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Immobilisation of Prototype Fast Reactor raffinate in a barium borosilicate glass matrix

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ABSTRACT

The vitrification of Dounreay Prototype Fast Reactor (PFR) Raffinate in a barium borosilicate glass matrix was investigated, with the aim of understanding process feasibility and the potential benefits over the current baseline of cement encapsulation. Laboratory scale glass melts demonstrated the production of homogeneous glasses incorporating at least 20 wt% simulant PFR waste (on an oxides basis), with no detectable crystalline accessory phases. The hardness and indentation fracture toughness of the simulant PFR waste glasses were determined to be comparable to those of current UK high level waste glass formulations. The normalised dissolution rate of boron from the simulant PFR glasses was determined to be 3×10^{-2} g m^{-2} d^{-1}, in 18.2 MΩ water at 90 °C and surface area/volume ratio of 1500 m^{-1}, only a factor of two greater than the French SON-68 simulant high level waste glass, under comparable conditions. Consequently, the simulant PFR waste glasses show considerable promise for meeting envisaged waste acceptance criteria for geological disposal. Overall, the superior stability of vitrified PFR wasteforms could enhance the safety case for long term near surface storage of radioactive wastes, mandated by current Scottish Government policy.

1. Introduction

The Prototype Fast Reactor (PFR) was the UK's second fast reactor and operated between 1974 and 1994, utilising a high plutonium content mixed oxide fuel (MOx) with a molten sodium coolant [1]. Spent fuel from the PFR was reprocessed on the Dounreay site by dissolution in nitric acid to recover the reusable fissile material. This process yielded approximately 200 m^3 of an aqueous radioactive liquor, known as PFR raffinate [2]. The PFR raffinate contains the majority of the radioactive material and fission products produced during the operation of the PFR reactor and on the Dounreay site as a whole [3]. Since the reprocessing of PFR fuel was completed in 1996, the waste raffinate has been stored in underground tanks on the Dounreay site. Having spent a decade in storage, PFR raffinate was reclassified as Intermediate Level Waste in 2004, ostensibly due to its low heat output [4].

The conditioning of PFR raffinate into a passively safe, wasteform is identified as a priority in the Dounreay Site Restoration Plan [5]. A best practical environmental option assessment, undertaken by the UKAEA, proposed neutralisation and cementation of the raffinate as the reference waste management strategy [6]. For this waste treatment option to be implemented, a new facility (to be known as D3900) is required, the construction of which is yet to begin at the time of writing.

Although laboratory studies have demonstrated that cement-encapsulated *inactive* raffinate has physical properties comparable to those of other cemented ILW streams (e.g. viscosity, initial setting time, bleed water), PFR raffinate has a specific activity 20 times greater than other encapsulated ILW streams [2,3,7,8]. The high concentration of ^{137}Cs in PFR raffinates, the porous nature and poor immobilisation of Cs observed in cementitious systems, may limit the ability of cement to retain the radioactive inventory of PFR [2,9–11]. It is not yet certain that environmental release rates from a cemented PFR raffinate wasteform will be within permitted limits over the relevant lifetime of the wasteform, particularly given the policy of the Scottish Government for long term near-surface storage at a coastal location, as in the case of Dounreay [12,13].

An issue that may be even more significant to safe interim storage of conditioned PFR raffinate is the high specific activity of

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the wastes and their significant alpha emitting component ($\beta/\gamma = 346$ TBq m^{-3}, $\alpha = 3.21$ TBq m^{-3}) [2]. It is known that the radiolysis of cementitious water will produce H_2, while the presence of significant nitrate concentrations in the waste (300–500 g l^{-1}) and alpha activity will also result in the formation of O_2 and NO_x [14–17]. These combined factors will increase the rate of gas generation when compared to existing UK ILW waste packages. As a result, these reactions could be expected to introduce significant complexities to the long-term management of cemented PFR raffinate waste packages through the need to monitor, vent and dissipate gases form the waste packages.

It should be noted that the near-surface storage policy was introduced after the strategic decision to encapsulate PFR raffinates in a cement wasteform. In its response to the Scottish Government consultation on higher activity wastes, the Committee on Radioactive Waste Management (CoRWM) highlighted that certain wastes from the Dounreay site were "*never likely to be suitable for near surface disposal and therefore greater efforts need to be made in the interest of safety, security and intergenerational equity to find a permanent solution for this waste*" [12].

The current investigation aims to demonstrate, in principle, an alternative processing option for PFR raffinate, which could enhance the safety case for long term near-surface storage and address the concerns of CoRWM. A derivative of the barium borosilicate glass, G73, previously investigated as a matrix for the immobilisation of UK ILWs arising at Magnox decommissioning sites [18–21], is here investigated as a disposal matrix for PFR raffinate, the composition of which incorporates ca. 7 wt% SO_3. Barium borosilicate glasses, such as G73, are reported to have a high aqueous durability and the presence of Ba is known to increase the solubility of sulphate species, which inhibits the formation of water soluble "yellow phase" salts [18–23]. We present an analysis of the composition, amorphous nature, aqueous durability, thermal behaviour and mechanical properties of vitrified PFR raffinate with waste loadings of 10 wt%, 15 wt% and 20 wt% (oxide basis), in a barium borosilicate glass. The results are discussed with reference to the potential benefits of PFR raffinate vitrification compared to cementation.

