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Immobilisation of Prototype Fast Reactor Raffinate using Barium Silicate ILW Glasses

Paul G. Heath, Claire L Corkhill, Martin C Stennett, Russell J Hand, Keiran M Whales, Neil C Hyatt

Immobilisation Science Laboratory, Sir Robert Hadfield Building, Mappin Street, The University of Sheffield, Sheffield, S1 JD, United Kingdom

Abstract

The vitrification of Dounreay Prototype Fast Reactor Raffinate (PFR) 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 0 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 x 10^{-} g m^{-} d^{-1}, in 18 MΩ water at 0°C and surface area / volume ratio of 1 00 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 are considered to 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

Keywords: Amorphous Materials, Waste Immobilisation, Mechanical properties

Introduction

The Prototype Fast Reactor (PFR) was the UK's second fast reactor and operated between 1   and 1   , 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 00 m of an aqueous radioactive liquor, known as PFR raffinate [ ] 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 [ ] Since the reprocessing of PFR fuel was completed in 1   6, 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 00 , ostensibly due to its low heat output [ ]

The conditioning of PFR raffinate into a passively safe, wasteform is identified as a priority in the Dounreay Site Restoration Plan [ ] 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 D   00) 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 0 times greater than other encapsulated ILW streams [, , ,8] The high concentration of ^{1} 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 [, –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 [1 ,1]

An issue that may be even more significant to safe interim storage is the high specific activity of the wastes and their significant alpha emitting component (β/γ = 6 TBq m^{-} , α = 1 TBq m^{-}) [ ] It is known that the radiolysis of cementitious water will produce H , while the presence of significant nitrate concentrations in the waste (00- 00 g l^{-1}) and alpha activity will also result in the formation of O and NO$_x$ [1 –1] 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*” [1]

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, G , previously investigated as a matrix for the immobilisation of UK ILWs arising at Magnox decommissioning sites [18- 1], is here investigated as a disposal matrix for PFR raffinate, the composition of which incorporates ca wt% SO Barium borosilicate glasses, such as G , 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-] 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%, 1 wt% and 0 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

Some variations in the elemental composition were necessary when batching the simulant For example, for reasons of practicality, any elements with concentrations < 1 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 ~1 0 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 [ ]

The omission of the elements noted above accounted for < 8 wt% of the mass of the total waste stream Radioactive elements with concentrations > 1 ppm were substituted by relevant concentrations of inactive surrogates (Ce for U and Sm for Am)

2.1.2 Glass Preparation

Three glasses were synthesised and characterised in this study These glasses were based on a derivative of the G barium-silicate base glass composition (referred to here as G , for simplicity), which was previously developed [18- 1], with PFR raffinate simulant incorporated at 10 wt%, 1 wt% and 0 wt% waste loading These glasses are identified as G -10, G -1 and G - 0, respectively The base glass composition, presented in Table for reference, is identified as G -00

Glasses were produced from batch chemicals to provide 0 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) , Na B O 10H O, BaCO , CaCO , CdO, CeO , Cr(NO) H O, Cs CO , CuO, Fe O , La O , Mn O , MoO , Na CO , Nd O , NiCO , Pr_6O_{11}, RuO , Na SO , SiO , Sm O , SrCO , TeO , TiO , Y O and ZnO The batched powders were heated in mullite crucibles with stirring to 1 00 °C at 10 °C min^{-1} and held at temperature for hours The glasses were poured into blocks and annealed at 00 °C for one hour before cooling to °C at 1 °C min^{-1} Glass monoliths were prepared for SEM-EDX, Vickers hardness testing and fracture toughness testing to a 0 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- µm size fraction was collected for use in XRD and XRF analysis and the -1 0 µm size fraction was collected for use in aqueous durability experiments and prepared according to ASTM standard C 1 8 – 0 [ ]

2.2 - Characterisation

Glass Characterisation

X-ray Fluorescence (XRF) analysis was performed using a Phillips PW 0 XRF Axios instrument to obtain compositional data B O content was determined by dissolution of glass powder in HF followed by analysis of leachate using a Perkin-Elmer Optima 00 dual view Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) The density of the glass wasteforms was measured using a < µm powder, using an AccuPyc 1 0 II helium pycnometer with the following analysis regime 00 purges of the chamber followed by 0 cycles using an equilibration rate of Pa min^{-1} at °C in a 1 cm chamber and a fill pressure of 86 KPa Scanning Electron Microscopy was performed using a JEOL JSM 6 00 SEM with an accelerating voltage of 0 kV and a working distance of 1 mm Concurrent Energy Dispersive Spectroscopy was acquired (INCA, Oxford Instruments) Additionally, an FEI Quanta 00 F SEM was utilised for high resolution imaging, using an accelerating voltage of 0 kV and working distance of 10 mm Concurrent Energy Dispersive X-ray analysis was performed (Genesis EDX)

Thermal and mechanical properties

The glass liquidus temperature for each sample was measured by placing a 0 cm long mullite boat, filled with sub- µm glass powder, into a tube furnace The samples were left to equilibrate at 1 00 °C for hours and the temperature gradient along the length of the boat at mm intervals was measured using a retractable thermocouple The boats were removed and rapidly quenched in air The point of crystallisation was measurable to within 1 mm by optical examination of the crucibles and this was then correlated with the associated temperature to estimate the liquidus temperature Alterations in chemical composition resulting from crucible corrosion were not accounted for, nor were the phases produced analysed As the purpose of this test was to check if the point of crystallisation was below 1100 °C, and the contaminants from crucible corrosion are likely to lower this value, the results presented are considered useful in this context

The Vickers hardness indentation method was used to determine both hardness (H_v) and the indentation fracture toughness (K_c) following the procedure described by Connelly et al [6] Indentation was performed on a Mitutayo HM-101 Sixty indents were made at each of three indentation loadings 0 8 N, 1 6 N and N (twenty indents at each force per sample, error ± 0 0 N) The load was held for 0 seconds Samples were left for hours prior to analysis using optical microscopy The Vickers hardness (Hv) in Pa and the Fracture Toughness (Kc) was calculated using Equations 1 and respectively

$$H_v = \frac{1.854P}{(2a)^2}$$ Equation 1

$$K_C = \frac{0.0824P}{c^{3/2}}$$ Equation

where P is the applied load (N), a is the half length of the indent diagonal (m) and c is the median/radial crack length (m) The results quoted are those obtained from the 1 6 N loading due to the higher number of acceptable indentations (a minimum of fifteen per sample)

Aqueous durability assessment

Aqueous durability assessment was performed according to ASTM standard C 1 8 – 0 (Product Consistency Test - PCT) utilising a µm – 1 0 µm size fraction in 18 MΩ H O at 0°C with a SA/V between 1 m^{-1} and 1 m^{-1} dependent on glass density, as provided in Table [ ] Experiments were performed in triplicate with duplicate blanks, sampling at , , 1 , 1 and 8 days Samples were filtered using a 0 µm PTFE filter and leachate analysis was performed using ICP-AES

The normalised elemental mass loss (NL$_i$) and normalised elemental dissolution rates (NR$_i$) were calculated according to Equations and , respectively using the analysed glass compositions

$$\mathrm{NL_i} = \frac{\mathrm{C_i}}{\mathrm{f_i} \times \frac{\mathrm{SA}}{\mathrm{V}}}$$ **Equation 3**

$$\mathrm{NR_i} = \frac{\mathrm{C_i}}{\mathrm{f_i} \times \frac{\mathrm{SA}}{\mathrm{V}} \times t}$$ **Equation 4**

where NL$_i$ is the normalised elemental mass loss of element *i* (g m^{-}), C$_i$ is the averaged, blank corrected concentration of element *i* in solution (g m^{-}), f$_i$ is the fraction of element *i* in the unleached glass, SA/V is the ratio of glass surface area to the volume of water (m^{-1}), NR$_i$ is the normalised elemental loss rate and t is time in days

Geochemical modelling of the solution leachate was performed using the PhreeqC geochemical modelling code (v -1 -8 8, provided by the United States Geological Survey) to identify solution saturation species, using the Lawrence Livermore National Laboratory (LLNL) thermodynamic database

3 - Results

3.1 - Glass Formation and Composition

It can be stated with confidence that the three simulant PFR waste loaded G glasses exist within a stable glass forming region of the phase diagram up to a 0 wt% loading. The glasses formed readily and poured from the melt at 1 00 °C, with no evidence of un-dissolved batch. However, a small degree of corrosion was evident inside the crucible, which is responsible for the elevated concentrations of alumina in the final composition. The composition of the three glasses was analysed using XRF and ICP-AES data are shown in Table , which compares the final composition with the nominal batched compositions.

Overall, it can be seen from Table that the batched and analysed compositions are in reasonable agreement for major and minor oxides, although with some notable exceptions Na_2O, B_2O_3, and SO_3, are, in general, analysed as lower than the batched composition, due to volatilisation from the melts during high temperature processing. SiO_2 and BaO are, respectively, systematically higher and lower in the analysed glass compositions compared to the batched. The complexity of the glass composition made deconvolution of overlapping X-ray emission lines, from multiple elements, challenging and may be responsible for this systematic discrepancy. The loss of such volatile components from the melts does not pose a challenge to the off-gas system of existing HLW melter systems and, therefore, is not expected to be problematic for full scale deployment. In addition, it should be noted that the lower surface area to volume ratio, and presence of a cold cap, in full scale melter systems will reduce volatilisation considerably, with respect to laboratory scale melts.

Analysis of the vitrified products by X-ray diffraction showed only diffuse scattering (Figure 1) characteristic of an amorphous material, with no evidence of phase separation or detectable crystallisation The lack of contrast in both the SEM-BSE imaging and SEM-EDX mapping analysis, displayed in Figure 1b and Figure , is indicative of a chemically homogeneous glass on a micron scale Each glass showed similar characteristics There was no evidence from XRD or SEM-EDX analysis of distinct segregated sulphate phases

Crystallisation in radioactive waste glasses, when produced from the melt, is undesirable for several reasons, including the possibility for the precipitation of soluble radionuclide containing phases the potential for decreased aqueous durability of the matrix, due to the removal of refractory components and the potential for swelling of crystal phases as a result of damage from self-irradiation The absence of significant crystallisation and minimal evidence of crucible corrosion indicate that a high-quality glass wasteform was obtained that should be both stable and amenable to the processing of PFR wastes

3.2 - Thermal Properties

Table shows the density, glass transition temperature and measured liquidus temperature of the simulant PFR glasses The values obtained for the T_g are comparable, within error, for the three waste-loadings and correspond well with the transition temperature previously reported for the same base glass loaded with organic exchange resins [18- 1]

The liquidus temperatures of the glasses were all below 1100 °C, and no correlation with increasing waste loading was observed Glass compositions with a liquidus temperature below 1100 °C are thought to be beneficial for nuclear waste vitrification as the lower temperatures minimise volatile losses of radioactive components during melting [-] Although not essential for all melter operations or wasteform acceptance criteria, the absence of crystalline products indicates that the wasteforms will be amenable to commercial application due to the associated simplification of wasteform qualification, improved efficiency of melter operation and predictability of process control [0].

As the glasses produced in this study have been shown to retain their Cs inventory after processing at 1 00 °C, the retention of Cs should be expected to be retained in full scale melts given the smaller melt surface area to volume ratio and possibility of operating with a cold cap [1].

