density as a function of sinter temperature and dwell time for four of the candidate ceramic wastefroms. Note that the figures given in Table I for sintering temperatures and the resulting density are optimum values. The use of lower fabrication temperatures may be beneficial in establishing a process route capable of immobilising what may be a large volume of material.

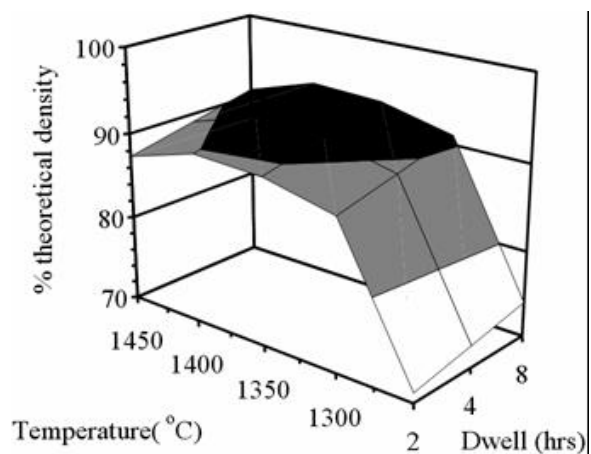
a) $(Ca_{0.9}Gd_{0.1})(Zr_{0.5}Ce_{0.2}Hf_{0.2}Gd_{0.1})Ti_2O_7$



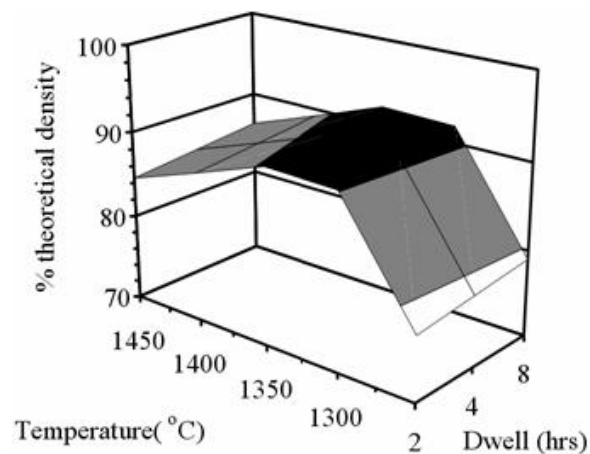
b) $Gd_2(Zr_{1.6}Ce_{0.2}Hf_{0.2})O_7$



c) $(Ca_3Y_5CeGd)Si_6O_{26}$



d) $Na_{1.2}(Zr_{1.4}Ce_{0.2}Hf_{0.2}Gd_{0.2})P_3O_{12}$



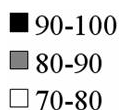


Fig. 1. % Theoretical density as a function of sinter temperature and dwell time for four ceramic-based plutonium wasteforms.

In addition to using a route based on CPS, there is the potential for using hot isostatic pressing (HIP) technology, which is being developed to immobilise a range of plutonium containing waste and residues currently stored on the Sellafield site [6]. Despite the restriction of operating temperature to ~1300 °C due to the selection of stainless steel containers for the HIP process, the simultaneous application of pressure (~100 MPa) produces fully dense wasteforms.

The ceramic programme has benefited in an number of areas from the development of the HIP process aimed at the plutonium waste and residues. Specifically, as part of this programme, a package of work has been carried out to assess the effect of processing plutonium contaminated with chlorine from the degradation of PVC storage bags. Calcination trials showed that up to half of the chlorine could be removed from PVC based materials when held at 750 °C for over 1 hour. More importantly it was shown that in both zirconolite and pyrochlore based compositions up to 0.2 wt% chloride could be accommodated in the wasteform without any deleterious effect. The work was carried out using a cerium surrogate.

Wasteforms containing plutonium will experience structural radiation damage through self irradiation over prolonged time periods. While different phases will respond differently to such exposure, e.g. crystalline or amorphous, it is important that any change in phase or dimensions must not have a deleterious effect on the wasteform's ability to retain radionuclides. Researchers have shown that following radiation damage, most ceramics convert to either a disordered form as is the case for the zirconate pyrochlore, or fully amorphous as for the zirconolite [7]. However the amorphisation does not necessarily lead to a reduction in durability [7].