2. Materials and experimental

2.1. Materials

2.1.1. Raffinate simulant

The inactive surrogate for PFR raffinate was formulated on the assumption that the waste would be treated using an evaporation or calcination step to produce a solid calcine prior to vitrification. The composition was thus formulated using the data available on the average composition of four PFR tanks at the Dounreay site [6]. The chemical composition of model PFR raffinate is provided in Table 1. The solids content of the raffinate calcine was calculated based on the reported elemental values in the raffinate (ppm) and then converted to their oxide form, which is reported in Table 2.

Some variation from the reported raffinate composition was necessary when batching the simulant. For example, for reasons of practicality, elements with concentrations <15 ppm were excluded (Ag, As, Cm, Dy, Eu, Gd, Ge, Hg, Ho, In, Nb, Np, P, Pb, Pd, Rb, Rh, Sb, Se, Sn and Tc). One exception was Pd, which was present at a concentration of ~150 ppm in the waste stream. This was excluded on grounds of cost, for this preliminary study, and its known propensity to exist as an insoluble noble metal in glass melts [24].

The omission of the elements noted above accounted for <2.8 wt% of the mass of the total waste stream. Radioactive elements with concentrations >15 ppm were substituted by relevant concentrations of inactive surrogates (Ce for U and Sm for Am).

Table 1
Average composition of PFR raffinate as characterised in Ref. [6]. (Brackets) indicate where the use of an appropriate inactive simulant was applied. The right-hand columns identifies elements excluded from the simulant based on either their low concentration in the raffinate or on an economic basis.

Included in Simulant (surrogate element used)		Excluded from Simulant	
Element	ppm	Element	ppm
Na	9711	Rh	15
Cu	8725	Cm	4
Fe	3837	Nb	3.5
Zn	3566	Dy	2.4
Cd	2540	Ag	<1.3
S	1351	As	<13
Ni	1277	Co	<0.4
Cr	669	Ge	<1.3
Cs	509	Hg	<0.3
Nd	462	Ho	<1.3
Am (Sm)	405	In	<4
Al	350	Np	<13
Ce	304	P	<2.7
U (Ce)	168	Pb	<1.1
La	163	Rb	<1.3
Pr	158	Sb	<1.3
Mo	154	Se	<1.3
Pd	150	Sn	<0.3
Ca	138	Tc	<1.3
Sm	123	Eu	15
Y	112	Gd	15
Te	74	Pd	150
Sr	60		
Mn	45		
Ru	60		
Ba	39		
Ti	36		
Total	35,186	Total	205

2.1.2. Glass preparation

Three glasses were synthesised and characterised in this study. These glasses were based on a derivative of the G73 barium-silicate base glass composition (referred to here as G73, for simplicity), which was previously developed [18–21], with PFR raffinate simulant incorporated at 10 wt%, 15 wt% and 20 wt% waste loading (on an oxides basis). These glasses are identified as G73-10, G73-15 and G73-20, respectively. The base glass composition, presented in Table 2 for reference, is identified as G73-00.

Glasses were produced from batch chemicals to provide 250 g of glass. The components of the raffinate simulant were batched in either their oxide or carbonate forms according to their molar proportions to obtain the specified waste loading. The following analytical grade chemicals were used for batching; $Al(OH)_3$, $Na_2B_4O_7.10H_2O$, $BaCO_3$, $CaCO_3$, CdO, CeO_2, $Cr(NO_3)_3.9H_2O$, Cs_2CO_3, CuO, Fe_2O_3, La_2O_3, Mn_2O_3, MoO_3, Na_2CO_3, Nd_2O_3, $NiCO_3$, Pr_6O_{11}, RuO_2, Na_2SO_4, SiO_2, Sm_2O_3, $SrCO_3$, TeO_2, TiO_2, Y_2O_3 and ZnO. The batched powders were heated in mullite crucibles with stirring to 1200 °C at 10 °C min^{-1} and held at temperature for 3 h. The glasses were poured into blocks and annealed at 500 °C for 1 h before cooling to 25 °C at 1 °C min^{-1}. Glass monoliths were prepared for SEM-EDX, Vickers hardness testing and fracture toughness testing to a 0.25 μm finish by successive grinding and polishing with SiC grit papers and diamond pastes. Powder samples were prepared using a hardened steel ring and puck mill. The sub-75 μm size fraction was collected for use in XRD and XRF analysis and the 75–150 μm size fraction was collected for use in aqueous durability experiments and prepared according to ASTM standard C 1285–02 [25].