3.3 - Mechanical Testing

The Vickers hardness and indentation fracture toughness of the PFR simulant glasses are plotted in Figure . The fracture toughness of the glass relates to the energy required to form a new surface and is relevant to qualifying the suitability of radioactive waste packages for transport, e.g. in estimating the likelihood of respirable fines formation in accident scenario [ ].

The lowest waste loaded glass, G -10, had the highest indentation fracture toughness and the hardness value of the glasses tested. G -1 and G - 0 glasses gave lower values and were equivalent within measurable precision. All compositions were comparable or superior to existing HLW glass compositions (e.g. UK MW glass and US PNL 6- 8 glass, Fig.) for indentation fracture toughness and were comparable, or superior, in terms of Vickers hardness [6,].

Although no specification for fracture toughness currently exists for UK vitreous waste packages, the results imply that, as the G based glasses are comparable to current wasteforms, they are likely to be compliant with storage in existing (HLW) canisters. Furthermore, the mechanical properties suggest that packaging in larger m boxes may also be possible, although in this case analysis of thermally induced cracking/stresses during processing requires investigation

3.4 - Aqueous Durability

The short-term chemical durability of the simulant raffinate glasses was investigated using the PCT methodology [ ] Figure shows the normalised mass loss of elements that were detectable by ICP-AES in concentrations higher than those measured in the blank solutions The normalised elemental mass loss (NL) and normalised dissolution rate (NR , 8 days) data are shown in Tables and , respectively The solution pH buffered to a value of pH 10 ± 0 after days (Fig) and there was no further measurable fluctuation of pH during the 8-day duration of the experiments

The normalised elemental loss rates (to 8 days) for boron were similar for each glass composition, giving an NR_B between x 10^{-} g m^{-} d^{-1} and x 10^{-} g m^{-} d^{-1} (± x 10^{-}) as stated in Table This indicates that varying the waste loading from 10 to 0 wt% did not appreciably alter the chemical durability on the timescales investigated Importantly, the glasses showed a comparable normalised mass loss and normalised dissolution rate to other high-level waste glass compositions destined for long-term disposal, tested under comparable conditions (Table) For example, the UK HLW MW glass, has a NR_B of 0 x 10^{-1} g m^{-} day^{-1} [ ], compared with x 10^{-} g m^{-} d^{-1} for the 0 wt% loaded simulant PFR raffinate glass (Table) The NR_B is approximately twice that of the SON68 French HLW base glass, however it should be noted that the specific activity in R T (the active analogue of SON68) will be substantially higher than that of the PFR loaded G glasses At production, R T contains an average specific activity ca 110 PBq m^{-} , approximately 0 times greater than the average ca

6 PBq m^{-} estimated for the G - 0 glass [ ] As such, these glasses could be considered suitable for the immobilisation and disposal of PFR raffinate

Glass dissolution was observed to be incongruent B and Na leached at similar rates ($NL_B > NL_{Na}$), however the normalised mass loss of all other elements was an order of magnitude lower than both B and Na (Table) The normalised mass loss of all elements was observed to be rapid for the first days of dissolution and, after this time, the normalised mass loss of Si, Na, B began to reduce indicating an approach to quasi-equilibrium, as indicated in Figure 6

The normalised mass loss of Ba and Ca differed as a function of glass composition, albeit without a notable trend For example, the normalised mass loss of Ba decreased after days for the 0 wt% waste loaded composition, and after 1 days for the 1 wt% glass (Fig b) There appeared to be little removal of Ba from solution from the 10 wt% loaded glass Additionally, the NL_{Sr} dropped after 1 days for all three glasses (Fig f) This behaviour may be attributed to the formation of Ca-, Ba- and Sr-containing alteration layers on the glass surface Indeed, geochemical modelling indicated that tobermorite ($Ca\ Si_6H_{11}O$) is likely to precipitate A number of recent investigations have also identified this phase in glasses containing Ca, or where Ca is present in solution [–] and have shown that its formation can significantly reduce the dissolution rate of nuclear waste glasses, by an order of magnitude compared to other media [ ] Other phases shown by geochemical modelling to be favourable precipitates were the Ca- Ba- and Sr-carbonate phases, calcite (CaCO), witherite (BaCO) and strontianite (SrCO) Arising from equilibrium of CO in air with the leaching medium, it is possible that these phases precipitated in solution, and when the samples were filtered for analysis, they were removed, leading to an apparent decrease in Ca, Ba and Sr leaching It will be necessary to perform further monolith leaching experiments to examine the properties of the altered layer so that the origin of the fluctuations in these elements can be determined and set in the context of recent mechanistic studies of UK HLW and ILW glass performance [0-]

4 - Discussion

Previous work has shown that cement may not have the capacity to effectively immobilise the diverse inventory of radioactive elements present in the PFR raffinate waste stream [ ] Cementitious wasteforms could be subject to increased dissolution and release rates due to their inherent porosity and high internal surface area The high solubility and potential for removal of many of the waste elements which sorb to the cement surface especially Cs, which makes up over 60% of the radioactive inventory by activity, is of potential concern [ ] These factors highlight the opportunity to vitrify PFR wastes to minimise radioisotope migration to the biosphere Vitrification, using G barium silicate glass described in this investigation, is likely to offer significant improvements in long term wasteform performance over the current baseline

The benefits of vitrification reach beyond the improvements in wasteform quality described and may also offer fiscal incentives, for example, by substantially reducing the waste volumes for storage and disposal The current lifecycle waste management plan is to cement the PFR raffinate in 00 L drums, with a target waste loading of 0 0 m per drum With 1 1 m of raffinate to process this would result in m of packaged waste for disposal (6 6 x 00 L drums with a displacement volume of 0 m each) [ ] If vitrification, at 0 wt% loading was to be utilised, the volume of waste produced would be reduced to < 1 m^3 of glass Conceivably, this volume of material could be readily processed in a small or modular plant, utilising one of a variety of thermal treatment options for ILW being developed in the UK e g plasma vitrification, resistive heating melters or Hot-Isostatic Pressing [ ]

Assuming packaging of vitrified PFR waste into m ILW boxes was preferable and 0% of the box capacity (m) could be filled, each m box would hold 1 8 m of vitrified product In this scenario, the waste could be fully conditioned using just eight m boxes, producing a total waste volume for disposal of 8 6 m This treatment methodology, when compared with cementation, would reduce the waste disposal inventory by more than 0%, and, in principle, could be achieved, using in-container Joule heated melter technology The heat generation, surface activity limits and containment limits for impact of this hypothetical G - 0 waste stream have been estimated to be within existing guidelines for a m^3 ILW box[1] [6] The substantial volume reduction achieved by the vitrification approach would enable transfer of the resulting waste packages to the Sellafield site for storage, potentially assisting earlier closure of the Dounreay site

Deriving a lifetime waste management cost for these wastes intended for near surface storage has not been attempted here However, it is believed the cost reductions associated with managing lower volumes of wastes in the rest of the NDA estate should be transferable to Scottish policy It is important to note that the volume reduction and concentration of the waste associated with this vitrification step would not result in the re-classification of the waste as HLW This is important as a reclassification to HLW would require consideration of heat dissipation in storage, introducing significant extra costs for disposal, as well as increasing the final volume required in a storage vault

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[1] Calculation based upon reported inventory of radioisotopes for this waste stream and accounting for the concentration of activity achieved by vitrification This packaged waste will meet stated specifications imposed for a square corner m box

The decreased risk to public health, superior quality of final wasteform, improved long term stability, smaller footprint on the Dounreay ILW stores and the reduced waste management cost, combine to provide a credible case for treatment of these wastes using vitrification over cementation

5 - Conclusion

A vitreous wasteform for simulant PFR raffinate was developed at a range of waste loadings up to 0 wt% The product was a stable and homogeneous amorphous solid with no observable crystal formation All glasses performed comparably to vitrified waste compositions currently in use, both in the UK and internationally, for the immobilisation of HLW The aqueous durability was superior to that of current UK HLW glasses under comparable experimental conditions Therefore, the glasses investigated here could be considered a stable matrix for ILW under both geological disposal and near-surface storage scenarios The mechanical properties of the wasteform also matched or exceeded those currently in use for HLW glasses, in both the UK and USA, and therefore, should be amenable to transport and storage in either 00 L HLW flasks or m ILW waste packages Additionally, we demonstrated that undertaking immobilisation of PFR raffinate through thermal treatment methods may also result in a decrease in the anticipated volume of waste from m to 8 6 m , potentially resulting in significant lifetime waste management cost savings and a more robust option to support the Scottish policy for at near surface storage and site closure

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6 Figures

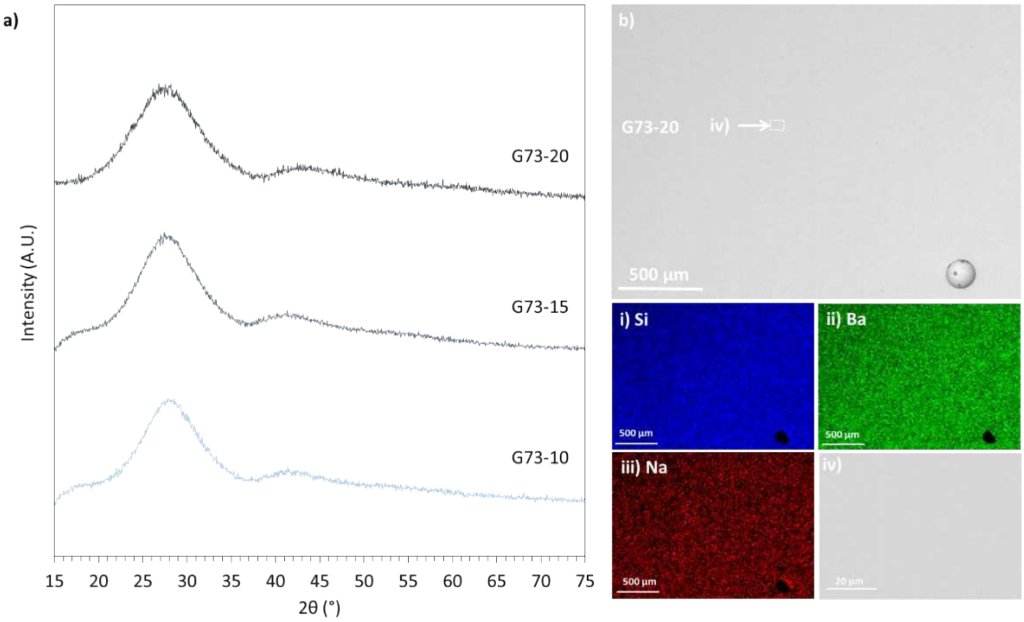

Figure 1 - a) Powder XRD patterns of G73 PFR raffinate loaded glasses, displaying diffuse scattering characteristic of amorphous material and b) SEM-BSE image displaying homogeneity of G73-20 glass matrix, set above i) - iii) SEM-EDX maps of key elements for b) and iv) a higher resolution BSE-SEM of G73-20 glass matrix identified in b) which taken illustrates the absence of crystalline materials in the final waste product.