Microscopy studies of Synroc-C based samples made over 20 years ago containing Pu-238 to accelerate aging have been carried out [8]. Note that whilst Synroc-C is not being considered for the immobilisation of separated PuO₂, these samples offer an invaluable insight into the long-term radiation stability of ceramic plutonium wasteforms. The decay dose averaged over whole sample was ~3 x 10¹⁹ alpha g⁻¹, with the decay dose averaged over the Pu-host phases ~6 x 10¹⁹ alpha g⁻¹, which although significant is still lower than can be found in natural analogues (up to 25 x 10¹⁹ alpha g⁻¹). SEM was used for bulk sample microstructural evaluation, i.e. investigation of cracking, phase distribution, homogeneity, Pu partitioning via Energy Dispersive X-Ray analysis (EDX). TEM was used for detailed sample nanostructural evaluation, i.e. investigation of effects on the nanometre scale, examination and EDX of very fine grained material, nanodiffraction studies, Pu partitioning assessment by EDX on individual grains. Fig. 2 shows typical high and low magnification SEM micrographs of a Pu-238 Synroc-C sample. The SEM / TEM examination confirmed all the main Synroc phases with no significant porosity. Fig. 2b shows the inhomogeneity in the samples, although this is consistent with the precursors used for their preparation. As expected, the Pu had partitioned into the zirconolite and perovskite phases, although the relative quantities have not been determined, and these were shown to be fully

amorphous. There was some cracking present, but this was only seen in the non-Pu bearing phases, i.e. rutile and hollandite, which were shown to still be crystalline. The cracking is caused by the swelling of the amorphised Pu-bearing phases introducing tensile strain into the crystalline phases.

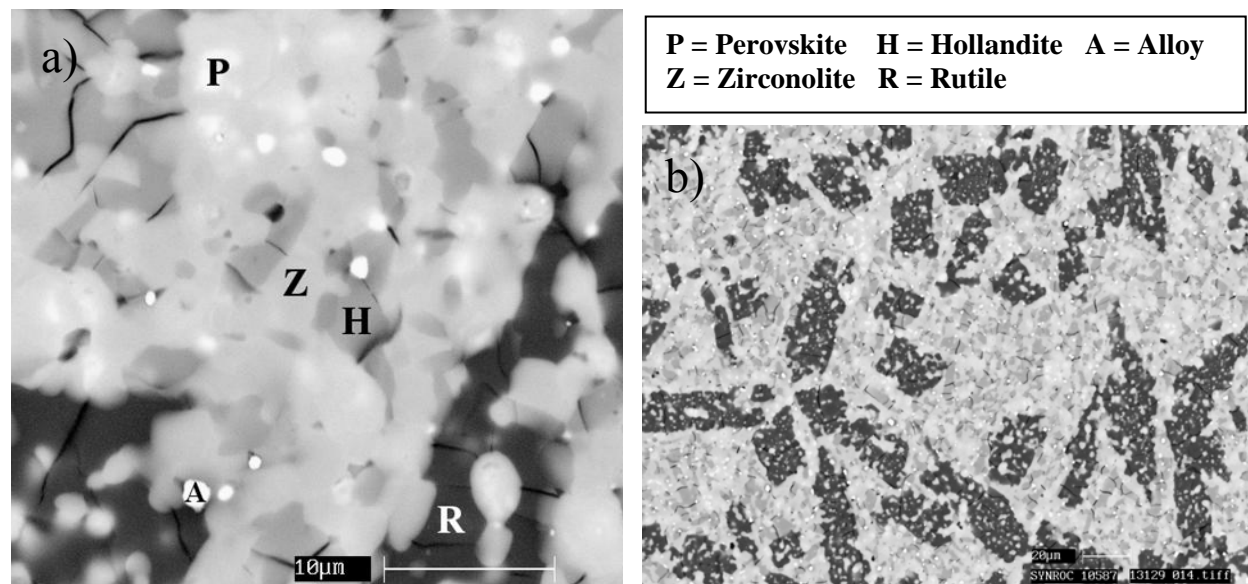


Fig. 2. Typical SEM micrographs from an aged Pu-238 Synroc C sample; a) High magnification showing Synroc-C phases, b) Low magnification showing inhomogeneity.

These microscopy studies show that although amorphisation has taken place, the samples remained mechanically robust giving confidence that while not optimised for plutonium immobilisation, these titanate-based materials remain intact over extended time periods and are tolerant of radiation damage effects.

Modelling work is being undertaken to understand the various damage and annealing mechanisms in zirconolite following heavy recoil atom damage. This will be backed up by experimental studies and will compare damaged structures with materials amorphised by other experimental methods. This will provide a more readily accessible assessment of the way zirconolite as a wasteform candidate behaves in the presence of radiation damage expected over disposal time scales.

Glass Wasteforms

A wide range of glass compositions have been fabricated and assessed for their suitability for the immobilisation of the UK's separated plutonium stocks. It has been demonstrated that plutonium vitrification is feasible and waste loading for surrogate materials of over 10 wt% in a number of silicate and phosphate glass matrices is practicable.

Following the initial evaluation of 10 candidate glass systems, *modified-MW (MMW)*, *lanthanum borosilicate (LaBS)*, *alkali tin silicate (ATS)*, *sodium aluminium phosphate (NAP)* and *iron*

phosphate (IP) compositions were selected to be taken forward for a more detailed 2nd stage assessment. Simple alkali borosilicate (MW), calcium borosilicate (CaBS), aluminium borosilicate (ABS), lanthanum aluminium silicate (LAS), and lead iron phosphate (LIP) were all rejected due to a number of factors including poor durability, inferior waste loading, evidence of crystallisation, and extremely high processing temperatures. The development programme has sought to maximise waste loading while at the same time reduce melt temperatures in order to facilitate ease of manufacturing. Initial melts were carried out using cerium as a plutonium surrogate. While cerium has given a good indication of plutonium solubility in glass, it has a tendency to auto-reduce at high temperatures and as such is not typical of the Pu⁴⁺ state. As such cerium has been replaced by hafnium as a surrogate, which has the additional advantage of having a more similar density to plutonium and as such has a more representative behaviour in glass melts where settling can be a problem.

The borosilicate glasses included in the 2nd stage assessment, which consisted of a temperature-composition study and powder based (PCT-B) leach testing, are described below. The base glass compositions are shown in Table II.

Modified-MW (MMW): One of the surprising results from the initial programme, the addition of Al₂O₃ along with a mixture of Pu-surrogates and neutron poisons (CeO₂, HfO₂, and Gd₂O₃) to MW yielded a highly durable product with waste loadings of at least 10 wt%.

Lanthanum Borosilicate (LaBS): The family of glasses developed in the US for actinide waste immobilisation [9]; Savannah River National Laboratory are currently proposing a LaBS formulation for the immobilisation of excess weapons-usable plutonium [10, 11]. It has been demonstrated as having a high capacity for Pu along with excellent durability, although it requires melting temperatures typically in excess of 1400 °C to achieve high waste loading.

Alkali Tin Silicate (ATS): Another actinide waste glass developed in the US, this formulation is not quite as durable as LaBS, but requires a significantly lower melting temperature to achieve the 10 wt% loading benchmark [12].

Table II. Base glass compositions used in the 2nd stage assessment (weight %)

MMW ^a	ATS	LaBS E	LaBS F	LaBS G	LaBS X
Al ₂ O ₃ 6.3	Al ₂ O ₃ 2.7	Al ₂ O ₃ 18.2	Al ₂ O ₃ 19.2	Al ₂ O ₃ 16.1	Al ₂ O ₃ 10.0
B ₂ O ₃ 17.9	B ₂ O ₃ 13.5	B ₂ O ₃ 10.4	B ₂ O ₃ 10.6	B ₂ O ₃ 10.0	B ₂ O ₃ 13.0
Gd ₂ O ₃ 12.5	Cs ₂ O 0.6	Gd ₂ O ₃ 12.2	Gd ₂ O ₃ 11.8	Gd ₂ O ₃ 13.3	Gd ₂ O ₃ 11.7
Li ₂ O 4.1	Gd ₂ O ₃ 3.8	La ₂ O ₃ 20.0	La ₂ O ₃ 29.5	La ₂ O ₃ 22.2	HfO ₂ 7.1
Na ₂ O 8.9	K ₂ O 5.9	Nd ₂ O ₃ 9.0	SiO ₂ 26.5	Nd ₂ O ₃ 13.3	La ₂ O ₃ 20.3
SiO ₂ 50.4	Li ₂ O 4.7	SiO ₂ 24.5	SrO 2.4	SiO ₂ 22.2	Nd ₂ O ₃ 15.4
	Na ₂ O 10.5	Sm ₂ O ₃ 3.2		SrO 2.8	SiO ₂ 20.0
	SiO ₂ 46.9	SrO 2.5			SrO 2.5
	SnO 3.0				
	TiO ₂ 2.2				
	ZrO ₂ 6.2				

^a The MW glass frit was used as received, with the Al₂O₃ and Gd₂O₃ added along with the Pu-surrogates during melting.

Four different base LaBS glass compositions were fabricated on the basis of two different approaches to optimising the melting conditions. Marra *et al* [10] predicted that compositions lying along the 1:3 stoichiometric axis in the Ln₂O₃-B₂O₃-(SiO₂+Al₂O₃) ternary phase diagram should have lower melting and liquidus temperature (T_L). Riley *et al* [13] measured a minimum T_L at a Ln₂O₃ content of ~45 wt% in the Al₂O₃-Ln₂O₃-SiO₂ phase fields. The *LaBS_X* glass is similar to the Savannah River composition ‘Frit X’ [10]. *LaBS_E* and *LaBS_F* are developments from the initial evaluation to attempt to minimise the required melting temperature using the approach of Riley, and *LaBS_G* is a hybrid composition that lies close to this 1:3 axis, but reduces the Ln₂O₃ content to as close to 45 wt% as possible.