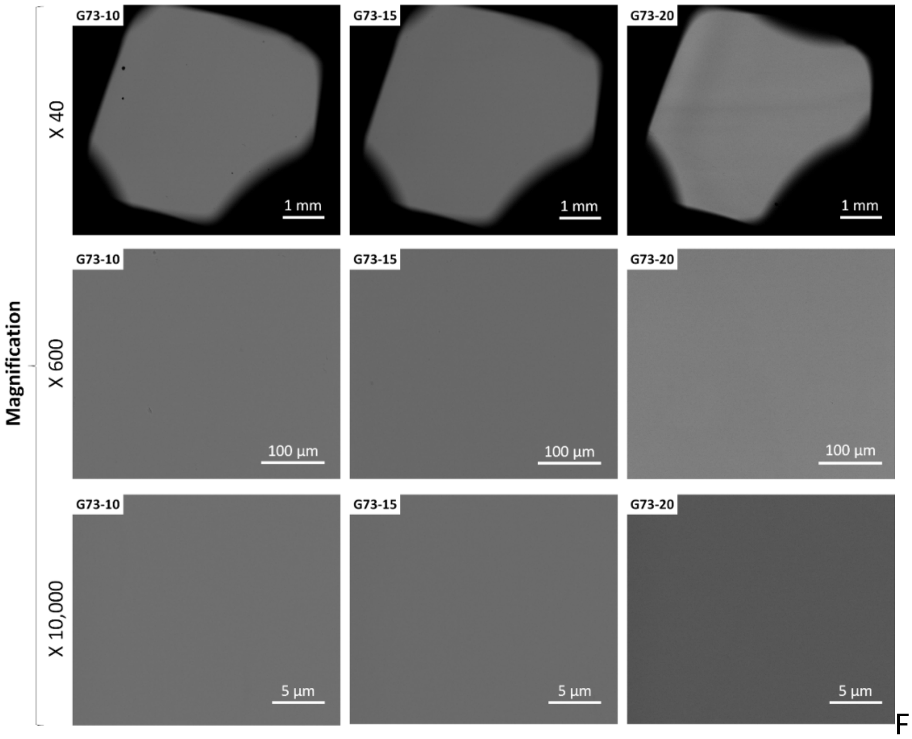

Figure 2 - SEM-BSE images of the three waste loaded glasses G73-10, G73-15 and G73-20 at various magnifications. The lack of image contrast suggests chemical homogeneity within the sample.

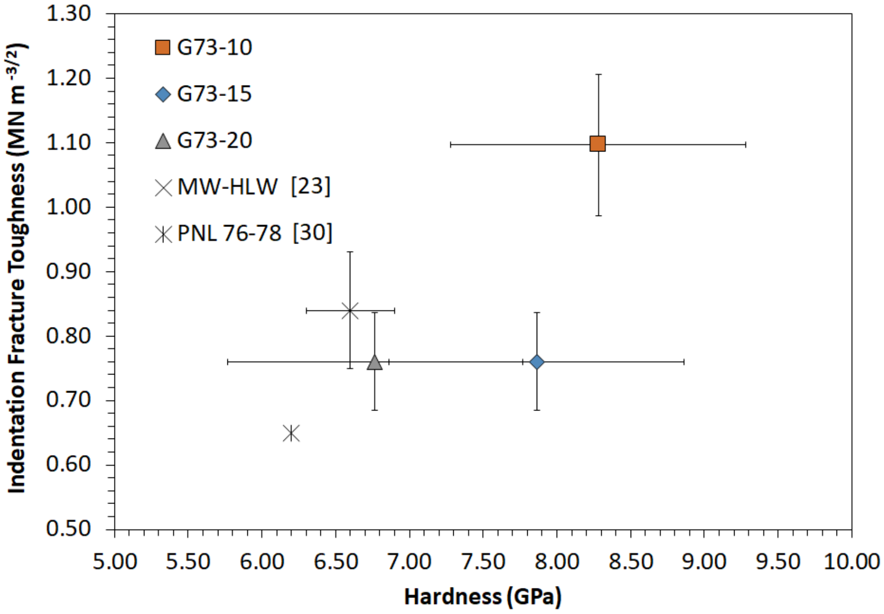

Figure 3 – Indentation fracture toughness and hardness values of G73 PFR raffinate waste loaded glasses obtained using the Vickers indentation methodology, with comparison to waste glasses currently used for HLW immobilisation [23,30]. Errors correspond to 3 x the measured standard deviation.

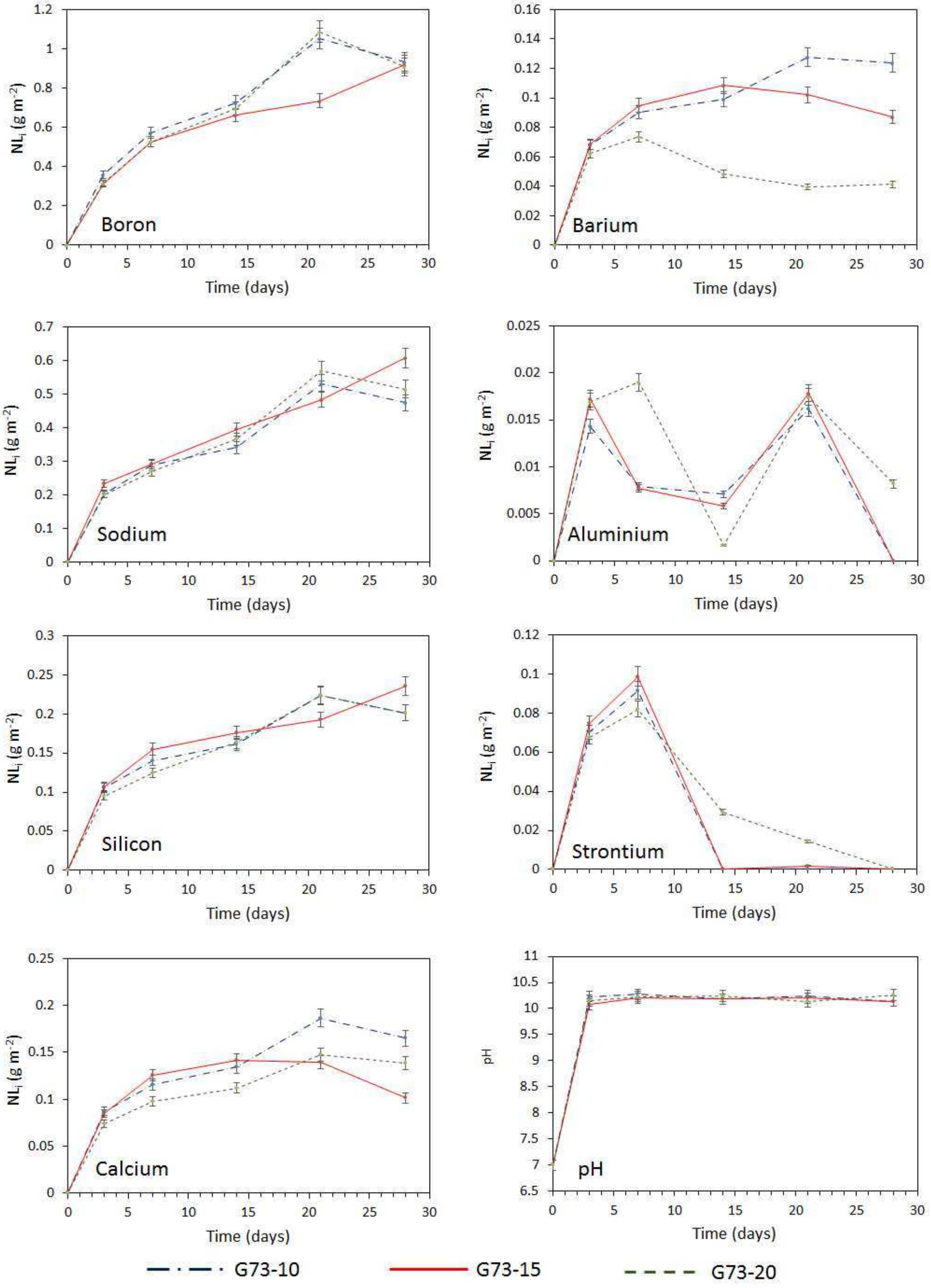

Figure 4 – Graphs displaying the normalised elemental mass loss with varying levels of PFR raffinate loading from PCT experiments at 90°C in 18.2 MΩ water with a SA/V of 1499 m^{-1} -1525 m^{-1} (dependant on glass density).

Tables

Included in Simulant (surrogate element used)		Excluded from Simulant	
Element	*ppm*	*Element*	*ppm*
Na	, 11	*Rh*	1
Cu	8,	*Cm*	
Fe	,8	*Nb*	
Zn	, 66	*Dy*	
Cd	, 0	*Ag*	<1
S	1, 1	*As*	<1
Ni	1,	*Co*	<0
Cr	66	*Ge*	<1
Cs	0	*Hg*	<0
Nd	6	*Ho*	<1
Am (Sm)	0	*In*	<
Al	0	*Np*	<1
Ce	0	*P*	<
U (Ce)	168	*Pb*	<1 1
La	16	*Rb*	<1
Pr	1 8	*Sb*	<1
Mo	1	*Se*	<1
Pd	1 0	*Sn*	<0
Ca	1 8	*Tc*	<1
Sm	1	*Eu*	1
Y	11	*Gd*	1
Te		*Pd*	1 0
Sr	60		
Mn			
Ru	60		
Ba			
Ti	6		
Total	,186	Total	0

Table 1 - Average composition of PFR raffinate as characterised in [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 both low concentrations in the raffinate and on an economic basis.

Table 2 - Compositions of base glass, simulant calcined PFR raffinate and glasses produced. Compositions of glasses provided both as batched and as measured by XRF (boron analysis via dissolution in HF and ICP-AES). *Note glasses were batched to 100 wt%; discrepancies reported result from rounding to 2 d,p.

Component (wt%)	G73-00 Base Glass	PFR Calcine	G73-10		G73-15		G73-20	
			Batch	Meas.	Batch	Meas.	Batch	Meas.
S O	0	0 00	80		0		60	8
BaO	0	0 0	81	1 1	1	1 61	6	8 61
Fe O	6 00	11 68	6	88	6 8	8	1	6
CaO	00	0 1			1		08	0
Na O	0	88	0	1 6	6 1	8	8	0
CuO	0	6 6	6	8		8		0
B O	00	0 00	1 80	0 6	1 0	0 6	1 60	0 6
ZnO	0		0	1 08	1	1	1 8	1
CdO	0	6 18	0 6	0	0	1 0	1	1
SO	0	18	0	0	1 08	0	1	0 86
Al O	0 0	1 1	0	0 86	0 6	0 8	0 68	1
N O	0	6	0	0	0	0 1	0 6	0 86
Cr O	0	08	0 1	0 8	0 1	0 6	0	0 66
Cs O	0	1 1	0 1	0 6	0 1	0	0	0
Nd O	0	1 1	0 1	0 1	0 1	0 00	0	0
Sm O	0	0 0	0 0	0 10	0 0	0 1	0 06	0 1
CeO	0	0	0 10	0 0	0 1	0 10	0 1	0 1
MoO	0	0	0 0	0 06	0 0	0 08	0 10	0 0
Y O	0	0 0	0 0	0 0	0 0	0 0	0 06	0 06
La O	0	0 0	0 00	0 0	0 01	0 00	0 01	0 0
Pr_6O_{11}	0	0 0	0 00	0 0	0 01	0 06	0 01	0 0
RuO	0	0 1	0 0	0 00	0 0	0 00	0 0	0 00
SrO	0	0 1	0 0	0 6	0 0	0 1	0 0	0 0
TeO	0	0 0	0 0	0 00	0 0	0 00	0 0	0 00
T O	0	0 1	0 01	0 00	0 0	0 00	0 0	0 00
Mn O	0	0 1	0 01	0 08	0 0	0 08	0 0	0 0
	100	-	100 1	8	100 0	100 81	100 6	100

Glass Property	Sample ID		
	G73-10	G73-15	G73-20
Density (g cm-)	1 ± 0 00	± 0 00	± 0 00
Glass Transition Temperature (°C)	0 ± 10	8 ± 10	8 ± 10
Liquidus Temperature (°C)	10 ± 10	10 ± 10	10 0 ± 10

Table 3 - Properties of glass wasteforms produced at varying PFR raffinate waste loadings including the density, liquidus temperature (measured in mullite crucibles – see main text for the implication of this) and glass transition temperature.