A summary of the results from the temperature-composition study is shown in Table III. A matrix of glass samples was prepared using the base glasses in Table II melted at a range of temperatures and HfO₂ (Pu-surrogate) loadings. For MMW, CeO₂ was included with the HfO₂ as the Pu-surrogate such that the *total* CeO₂ plus HfO₂ loading was 20 wt%, as it seemed that the mixture of oxides gave the beneficial properties of MMW. It was found that a HfO₂ loading of 10 wt% is readily achievable with temperatures of 1200, 1300 and 1400 °C for ATS, MMW and LaBS respectively. For ATS and MMW, HfO₂ loadings of 15 wt% are also possible at these temperatures, but for the LaBS glasses, temperatures in excess of 1400 °C are required to dissolve >10 wt% HfO₂. In addition, for the MMW glasses it was observed that at temperatures below 1300 °C, it was the CeO₂ that tended not to dissolve. Hence, a MMW sample was fabricated at 1350 °C with all the cerium replaced by hafnium, i.e. 20 wt% HfO₂, in order to investigate whether the cerium is required for the high waste loading and durability of these glasses. A fully homogeneous material was formed with all the HfO₂ dissolved, demonstrating the capacity of MMW for tetravalent species, but the full glass forming temperature range of MMW using solely Hf as a Pu-surrogate still needs to be investigated. It was also noted that the viscosity of 10 wt% HfO₂ ATS at 1200 °C was fairly high, which could potentially lead to difficulties in pouring. Therefore, a series of glass viscosity measurements have been carried out on the candidate glasses and these will give an indication as to the ability to “work” these glasses at a range of temperatures. This will support the development of a processing route.

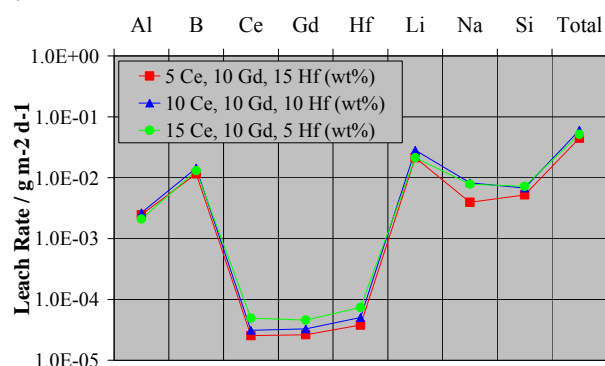
Table III. Summary of the temperature-composition study of candidate glass wasteforms for Pu-immobilisation.

Glass	Pu-Surrogate (Neutron Poison)	Surrogate loading (wt%)	Spatial Density 10 wt% PuO ₂ (kg m ⁻³)	Melt Temp. (°C)	Comments
MMW	Ce & Hf (Gd)	>10	300	1300	Requires validation using solely Hf as Pu-surrogate
ATS	Hf (Gd)	>10	290	1200	High viscosity at 1200 °C may give pouring problems
LaBS	Hf (Gd)	≤10	400	1400	Significant decrease in

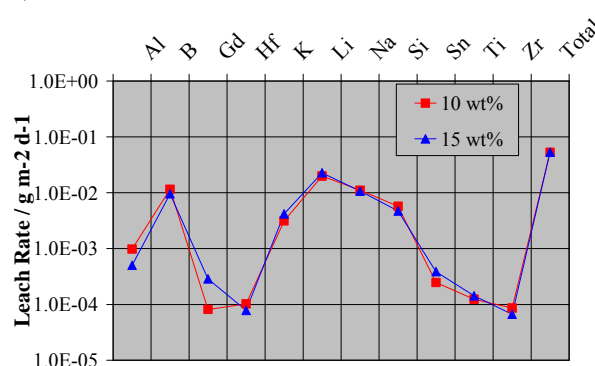
					durability at low pH
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Durability has also been tested using a modified PCT-B test over a range of pHs at elevated temperatures. These were performed statically on powdered samples (75-150 μm), with surface-area to leachate volume ratios of about 1800, 1850 and 1300 m^{-1} for MMW, ATS and LaBS respectively, at 90 $^{\circ}\text{C}$, in low density polyethylene bottles. Fig. 3 shows the elemental leach rates after 27 days in de-ionised water (DIW) for MMW, ATS, and LaBS fabricated at 1300, 1200 and 1400 $^{\circ}\text{C}$ respectively. In Fig. 3a, the three variations of $\text{HfO}_2/\text{CeO}_2$ loading used for the MMW glass are shown; Fig. 3b shows the ATS samples with 10 and 15 wt% HfO_2 loading; and Fig. 3c shows the values from the four different LaBS base glasses with 10 wt% HfO_2 -loading. All glasses examined showed low elemental leach rates (ELRs) for the Pu-surrogates in DIW, i.e. 10^{-4} to 10^{-5} $\text{g m}^{-2} \text{d}^{-1}$ for MMW and ATS, and 10^{-5} to 10^{-6} for LaBS. Overall wasteform durability, however, was shown to be dominated by the corrosion of the base glass matrix with the Pu-surrogates remaining in insoluble phases. For example, the boron ELRs, which is used as an indicator for matrix dissolution, were $\sim 10^{-2}$ $\text{g cm}^{-2} \text{d}^{-1}$ for MMW and ATS, and $\sim 10^{-3}$ $\text{g cm}^{-2} \text{d}^{-1}$ for the LaBS glasses.

a) MMW



b) ATS



c) LaBS

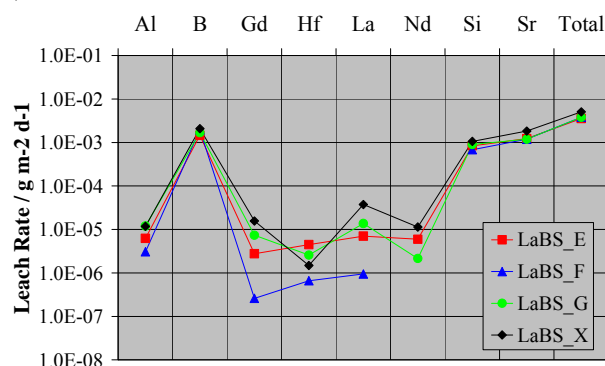


Fig. 3. Modified PCT-B leach test data for a) MMW at 1300 $^{\circ}\text{C}$ (20 wt% total of CeO_2 and HfO_2); b) ATS at 1200 $^{\circ}\text{C}$ (10 and 15 wt% HfO_2); and c) LaBS at 1400 $^{\circ}\text{C}$ (10 wt% HfO_2).

Both modified PCT-B (powder) and MCC-1 (monolith) leach tests were repeated using buffer solutions at pH 4, 7 and 10. Table IV shows the bulk leach rates, calculated from a simple weight loss measurement of the MCC-1 monolithic samples, for representative MMW, ATS and LaBS glasses. MMW shows a small decrease in durability at higher and lower pHs, while ATS shows a small increase. However, the most pronounced effect is for LaBS at low pHs, where there is a substantial (~2 orders of magnitude) increase in the bulk leach rate. Hence, LaBS may well have the best durability in DIW, but performs very poorly in acidic conditions [14]. Whilst this may not be important for the typical conditions expected in a repository environment, it is significant for the potential retrievability of Pu from the wastefrom, raising concerns about its proliferation resistance. The LaBS_G glass also forms substantial quantities of precipitated secondary phases on the surface of the leached sample in the buffer solutions, which yields an overall sample weight gain, and hence an apparent negative leach rate in the case of pH 7 and 10. Work is continuing to analyse PCT-B (powder) based leach data in order to compare elemental leach rates at the different pHs, and also to identify alteration phases.

Table IV. Bulk leach rates for MMW, ATS and LaBS_G in pH 4, 7 and 10 buffers, compared with the value in DIW.

Glass Sample	Melt Temp. / °C	pH Buffer BLR / g m ⁻² d ⁻¹			DIW BLR / g m ⁻² d ⁻¹
		4	7	10	
MMW ^a	1350	2.08 x 10 ⁻¹	1.04 x 10 ⁻¹	1.06 x 10 ⁻¹	3.32 x 10 ⁻²
ATS ^b	1300	6.05 x 10 ⁻²	9.61 x 10 ⁻²	2.14 x 10 ⁻²	9.66 x 10 ⁻²
LaBS_G ^c	1400	1.55	-1.72 x 10 ⁻²	-1.71 x 10 ⁻³	3.36 x 10 ⁻²

^a The MMW sample had a waste loading (in wt%) of 15 HfO₂, 10 Gd₂O₃ and 5 CeO₂.

^b The ATS sample had a waste loading of 10 wt% HfO₂.

^c The LaBS_G sample had a waste loading of 10 wt% HfO₂.