NR$_i$ (g m^{-2} day^{-1})	Glass Composition		
	G73-10	**G73-15**	**G73-20**
B	x 10^{-}	8 x 10^{-}	x 10^{-}
Na	1 6 x 10^{-}	1 x 10^{-}	1 8 x 10^{-}
S	18 x 10^{-}	8 0 x 10^{-}	1 x 10^{-}
Ca	8 x 10^{-}	6 x 10^{-}	x 10^{-}
Mo	x 10^{-}	8 x 10^{-}	6 8 x 10^{-}
Ba	x 10^{-}	10 x 10^{-}	1 x 10^{-}
Cr	8 x 10^{-}	1 6 x 10^{-}	0 x 10^{-}
Cu	x 10^{-6}	1 x 10^{-6}	0 00
Al	0 00	0 00	1 x 10^{-}
Fe	0 00	0 00	0 00
N	0 00	0 00	0 00
Sr	0 00	0 00	0 00
Zn	0 00	0 00	0 00

Table 4 – Normalised elemental loss rates for the three waste PFR waste loaded glasses measured after 28 days. Data is from PCT experiments of the wasteforms at 90 °C in 18.2 MΩ water.

Glass Composition	NL_i after 28 days (g m^{-2})		NR_i after 28 days (g m^2 day^{-1})		SA/V (m^{-1})	pH (25 °C)
	NL_B	NL_{Si}	NR_B	NR_{Si}		
G - 0	0 0 6	0 01	0 0	0 00	1	10 6
SON68 [40]	0 886	0 1	0 01	0 00	1	
MW [31]	8 8	0 8	0	0 0 0	1 00	-

Table 5 – Comparison of network dissolution limiting normalised elemental mass losses and normalised elemental dissolution rates between SON68 glass, British Magnox waste HLW glass and G73-15 waste loaded glasses tested, under PCT conditions at 90 °C in 18.2 MΩ water.

Immobilisation of Prototype Fast Reactor Raffinate using Barium Silicate ILW Glasses

Paul G. Heath, Claire L. Corkhill, Martin C. Stennett, Russell J. Hand, Kieran M. Whales, Neil C. Hyatt

Immobilisation Science Laboratory, Sir Robert Hadfield Building, Mappin Street, The University of Sheffield, Sheffield, S1 JD, United Kingdom

Abstract

The vitrification of Dounreay Prototype Fast Reactor Raffinate (PFR) 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 0 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 x 10^{-} g m^{-} d^{-1}, in 18 MΩ water at 0^{o}C and surface area / volume ratio of 1 00 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 are considered to 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

Keywords Amorphous Materials, Waste Immobilisation, Mechanical properties

Introduction

The Prototype Fast Reactor (PFR) was the UK's second fast reactor and operated between 1 and 1 , 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 00 m of an aqueous radioactive liquor, known as PFR raffinate [ ] 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 [ ] Since the reprocessing of PFR fuel was completed in 1 6, 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 00 , ostensibly due to its low heat output [ ]

The conditioning of PFR raffinate into a passively safe, wasteform is identified as a priority in the Dounreay Site Restoration Plan [ ] 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 D 00) 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 0 times greater than other encapsulated ILW streams [, , ,8] The high concentration of ^{1}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 [, –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 [1 ,1]

An issue that may be even more significant to safe interim storage is the high specific activity of the wastes and their significant alpha emitting component ($\beta/\gamma =$ 6 TBq m^{-} , $\alpha =$ 1 TBq m^{-}) [ ] It is known that the radiolysis of cementitious water will produce H , while the presence of significant nitrate concentrations in the waste (00- 00 g l^{-1}) and alpha activity will also result in the formation of O and NO$_x$ [1 –1] 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"* [1]

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, G , previously investigated as a matrix for the immobilisation of UK ILWs arising at Magnox decommissioning sites [18- 1], is here investigated as a disposal matrix for PFR raffinate, the composition of which incorporates ca wt% SO Barium borosilicate glasses, such as G , 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-] 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%, 1 wt% and 0 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

Some variations in the elemental composition were necessary when batching the simulant For example, for reasons of practicality, any elements with concentrations < 1 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 ~1 0 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 [ ] The omission of the elements noted above accounted for < 8 wt% of the mass of the total waste stream Radioactive elements with concentrations > 1 ppm were substituted by relevant concentrations of inactive surrogates (Ce for U and Sm for Am)

2.1.2 Glass Preparation

Three glasses were synthesised and characterised in this study These glasses were based on a derivative of the G barium-silicate base glass composition (referred to here as G , for simplicity), which was previously developed [18- 1], with PFR raffinate simulant incorporated at 10 wt%, 1 wt% and 0 wt% waste loading These glasses are identified as G -10, G -1 and G - 0, respectively The base glass composition, presented in Table for reference, is identified as G -00

Glasses were produced from batch chemicals to provide 0 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) , Na B O 10H O, BaCO , CaCO , CdO, CeO , Cr(NO) H O, Cs CO , CuO, Fe O , La O , Mn O , MoO , Na CO , Nd O , NiCO , Pr_6O_{11}, RuO , Na SO , SiO , Sm O , SrCO , TeO , TiO , Y O and ZnO The batched powders were heated in mullite crucibles with stirring to 1 00 °C at 10 °C min^{-1} and held at temperature for hours The glasses were poured into blocks and annealed at 00 °C for one hour before cooling to °C at 1 °C min^{-1} Glass monoliths were prepared for SEM-EDX, Vickers hardness testing and fracture toughness testing to a 0 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- µm size fraction was collected for use in XRD and XRF analysis and the -1 0 µm size fraction was collected for use in aqueous durability experiments and prepared according to ASTM standard C 1 8 – 0 [ ]

2.2 - Characterisation

Glass Characterisation

X-ray Fluorescence (XRF) analysis was performed using a Phillips PW 0 XRF Axios instrument to obtain compositional data B O content was determined by dissolution of glass powder in HF followed by analysis of leachate using a Perkin-Elmer Optima 00 dual view Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) The density of the glass wasteforms was measured using a < µm powder, using an AccuPyc 1 0 II helium pycnometer with the following analysis regime 00 purges of the chamber followed by 0 cycles using an equilibration rate of Pa min^{-1} at °C in a 1 cm chamber and a fill pressure of 86 KPa Scanning Electron Microscopy was performed using a JEOL JSM 6 00 SEM with an accelerating voltage of 0 kV and a working distance of 1 mm Concurrent Energy Dispersive Spectroscopy was acquired (INCA, Oxford Instruments) Additionally, an FEI Quanta 00 F SEM was utilised for high resolution imaging, using an accelerating voltage of 0 kV and working distance of 10 mm Concurrent Energy Dispersive X-ray analysis was performed (Genesis EDX)

Thermal and mechanical properties

The glass liquidus temperature for each sample was measured by placing a 0 cm long mullite boat, filled with sub- µm glass powder, into a tube furnace The samples were left to equilibrate at 1 00 °C for hours and the temperature gradient along the length of the boat at mm intervals was measured using a retractable thermocouple The boats were removed and rapidly quenched in air The point of crystallisation was measurable to within 1 mm by optical examination of the crucibles and this was then correlated with the associated temperature to estimate the liquidus temperature Alterations in chemical composition resulting from crucible corrosion were not accounted for, nor were the phases produced analysed As the purpose of this test was to check if the point of crystallisation was below 1100 °C, and the contaminants from crucible corrosion are likely to lower this value, the results presented are considered useful in this context

The Vickers hardness indentation method was used to determine both hardness (H_v) and the indentation fracture toughness (K_c) following the procedure described by Connelly et al [6] Indentation was performed on a Mitutayo HM-101 Sixty indents were made at each of three indentation loadings 0 8 N, 1 6 N and N (twenty indents at each force per sample, error ± 0 0 N) The load was held for 0 seconds Samples were left for hours prior to analysis using optical microscopy The Vickers hardness (Hv) in Pa and the Fracture Toughness (Kc) was calculated using Equations 1 and respectively

$$H_v = \frac{1.854P}{(2a)^2}$$ Equation 1

$$K_C = \frac{0.0824P}{c^{3/2}}$$ Equation

where P is the applied load (N), a is the half length of the indent diagonal (m) and c is the median/radial crack length (m) The results quoted are those obtained from the 1 6 N loading due to the higher number of acceptable indentations (a minimum of fifteen per sample)

Aqueous durability assessment

Aqueous durability assessment was performed according to ASTM standard C 1 8 – 0 (Product Consistency Test - PCT) utilising a µm – 1 0 µm size fraction in 18 MΩ H O at 0°C with a SA/V between 1 m^{-1} and 1 m^{-1} dependent on glass density, as provided in Table [ ] Experiments were performed in triplicate with duplicate blanks, sampling at , , 1 , 1 and 8 days Samples were filtered using a 0 µm PTFE filter and leachate analysis was performed using ICP-AES

The normalised elemental mass loss (NL) and normalised elemental dissolution rates (NR) were calculated according to Equations and , respectively using the analysed glass compositions

$$\mathrm{NL_i} = \frac{\mathrm{C_i}}{\mathrm{f_i} \times \frac{\mathrm{SA}}{\mathrm{V}}}$$ **Equation 3**

$$\mathrm{NR_i} = \frac{\mathrm{C_i}}{\mathrm{f_i} \times \frac{\mathrm{SA}}{\mathrm{V}} \times t}$$ **Equation 4**

where NL is the normalised elemental mass loss of element *i* (g m^{-}), C is the averaged, blank corrected concentration of element *i* in solution (g m^{-}), f is the fraction of element *i* in the unleached glass, SA/V is the ratio of glass surface area to the volume of water (m^{-1}), NR is the normalised elemental loss rate and t is time in days

Geochemical modelling of the solution leachate was performed using the PhreeqC geochemical modelling code (v -1 -8 8, provided by the United States Geological Survey) to identify solution saturation species, using the Lawrence Livermore National Laboratory (LLNL) thermodynamic database

3 - Results

3.1 - Glass Formation and Composition

It can be stated with confidence that the three simulant PFR waste loaded G glasses exist within a stable glass forming region of the phase diagram up to a 0 wt% loading. The glasses formed readily and poured from the melt at 1 00 °C, with no evidence of un-dissolved batch. However, a small degree of corrosion was evident inside the crucible, which is responsible for the elevated concentrations of alumina in the final composition. The composition of the three glasses was analysed using XRF and ICP-AES; data are shown in Table , which compares the final composition with the nominal batched compositions.

Overall, it can be seen from Table that the batched and analysed compositions are in reasonable agreement for major and minor oxides, although with some notable exceptions. Na_2O, B_2O_3, and SO_3, are, in general, analysed as lower than the batched composition, due to volatilisation from the melts during high temperature processing. SiO_2 and BaO are, respectively, systematically higher and lower in the analysed glass compositions compared to the batched. The complexity of the glass composition made deconvolution of overlapping X-ray emission lines, from multiple elements, challenging and may be responsible for this systematic discrepancy. The loss of such volatile components from the melts does not pose a challenge to the off-gas system of existing HLW melter systems and, therefore, is not expected to be problematic for full scale deployment. In addition, it should be noted that the lower surface area to volume ratio, and presence of a cold cap, in full scale melter systems will reduce volatilisation considerably, with respect to laboratory scale melts.

Analysis of the vitrified products by X-ray diffraction showed only diffuse scattering (Figure 1) characteristic of an amorphous material, with no evidence of phase separation or detectable crystallisation The lack of contrast in both the SEM-BSE imaging and SEM-EDX mapping analysis, displayed in Figure 1b and Figure , is indicative of a chemically homogeneous glass on a micron scale Each glass showed similar characteristics There was no evidence from XRD or SEM-EDX analysis of distinct segregated sulphate phases

Crystallisation in radioactive waste glasses, when produced from the melt, is undesirable for several reasons, including the possibility for the precipitation of soluble radionuclide containing phases the potential for decreased aqueous durability of the matrix, due to the removal of refractory components and the potential for swelling of crystal phases as a result of damage from self-irradiation The absence of significant crystallisation and minimal evidence of crucible corrosion indicate that a high-quality glass wasteform was obtained that should be both stable and amenable to the processing of PFR wastes

3.2 - Thermal Properties

Table shows the density, glass transition temperature and measured liquidus temperature of the simulant PFR glasses The values obtained for the T_g are comparable, within error, for the three waste-loadings and correspond well with the transition temperature previously reported for the same base glass loaded with organic exchange resins [18- 1]

The liquidus temperatures of the glasses were all below 1100 °C, and no correlation with increasing waste loading was observed Glass compositions with a liquidus temperature below 1100 °C are thought to be beneficial for nuclear waste vitrification as the lower temperatures minimise volatile losses of radioactive components during melting [-] Although not essential for all melter operations or wasteform acceptance criteria, the absence of crystalline products indicates that the wasteforms will be amenable to commercial application due to the associated simplification of wasteform qualification, improved efficiency of melter operation and predictability of process control [0]

As the glasses produced in this study have been shown to retain their Cs inventory after processing at 1 00 °C, the retention of Cs should be expected to be retained in full scale melts given the smaller melt surface area to volume ratio and possibility of operating with a cold cap [1]

3.3 - Mechanical Testing

The Vickers hardness and indentation fracture toughness of the PFR simulant glasses are plotted in Figure The fracture toughness of the glass relates to the energy required to form a new surface and is relevant to qualifying the suitability of radioactive waste packages for transport, e g in estimating the likelihood of respirable fines formation in accident scenario [ ]

The lowest waste loaded glass, G -10, had the highest indentation fracture toughness and the hardness value of the glasses tested G -1 and G - 0 glasses gave lower values and were equivalent within measurable precision All compositions were comparable or superior to existing HLW glass compositions (e g UK MW glass and US PNL 6- 8 glass, Fig) for indentation fracture toughness and were comparable, or superior, in terms of Vickers hardness [6,]

Although no specification for fracture toughness currently exists for UK vitreous waste packages, the results imply that, as the G based glasses are comparable to current wasteforms, they are likely to be compliant with storage in existing (HLW) canisters Furthermore, the mechanical properties suggest that packaging in larger m boxes may also be possible, although in this case analysis of thermally induced cracking/stresses during processing requires investigation

3.4 - Aqueous Durability

The short-term chemical durability of the simulant raffinate glasses was investigated using the PCT methodology [ ] Figure shows the normalised mass loss of elements that were detectable by ICP-AES in concentrations higher than those measured in the blank solutions The normalised elemental mass loss (NL) and normalised dissolution rate (NR , 8 days) data are shown in Tables and , respectively The solution pH buffered to a value of pH 10 ± 0 after days (Fig) and there was no further measurable fluctuation of pH during the 8-day duration of the experiments

The normalised elemental loss rates (to 8 days) for boron were similar for each glass composition, giving an NR_B between x 10^{-} g m^{-} d^{-1} and x 10^{-} g m^{-} d^{-1} (± x 10^{-}) as stated in Table This indicates that varying the waste loading from 10 to 0 wt% did not appreciably alter the chemical durability on the timescales investigated Importantly, the glasses showed a comparable normalised mass loss and normalised dissolution rate to other high-level waste glass compositions destined for long-term disposal, tested under comparable conditions (Table) For example, the UK HLW MW glass, has a NR_B of 0 x 10^{-1} g m^{-} day^{-1} [ ], compared with x 10^{-} g m^{-} d^{-1} for the 0 wt% loaded simulant PFR raffinate glass (Table) The NR_B is approximately twice that of the SON68 French HLW base glass, however It should be noted that the specific activity in R T (the active analogue of SON68) will be substantially higher than that of the PFR loaded G glasses At production, R T contains an average specific activity ca 110 PBq m^{-} , approximately 0 times greater than the average ca

6 PBq m^{-} estimated for the G - 0 glass [ ] As such, these glasses could be considered suitable for the immobilisation and disposal of PFR raffinate

Glass dissolution was observed to be incongruent B and Na leached at similar rates (NL_B > NL_{Na}), however the normalised mass loss of all other elements was an order of magnitude lower than both B and Na (Table) The normalised mass loss of all elements was observed to be rapid for the first days of dissolution and, after this time, the normalised mass loss of Si, Na, B began to reduce indicating an approach to quasi-equilibrium, as indicated in Figure

The normalised mass loss of Ba and Ca differed as a function of glass composition, albeit without a notable trend For example, the normalised mass loss of Ba decreased after days for the 0 wt% waste loaded composition, and after 1 days for the 1 wt% glass (Fig b) There appeared to be little removal of Ba from solution from the 10 wt% loaded glass Additionally, the NL_{Sr} dropped after 1 days for all three glasses (Fig f) This behaviour may be attributed to the formation of Ca-, Ba- and Sr-containing alteration layers on the glass surface Indeed, geochemical modelling indicated that tobermorite ($Ca\,Si_6H_{11}O$) is likely to precipitate A number of recent investigations have also identified this phase in glasses containing Ca, or where Ca is present in solution [–] and have shown that its formation can significantly reduce the dissolution rate of nuclear waste glasses, by an order of magnitude compared to other media [ ] Other phases shown by geochemical modelling to be favourable precipitates were the Ca- Ba- and Sr-carbonate phases, calcite ($CaCO$), witherite ($BaCO$) and strontianite ($SrCO$) Arising from equilibrium of CO in air with the leaching medium, it is possible that these phases precipitated in solution, and when the samples were filtered for analysis, they were removed, leading to an apparent decrease in Ca, Ba and Sr leaching It will be necessary to perform further monolith leaching experiments to examine the properties of the altered layer so that the origin of the fluctuations in these elements can be determined and set in the context of recent mechanistic studies of UK HLW and ILW glass performance [0-]

4 - Discussion

Previous work has shown that cement may not have the capacity to effectively immobilise the diverse inventory of radioactive elements present in the PFR raffinate waste stream [ ] Cementitious wasteforms could be subject to increased dissolution and release rates due to their inherent porosity and high internal surface area The high solubility and potential for removal of many of the waste elements which sorb to the cement surface especially Cs, which makes up over 60% of the radioactive inventory by activity, is of potential concern [ ] These factors highlight the opportunity to vitrify PFR wastes to minimise radioisotope migration to the biosphere Vitrification, using G barium silicate glass described in this investigation, is likely to offer significant improvements in long term wasteform performance over the current baseline

The benefits of vitrification reach beyond the improvements in wasteform quality described and may also offer fiscal incentives, for example, by substantially reducing the waste volumes for storage and disposal The current lifecycle waste management plan is to cement the PFR raffinate in 00 L drums, with a target waste loading of 0 0 m per drum With 1 1 m of raffinate to process this would result in m of packaged waste for disposal (6 6 x 00 L drums with a displacement volume of 0 m each) [ ] If vitrification, at 0 wt% loading was to be utilised, the volume of waste produced would be reduced to < 1 m^3 of glass Conceivably, this volume of material could be readily processed in a small or modular plant, utilising one of a variety of thermal treatment options for ILW being developed in the UK e g plasma vitrification, resistive heating melters or Hot-Isostatic Pressing [ ] Assuming packaging of vitrified PFR waste into m ILW boxes was preferable and 0% of the box capacity (m) could be filled, each m box would hold 1 8 m of vitrified product In this scenario, the waste could be fully conditioned using just eight m boxes, producing a total waste volume for disposal of 8 6 m This treatment methodology, when compared with cementation, would reduce the waste disposal inventory by more than 0%, and, in principle, could be achieved, using in-container Joule heated melter technology The heat generation, surface activity limits and containment limits for impact of this hypothetical G - 0 waste stream have been estimated to be within existing guidelines for a m^3 ILW box[1] [6] The substantial volume reduction achieved by the vitrification approach would enable transfer of the resulting waste packages to the Sellafield site for storage, potentially assisting earlier closure of the Dounreay site

Deriving a lifetime waste management cost for these wastes intended for near surface storage has not been attempted here However, it is believed the cost reductions associated with managing lower volumes of wastes in the rest of the NDA estate should be transferable to Scottish policy It is important to note that the volume reduction and concentration of the waste associated with this vitrification step would not result in the re-classification of the waste as HLW This is important as a reclassification to HLW would require consideration of heat dissipation in storage, introducing significant extra costs for disposal, as well as increasing the final volume required in a storage vault

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[1] Calculation based upon reported inventory of radioisotopes for this waste stream and accounting for the concentration of activity achieved by vitrification This packaged waste will meet stated specifications imposed for a square corner m box

The decreased risk to public health, superior quality of final wasteform, improved long term stability, smaller footprint on the Dounreay ILW stores and the reduced waste management cost, combine to provide a credible case for treatment of these wastes using vitrification over cementation

5 - Conclusion

A vitreous wasteform for simulant PFR raffinate was developed at a range of waste loadings up to 0 wt% The product was a stable and homogeneous amorphous solid with no observable crystal formation All glasses performed comparably to vitrified waste compositions currently in use, both in the UK and internationally, for the immobilisation of HLW The aqueous durability was superior to that of current UK HLW glasses under comparable experimental conditions Therefore, the glasses investigated here could be considered a stable matrix for ILW under both geological disposal and near-surface storage scenarios The mechanical properties of the wasteform also matched or exceeded those currently in use for HLW glasses, in both the UK and USA, and therefore, should be amenable to transport and storage in either 00 L HLW flasks or m ILW waste packages Additionally, we demonstrated that undertaking immobilisation of PFR raffinate through thermal treatment methods may also result in a decrease in the anticipated volume of waste from m to 8 6 m , potentially resulting in significant lifetime waste management cost savings and a more robust option to support the Scottish policy for at near surface storage and site closure