For the phosphate glasses, initial fabrication and assessment was performed by the ISL [3]. Taking into account ease of melting, potential plutonium waste loading capacity, glass stability, chemical durability and proliferation resistance, the most promising candidates are the *iron phosphate (IP)* and *sodium aluminium phosphate (NAP)* families. Further work is planned on phosphate glasses to bring to the same level of understanding as the borosilicate based glasses, at which point an assessment will be made and the most appropriate systems taken forward.

An in-house criticality assessment has been carried out for MMW and ABS glasses assuming a homogeneous distribution of PuO₂. Due to the high concentrations of neutron absorbing elements (B and Gd), both glasses provide adequate criticality control in the melter, e.g. for MMW with 25 wt% PuO₂ and 10 wt% Gd₂O₃, a cylindrical melter with diameter <86 cm would be criticality safe.

‘Immobilisation’ MOX

An option for plutonium disposition is the utilisation of unirradiated MOX pellets as a wastefrom which would subsequently be disposed in a geological repository. To test the suitability of MOX

pellets as a wastefrom, samples with varying plutonium content (4.7, 5.8, and 11.1% Pu) have been sent to ITU for leach testing (November 2005). This package of work is similar to an existing package of work carried out by ITU on irradiated MOX pellets. The pellets have been sectioned to 1.3 mm disks (surface area of 1.3 - 1.6 cm²), ground and polished to 0.25 µm on one side, annealed, and a surface characterisation performed.

Short static leach tests (200 hours) have been carried out at ambient temperature and under reducing conditions (nitrogen atmosphere with <0.4% oxygen). These tests have used a range of leaching media, i.e. pure (milli-Q) water, granitic water and carbonated water. Preliminary results show that the initial normalised leach rates for plutonium are ~10⁻⁵ g m⁻² d⁻¹ in milli-Q and carbonated water, and lower for granitic water. For uranium, the leach rates are higher; ~10⁻³ g m⁻² d⁻¹ for carbonated water, and ~10⁻⁴ g m⁻² d⁻¹ for milli-Q and granitic water. Longer term (2 year) static leach tests are also being performed, and when full analyses become available these results will be compared to those obtained under similar test scenarios on ceramic and glass wastefroms.

Criticality Issues

One of the key influences on the design of plutonium containing wastefroms is the ability to mitigate against criticality in both storage and disposal scenarios. Various modes of criticality have been previously identified by US researchers and the use of neutron poisons or absorbers has been proposed in order to mitigate against such an event. These include the use of Hf and Gd to poison the plutonium, and uranium as a diluent for the Pu daughter radionuclides, e.g. U-235. The focus of their work was to ensure compatibility of the wastefrom for disposal in Yucca Mountain. A similar study may be required to underpin disposal in a UK repository, however in the absence of a defined repository a number of scenarios are being modelled, the results of which will feed into wastefrom formulation.

The three types of criticality scenarios that have been identified by US workers are:

- *Internal*: the wastefrom as emplaced
- *Degraded*: leaching of Pu from the wastefrom
- *Extended*: transport of Pu through the repository

Current modelling is aimed at the *internal* scenario, and has been carried out for a ceramic, glass and immobilisation MOX wastefroms. The model allows different poison strategies to be tested along with waste loading and packaging densities. Similarly, the presence of interstitial materials between an array of canisters is being tested. Modelling of all variants has yet to be completed but initial results show that K_{eff} (a measure of likelihood of criticality) can vary substantially as a result of removing neutron poisons and changing interstitial materials. The value of K_{eff} also varies depending on the type of Pu, with the product arising from the reprocessing of Magnox fuel showing higher values. MOX with the highest Pu-loading (12.6%) and ceramics without neutron poisons show K_{eff} values greater than 0.9 (criticality occurs when $K_{eff} \geq 1$), and therefore may be unsuitable for disposal as a result of potential criticality concerns. Note that this is for PWR plutonium and may well increase should Magnox plutonium be used. This programme of

models will continue to evaluate the full range of plutonium contents and neutron poisons for the range of possible wasteforms.

Immobilisation of Plutonium Dioxide in Hydraulic Cement

A desk study is examining the viability of immobilising a stockpile of plutonium dioxide powder in hydraulic cement. The study has involved a series of calculations to predict the maximum loading of plutonium dioxide powder which could be incorporated into conventional intermediate level waste cement monoliths manufactured at Sellafield. These waste monoliths include 500 litre and 3 m³ cement monoliths made from hydraulic cement consisting of formulations of ordinary Portland cement blended with blast furnace slag or pulverised fuel ash. The calculations compare the internal gas pressure developed inside each monolith from the alpha radiolysis of cement pore water with the strength of the cement at a given age to assess maximum plutonium dioxide loadings. This work is currently progressing, and when available the results will be used to assess the viability of the cementation approach.