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Figures

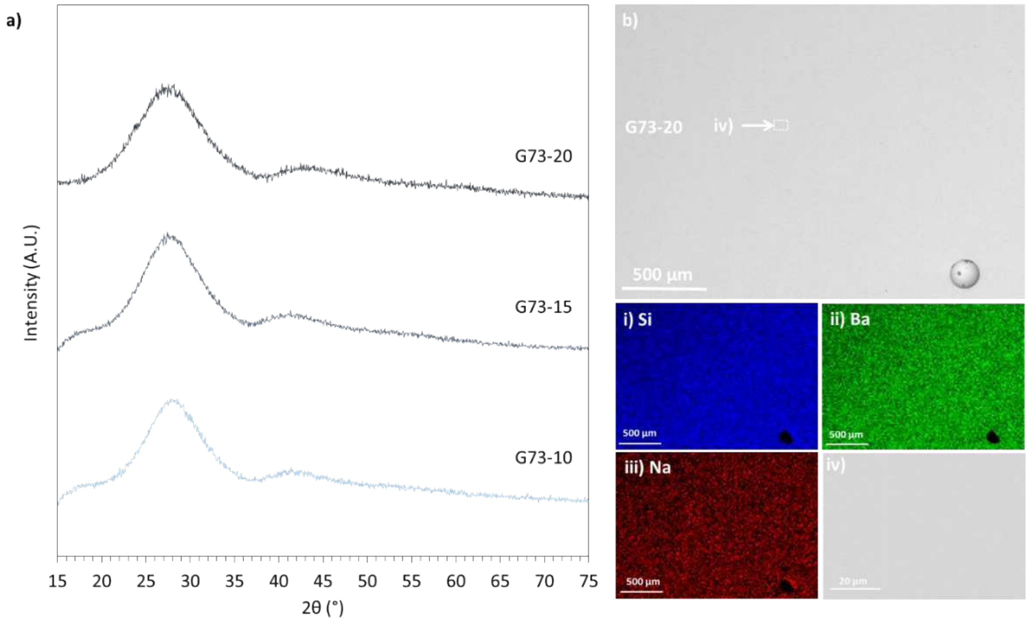

Figure 1 - a) Powder XRD patterns of G73 PFR raffinate loaded glasses, displaying diffuse scattering characteristic of amorphous material and b) SEM-BSE image displaying homogeneity of G73-20 glass matrix, set above i) - iii) SEM-EDX maps of key elements for b) and iv) a higher resolution BSE-SEM of G73-20 glass matrix identified in b) which taken illustrates the absence of crystalline materials in the final waste product.

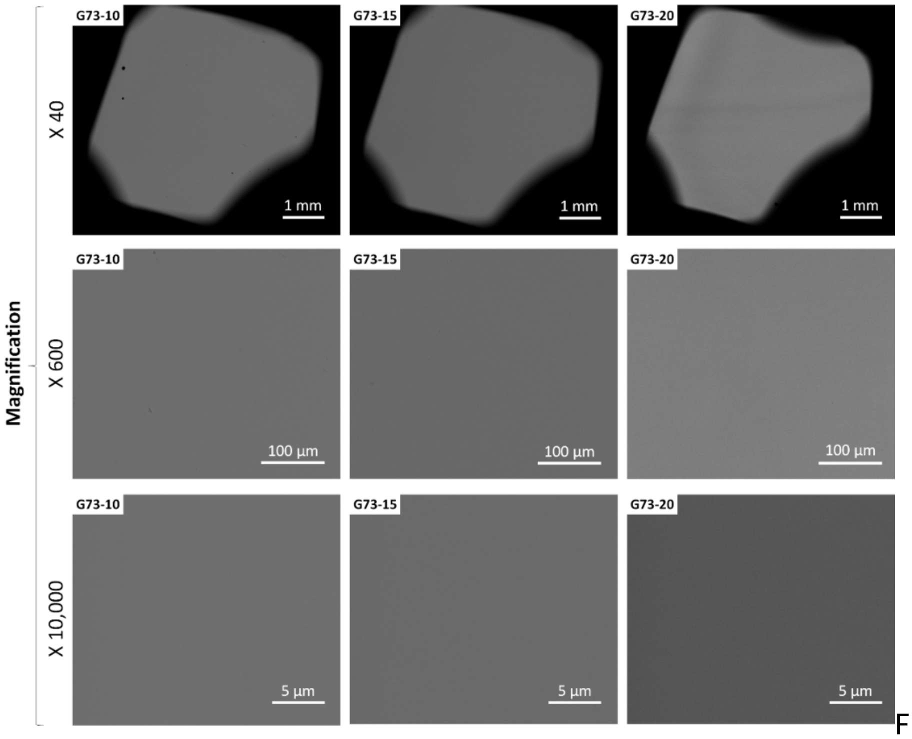

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Figure 2 - SEM-BSE images of the three waste loaded glasses G73-10, G73-15 and G73-20 at various magnifications. The lack of image contrast suggests chemical homogeneity within the sample.

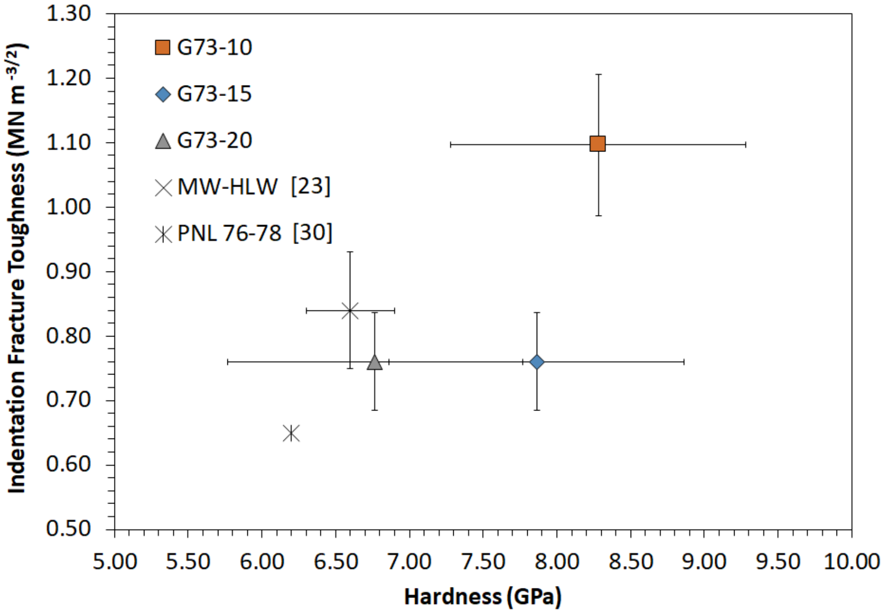


Figure 3 – Indentation fracture toughness and hardness values of G73 PFR raffinate waste loaded glasses obtained using the Vickers indentation methodology, with comparison to waste glasses currently used for HLW immobilisation [23,30]. Errors correspond to 3 x the measured standard deviation.

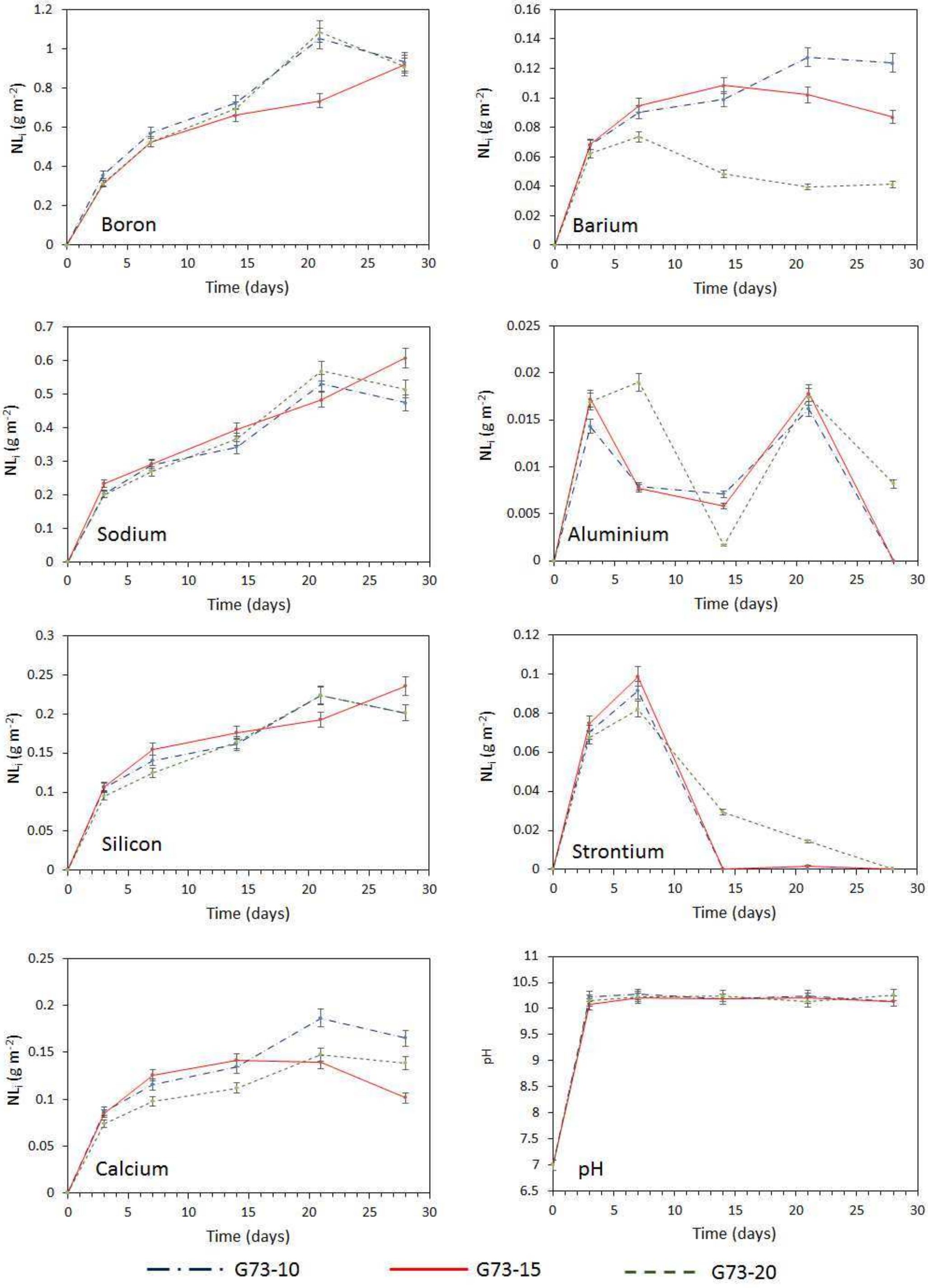


Figure 4 – Graphs displaying the normalised elemental mass loss with varying levels of PFR raffinate loading from PCT experiments at 90°C in 18.2 MΩ water with a SA/V of 1499 m^{-1} -1525 m^{-1} (dependant on glass density).

Tables

Included in Simulant (surrogate element used)		Excluded from Simulant	
Element	*ppm*	*Element*	*ppm*
Na	, 11	*Rh*	1
Cu	8,	*Cm*	
Fe	,8	*Nb*	
Zn	, 66	*Dy*	
Cd	, 0	*Ag*	<1
S	1, 1	*As*	<1
Ni	1,	*Co*	<0
Cr	66	*Ge*	<1
Cs	0	*Hg*	<0
Nd	6	*Ho*	<1
Am (Sm)	0	*In*	<
Al	0	*Np*	<1
Ce	0	*P*	<
U (Ce)	168	*Pb*	<1 1
La	16	*Rb*	<1
Pr	1 8	*Sb*	<1
Mo	1	*Se*	<1
Pd	1 0	*Sn*	<0
Ca	1 8	*Tc*	<1
Sm	1	*Eu*	1
Y	11	*Gd*	1
Te		*Pd*	1 0
Sr	60		
Mn			
Ru	60		
Ba			
Ti	6		
Total	,186	Total	0

Table 1 - Average composition of PFR raffinate as characterised in [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 both low concentrations in the raffinate and on an economic basis.

Table 2 - Compositions of base glass, simulant calcined PFR raffinate and glasses produced. Compositions of glasses provided both as batched and as measured by XRF (boron analysis via dissolution in HF and ICP-AES). *Note glasses were batched to 100 wt%; discrepancies reported result from rounding to 2 d,p.

Component (wt%)	G73-00 Base Glass	PFR Calcine	G73-10		G73-15		G73-20	
			Batch	Meas.	Batch	Meas.	Batch	Meas.
S O	0	0 00	80		0		60	8
BaO	0	0 0	81	1 1	1	1 61	6	8 61
Fe O	6 00	11 68	6	88	6 8	8	1	6
CaO	00	0 1			1		08	0
Na O	0	88	0	1 6	6 1	8	8	0
CuO	0	6 6	6	8		8		0
B O	00	0 00	1 80	0 6	1 0	0 6	1 60	0 6
ZnO	0		0	1 08	1	1	1 8	1
CdO	0	6 18	0 6	0	0	1 0	1	1
SO	0	18	0	0	1 08	0	1	0 86
Al O	0 0	1 1	0	0 86	0 6	0 8	0 68	1
N O	0	6	0	0	0	0 1	0 6	0 86
Cr O	0	08	0 1	0 8	0 1	0 6	0	0 66
Cs O	0	1 1	0 1	0 6	0 1	0	0	0
Nd O	0	1 1	0 1	0 1	0 1	0 00	0	0
Sm O	0	0 0	0 0	0 10	0 0	0 1	0 06	0 1
CeO	0	0	0 10	0 0	0 1	0 10	0 1	0 1
MoO	0	0	0 0	0 06	0 0	0 08	0 10	0 0
Y O	0	0 0	0 0	0 0	0 0	0 0	0 06	0 06
La O	0	0 0	0 00	0 0	0 01	0 00	0 01	0 0
Pr_6O_{11}	0	0 0	0 00	0 0	0 01	0 06	0 01	0 0
RuO	0	0 1	0 0	0 00	0 0	0 00	0 0	0 00
SrO	0	0 1	0 0	0 6	0 0	0 1	0 0	0 0
TeO	0	0 0	0 0	0 00	0 0	0 00	0 0	0 00
T O	0	0 1	0 01	0 00	0 0	0 00	0 0	0 00
Mn O	0	0 1	0 01	0 08	0 0	0 08	0 0	0 0
	100	-	100 1	8	100 0	100 81	100 6	100

Glass Property	Sample ID		
	G73-10	G73-15	G73-20
Density (g cm⁻)	1 ± 0 00	± 0 00	± 0 00
Glass Transition Temperature (°C)	0 ± 10	8 ± 10	8 ± 10
Liquidus Temperature (°C)	10 ± 10	10 ± 10	10 0 ± 10

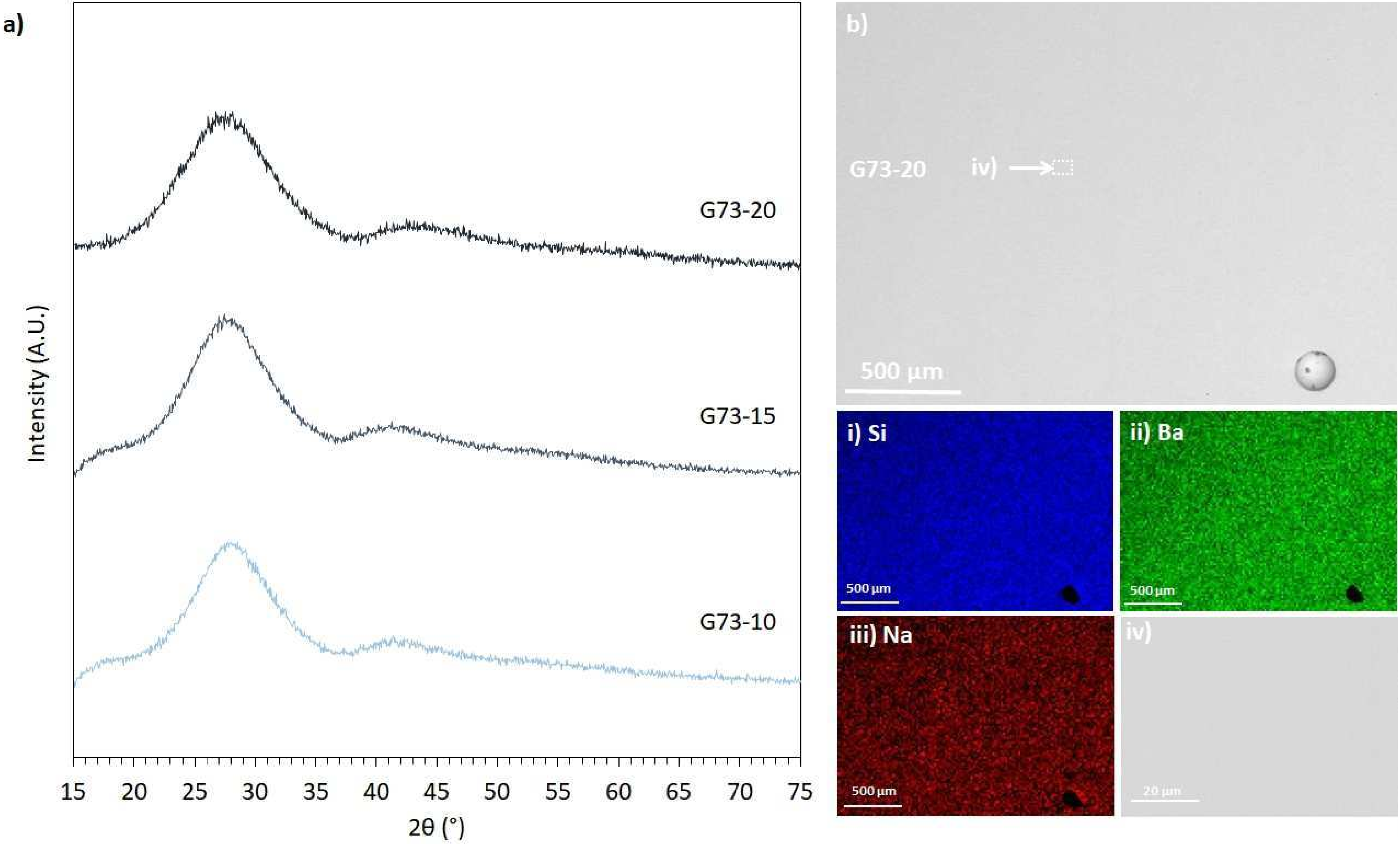
Table 3 - Properties of glass wasteforms produced at varying PFR raffinate waste loadings including the density, liquidus temperature (measured in mullite crucibles – see main text for the implication of this) and glass transition temperature.

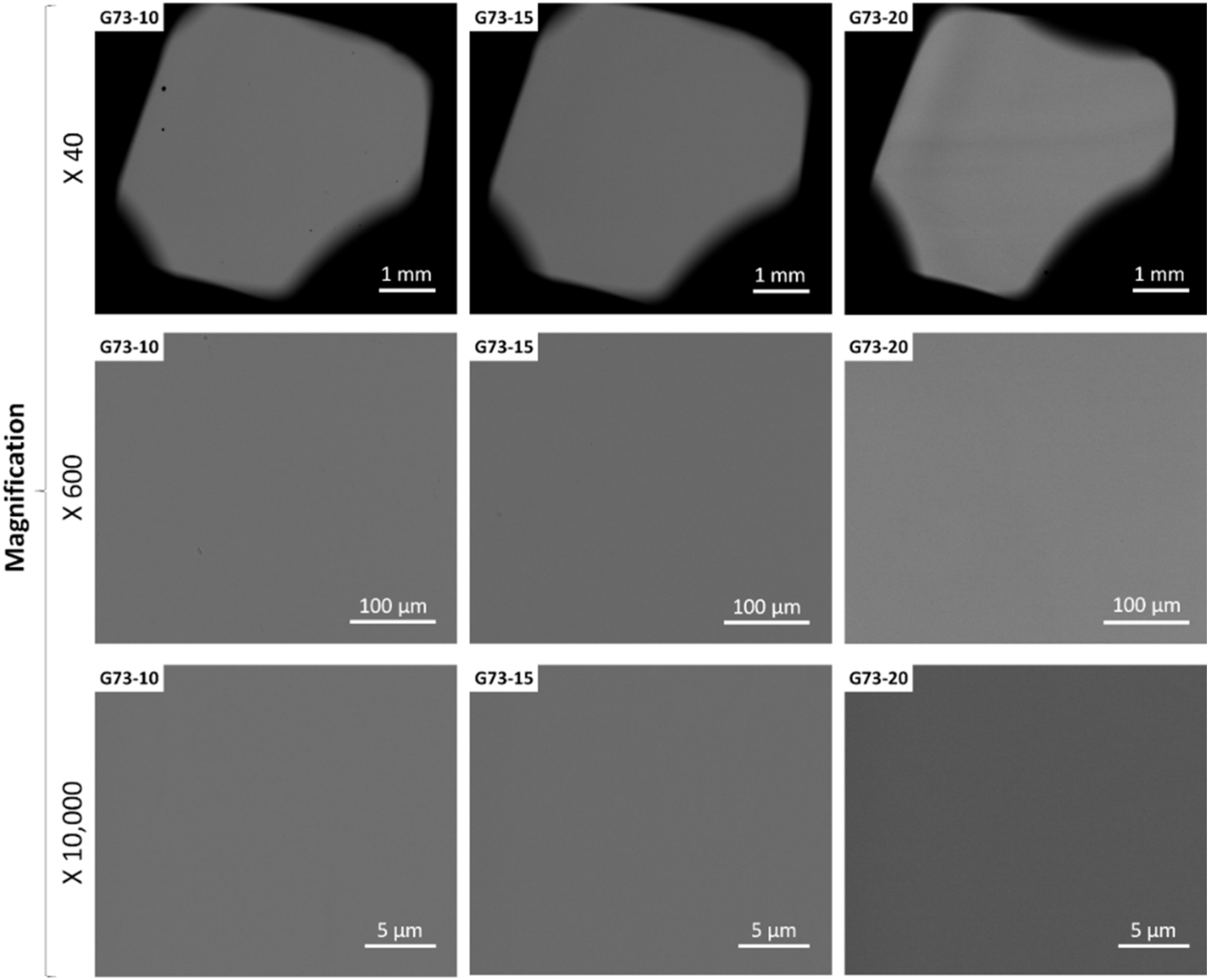
NR$_i$ (g m^{-2} day^{-1})	Glass Composition		
	G73-10	**G73-15**	**G73-20**
B	x 10^{-}	8 x 10^{-}	x 10^{-}
Na	1 6 x 10^{-}	1 x 10^{-}	1 8 x 10^{-}
S	18 x 10^{-}	8 0 x 10^{-}	1 x 10^{-}
Ca	8 x 10^{-}	6 x 10^{-}	x 10^{-}
Mo	x 10^{-}	8 x 10^{-}	6 8 x 10^{-}
Ba	x 10^{-}	10 x 10^{-}	1 x 10^{-}
Cr	8 x 10^{-}	1 6 x 10^{-}	0 x 10^{-}
Cu	x 10^{-6}	1 x 10^{-6}	0 00
Al	0 00	0 00	1 x 10^{-}
Fe	0 00	0 00	0 00
N	0 00	0 00	0 00
Sr	0 00	0 00	0 00
Zn	0 00	0 00	0 00