SELECTION OF IMMOBILISATION OPTIONS

Three immobilisation options remain feasible; the use of a ceramic option involving the consolidation of powder stocks with a suitable precursor, a vitrification option involving the use of melting technology, and the employment of immobilisation MOX. Within each of the first two there exist a number of sub-options which will utilise primarily the same processing route but have radically different compositions each with its own strengths and weaknesses.

The selection of a wasteform for the UK's excess civil plutonium is expected to be carried out against a NDA-agreed specification, which would be developed by means of stakeholder consultation. Although the wasteform criteria and their relative weightings have still to be decided, there are a number of questions that might be considered by the selection process, for example:

What level of durability is adequate for a plutonium wasteform?

The project is assembling extensive data on the aqueous behaviour of the candidate wasteforms. In general, all have better durability than the typical glass wasteform used for the stabilisation of Highly Active (HA) waste. However, what level of durability will a possible disposal regime require and under what conditions?

What level of criticality protection is required, be it in internal, degraded or extended modes?

Allied to the question of durability is that of criticality. Modelling can make a case for the *internal* criticality safety of a given wasteform. However, the status of the altered materials relates both to the durability and to the amount of neutron poisons incorporated. The need for poisons rests very much on the strategy for criticality mitigation. The project is looking at a range of scenarios and will make recommendations on the basis of feedback from the UK organisation responsible for the final disposal of plutonium wasteforms.

What level of security or non-proliferation protection will be required?

Disposal of plutonium will create security issues. The disposition of ex-weapons plutonium in the US recommended that disposed plutonium should comply with the spent fuel standard thus

having a radiation spike to prevent would-be theft. The US approach of using HA glass to produce that spike was not recommended by the plutonium stakeholder review in the *Environment Council Report* (2003) on the grounds that HA waste could not be held back to fulfil such a mission in addition to the fact verification of safeguards would then become impossible [2]. It was felt that better routes to provide such security could be found. Whilst this needs to be addressed at stakeholder level, the wastefrom could provide a significant proportion of that security by providing any would-be miscreant with a retrieval challenge that would be beyond the scope of any rogue operator, although not beyond the capability of the host nation. It is proposed to set up retrieval tests involving extracting plutonium (or its surrogates) from the proposed wastefrom candidates using mineral acids.

Whereas nominal values have been used to eliminate some of the previous candidate options on technical grounds, further de-selection may require consideration of the relative merit and weightings of the various evaluation criteria coupled with their effect on a range of economic and societal issues. For example, cost effectiveness, viability and timeliness, technology maturity, and environmental, health, and safety (EH&S) standards, may all need to be taken into account in the final analysis, although currently these are not expected to be major discriminators between the various wastefrom options.

The choice of immobilisation matrix should not be considered in isolation. The ultimate decision may need to be based on a balance of ease of processing and product performance. A review of processing options and identification of preferred routes understanding the issue of criticality in the process is recommended. This will establish the confidence that the chosen wasteforms can be fabricated in an economic and timely manner, and will identify any potential showstoppers.

CONCLUSIONS

The results of the work carried out to date on the immobilisation of separated civil plutonium has built upon the existing store of publicly available information, and has evaluated a range of vitrification and ceramic options, along with that of immobilisation MOX, in the light of UK requirements. The experimental programme has shown that there exists a wide range of glass compositions and ceramic phases that are capable of accommodating plutonium surrogates at levels in excess of 10% plutonium by weight.

The research has also demonstrated that neutron poisons can also be accommodated allowing a protection against criticality in the repository. Preliminary modelling of the behaviour of ceramic and glass wasteforms containing neutron poisons has shown the benefit of their inclusion to criticality safety.

Of the wide range of ceramics and glass options explored it has already been possible to eliminate some of the compositions either on the grounds of poor leachability, e.g. simple MW glass, and difficulty of fabrication, e.g. murataite.

The durability of the candidate borosilicate glasses has been investigated using a powder based static leach test (modified PCT-B) in DIW. All of the glasses exhibit low elemental leach rates, especially for the Pu-surrogates (Hf, Gd and Ce), with the best performance demonstrated by the LaBS compositions. Although preliminary results from a study of the pH dependence of the

candidate glasses' durability have shown that LaBS has the best performance at high and neutral pHs, this is drastically reduced at low pHs dissolving at least an of magnitude faster than MMW and ATS. This has significant implications for the retrievability of plutonium from the wasteform.