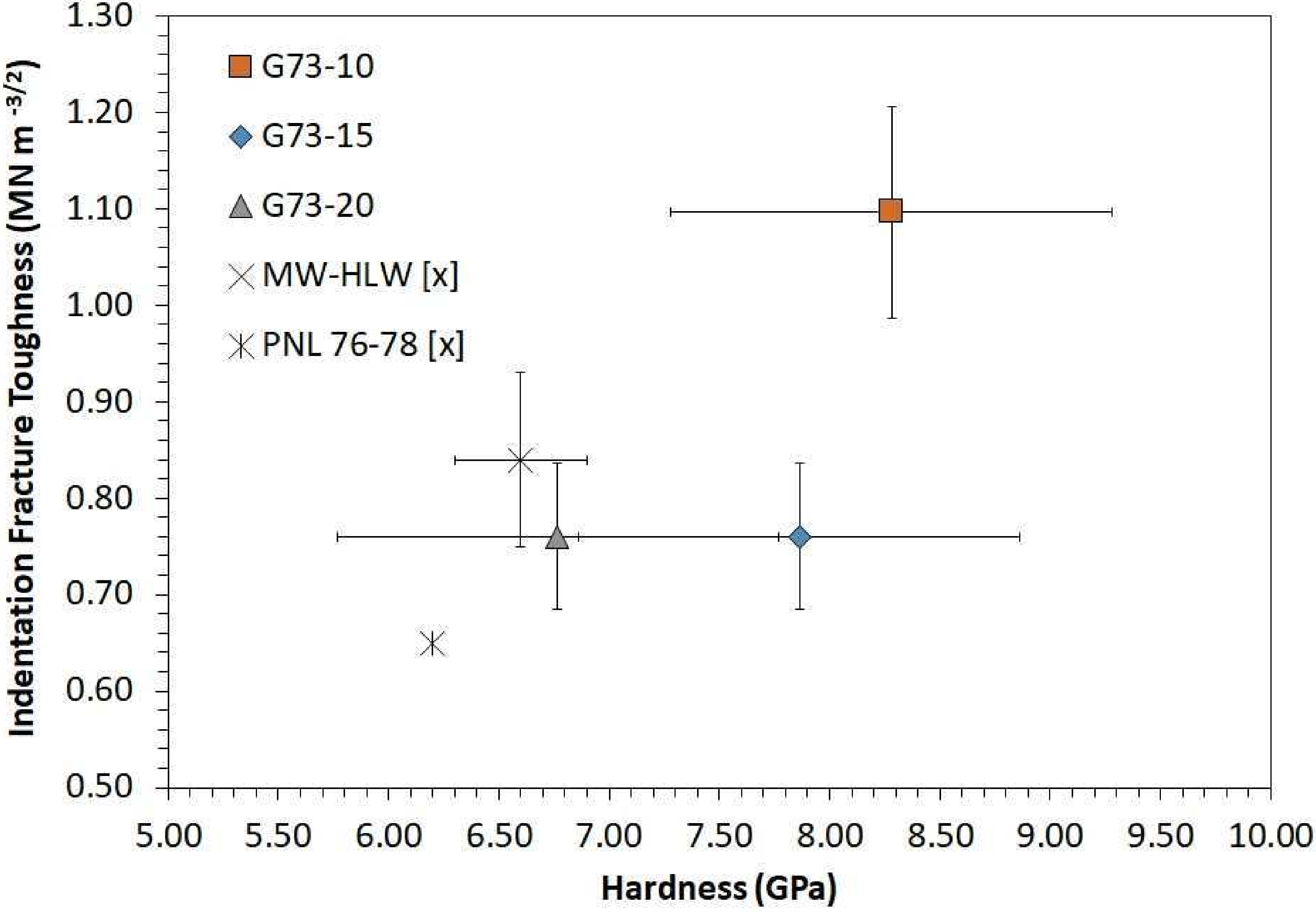
Table 4 – Normalised elemental loss rates for the three waste PFR waste loaded glasses measured after 28 days. Data is from PCT experiments of the wasteforms at 90 °C in 18.2 MΩ water.

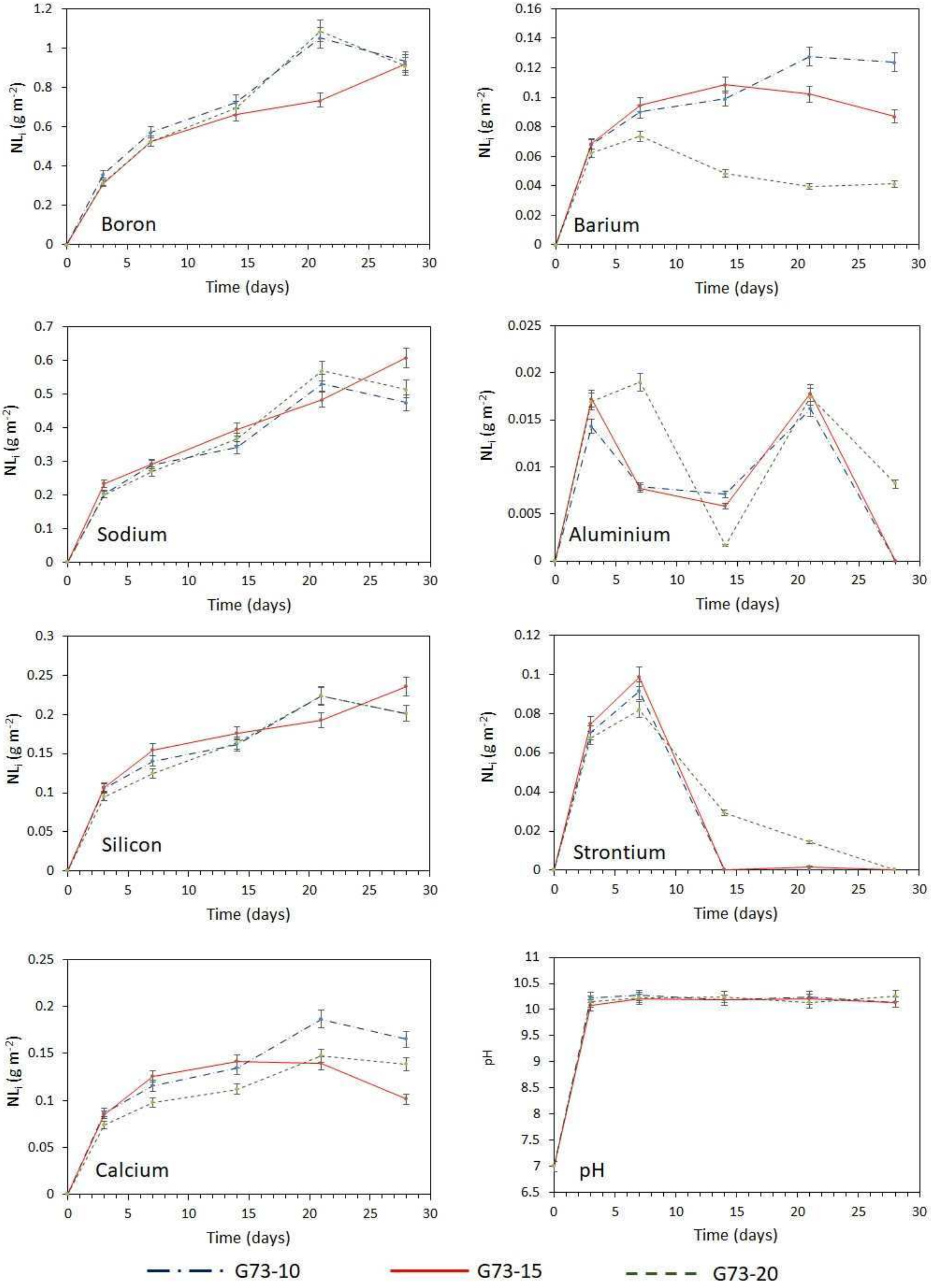
Glass Composition	NL$_i$ after 28 days (g m^{-2})		NR$_i$ after 28 days (g m^{2} day^{-1})		SA/V (m^{-1})	pH (25 °C)
	NL_B	NL_{Si}	NR_B	NR_{Si}		
G - 0	0 0 6	0 01	0 0	0 00	1	10 6
SON68 [40]	0 886	0 1	0 01	0 00	1	
MW [31]	8 8	0 8	0	0 0 0	1 00	-

Table 5 – Comparison of network dissolution limiting normalised elemental mass losses and normalised elemental dissolution rates between SON68 glass, British Magnox waste HLW glass and G73-15 waste loaded glasses tested, under PCT conditions at 90 °C in 18.2 MΩ water.


a)
Intensity (A.U.)
G73-20
G73-15
G73-10
15
20
25
30
35
40
45
50
55
60
65
70
75
2θ (°)
b)
G73-20
iv)
500 µm
i) Si
500 µm
ii) Ba
500 µm
iii) Na
500 µm
iv)
20 µm


Magnification
X 40
X 600
X 10,000
G73-10
G73-15
G73-20
G73-10
G73-15
G73-20
G73-10
G73-15
G73-20
1 mm
1 mm
1 mm
100 µm
100 µm
100 µm
5 µm
5 µm
5 µm


G73-10
G73-15
G73-20
MW-HLW [x]
PNL 76-78 [x]
Indentation Fracture Toughness (MN m -3/2)
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
9.00
9.50
10.00
Hardness (GPa)


Boron
Barium
Sodium
Aluminium
Silicon
Strontium
Calcium
pH
NL$_i$ (g m^{-2})
pH
Time (days)
0
5
10
15
20
25
30
1.2
1
0.8
0.6
0.4
0.2
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.025
0.02
0.015
0.01
0.005
0.3
0.25
0.2
0.15
0.1
0.05
0.12
0.1
0.08
0.06
0.04
0.02
0.25
0.2
0.15
0.1
0.05
11
10.5
10
9.5
9
8.5
8
7.5
7
6.5
G73-10
G73-15
G73-20