Samples of Synroc containing plutonium Pu-238 manufactured ~20 years ago have been shown to be mechanically intact despite suffering extensive radiation damage. This gives confidence to the approach of using ceramics as a plutonium wasteform.

Assessment of immobilisation MOX as a wasteform is underway with some short-term leach tests results now available. These indicate that the leach rates for Pu are about an order of magnitude lower than for U. Results from the longer-term (2 year) tests will allow a better comparison to with other wasteforms to be made.

Assessment of processing routes for glasses and ceramics has commenced. This study is benefiting from allied work carried out in the plutonium residues immobilisation project on the use of HIP technology for the fabrication of ceramic wasteforms, as well as that in cold press and sinter technology gained from the Sellafield MOX Plant (SMP) design and operation.

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REFERENCES

1. C. R. SCALES, E. R. MADDRELL, and M. T. HARRISON, "Options for the Immobilisation of UK Civil Plutonium – 7214", WM07 Conference, February 25 - March 1, 2007, Tucson, AZ.
2. BNFL National Stakeholder Dialogue – Plutonium working group, The Environment Council, Final Report, March 2003 (available from: www.the-environment-council.org.uk).
3. M. T. HARRISON, C. R. SCALES, P. A. BINGHAM, and R. J. HAND, "Survey of Potential Glass Compositions for the Immobilisation of the UK's Separated Plutonium Stocks", Mater. Res. Soc. Symp. Proc. **985**, 151-156 (2007).
4. M. C. STENNETT, E. R. MADDRELL, C. R. SCALES, F. R. LIVENS, M. GILBERT, and N. C. HYATT, "An evaluation of single phase ceramic formulations for plutonium disposition", Mater. Res. Soc. Symp. Proc. **985**, 145-150 (2007).
5. E. M. LEVIN, C. R. ROBBINS, and H. F. McMURDIE, Phase Diagrams for Ceramists 1969 Supplement, Vol. II, Fig. 2224, p. 60, American Ceramic Society (1969).
6. M. W. A. STEWART, S.A. MORICCA, B. D. BEGG, R. A. DAY, C. R. SCALES, E. R. MADDRELL and A. B. EILBECK, "Flexible Process Options for the Immobilisation of Residues and Wastes containing Plutonium", Proceedings of the 11th International Conference on Environmental Remediation and Radioactive Waste Management (ICEM2007), September 2-6, 2007, Oud Sint-Jan Hospital Conference Center, Bruges, Belgium.

7. D. M. STRACHAN, R. D. SCHEELE, J. P. ICENHOWER, E. C. BUCK, A. E. KOZELISKY, R. L. BELL, R. J. ELOVICH, and W. C. BUCKMILLER, "Radiation damage effects in candidate ceramics for plutonium immobilisation: Final Report", PNNL Report 14588, Feb. 2004.
8. M. J. HAMBLEY, S. DUMBILL, E. R. MADDRELL, and C. R. SCALES, "Characterisation of 20 year old Pu-238 doped Synroc C", MRS 2007 Scientific Basis For Nuclear Waste Management XXXI, 16-21 September 2007, Sheffield, UK.
9. N. E. BIBLER, W. G. RAMSEY, T. F. MEAKER, and J. M. PAREIZS, "Durabilities and microstructures of radioactive glasses for immobilisation of excess actinides at the Savannah River Site", Mat. Res. Soc. Symp. Proc. 412, 65-72 (1996).
10. J. C. MARRA, D. K. PEELER, and C. M. JANTZEN, "Development of an alternative glass formulation for vitrification of excess plutonium", SNRL Report WSRC-TR-2006-00031, Jan 2006.
11. J. R. ZAMECNIK, T. M. JONES, D. H. MILLER, D. T. HERMAN, and J. C. MARRA, "Process testing to support the conceptual design of a plutonium vitrification facility - 7358", WM07 Conference, February 25 - March 1, 2007, Tucson, AZ.
12. J. K. BATES, A. J. G. ELLISON, J. W. EMERY, and J. C. HOH, "Glass as a waste form for the immobilisation of plutonium", Mat. Res. Soc. Symp. Proc. 412, 57-64 (1996).
13. B. J. RILEY, J. D. VIENNA, and M.J. SCHWEIGER, "Liquidus temperature of rare earth-alumino-borosilicate glasses for treatment of americium and curium", Mat. Res. Soc. Symp. Proc. 608, 677-682 (2000).
14. T. S. RUDISILL, D. K. PEELER, and T. B. EDWARDS, "Demonstration of the feasibility of recovering americium and curium isotopes from a lanthanide borosilicate glass", Mat. Res. Soc. Symp. Proc. 713, 915-920 (2002).