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Article:

Characterisation and Durability of a Vitrified Wasteform for Simulated Chrompik III Waste

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Legacy waste from the decommissioned A-1 nuclear power plant in the Slovak Republic is scheduled for immobilisation within a tailored alkali borosilicate glass formulation, as part of ongoing site cleanup. The aqueous durability and characterisation of a simulant glass wasteform for Chrompik III legacy waste, was investigated, including dissolution experiments up to 112 days (90°C, ASTM Type 1 water). The wasteform was an amorphous, light green glassy product, with no observed phase separation or crystalline inclusions. Aqueous leach testing revealed a suitably durable product over the timescale investigated, comparing positively to other simulant nuclear waste glasses and vitreous products tested under similar conditions. Iron and titanium rich precipitates were observed to form at the surface of monolithic samples during leaching, with the formation of an alkali deficient alteration layer behind these at later ages. Overall this glass appears to perform well, and in line with expectations for this chemistry, although longer-term testing would be required to predict overall durability. This work will contribute to developing confidence in the disposability of vitrified Chrompik legacy wastes.

Keywords: Higher activity waste, Vitrification, Glass, Durability, Characterisation, Chrompik

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1. Introduction

The safe conditioning and disposal of nuclear wastes is of paramount importance for hazard minimisation on nuclear licensed sites. Legacy materials, especially if arising from novel process or experimental reactors, can prove challenging to manage owing to their different chemistries, physical properties, or due to historical poor documentation. Certain waste materials arising from the A-1 nuclear power plant in the Slovak Republic fall into this category, with quantities of liquid / sludge wastes generated of an atypical chemistry arising from the now closed reactor of novel design.

The A-1 power plant was a KS-150 design gas-cooled (CO_2), heavy water moderated reactor utilising natural uranium metallic fuel in a magnesium-beryllium cladding. The plant was built at Jaslovské Bohunice, Slovak Republic (formerly Czechoslovakia) with commercial operations commencing in 1972 [1]. The plant was closed in 1977 following an accident during a refuelling procedure in which fuel cladding was damaged, resulting in the contamination of several coolant facilities. The cost of the required repair and clean up, to enable recommissioning and reactor operation, was considered prohibitive [2, 3]. During commercial operation, and post-operation, some spent fuel assemblies (including damaged fuel) were stored in a mix of potassium chromate and dichromate aqueous solution (referred to as Chrompik), as a cooling medium for up to 20 years, prior to transfer of the fuel to Russia for processing. These suboptimal fuel storage conditions resulted in the accumulation of legacy liquids and sludges that require conditioning to reduce associated hazards [4, 5].

The original Chrompik solution consisted of either 1–3wt% potassium dichromate ($K_2Cr_2O_7$) with 0.5wt% potassium fluoride (KF) or 1–3wt% potassium chromate (K_2CrO_4), and was used for short-term cooling, with waste Chrompik solution having an activity of ~1 GBq·dm^{-3} for ^{137}Cs. These wastes, now owned by JAVYS (Jadrova a vyrad'ovacia spoločnost – Nuclear and Decommissioning

Company), were vitrified at the VICHR plant (Vitrification facility of Chrompik) by 2001 [6]. A batch melting process is employed, with both the fine sludge and liquids treated together, and the vitrified product cast into steel containers [4]. The glass frit utilised is a typical sodium-lithium borosilicate, but with significant TiO_2 and Fe_2O_3 additions [7]. This facility was licenced for solutions that contain up to 100 GBq·L^{-1}, and thus, legacy wastes containing higher activities (> 100 GBq·L^{-1}) have been awaiting conditioning [5]. The more challenging waste is designated as Chrompik III – having been used for long-term fuel storage, recording 100 GBq·dm^{-3} ^{137}Cs. The Cr content of this material is much lower than the vitrified wastes, as the result of chromium reduction, forming insoluble Cr(III) compounds, which are one component of the sludge located at the bottom of the storage tank. Due to the increased activity and different chemistry of this material, modification of the existing vitrification rig has be required before processing of Chrompik III waste [6], with Chrompik III processing on the vitrification rig since 2017.

This study focusses on the characteristics and durability of a simulated Chrompik III glass wasteform, as part of a research programme undertaken by Vuje to determine the optimum processing conditions for the remaining Chrompik III liquors. This simulant Chrompik III vitrified product was characterised, and subjected to standardised leaching tests up to 112 days, both as a crushed powder and as monolithic glass blocks to determine the formation of any alteration layers which may affect longer term aqueous durability.

2. Experimental Methodology

2.1 Materials

Surrogate inactive Chrompik III glass materials were produced by Vuje using a mixture of glass frit, additives (aluminosilicates to reduce Cs volatility during melt), and Chrompik surrogate solution (composition in Table 1) in

Table 1. Surrogate material composition [8]

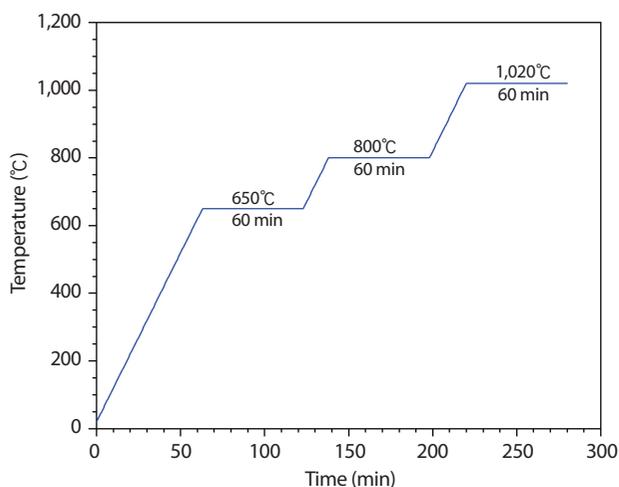| Chrompik III solution	K (7.6 g·L^{-1}), HCO$_3^-$ (7.3 g·L^{-1}), CO$_3^{2-}$ (1.8 g·L^{-1}), Cr (0.06 g·L^{-1})
Glass frit	SiO$_2$ (57wt%), B$_2$O$_3$ (14.8wt%), Na$_2$O (8.5wt%), TiO$_2$ (5.5wt%), Al$_2$O$_3$ (5.3wt%), Fe$_2$O$_3$ (4.5wt%), Li$_2$O (3.5wt%)
Additives	Aluminosilicate / geopolymer material

Fig. 1. Temperature profile for Chrompik III glass simulant laboratory fabrication.

a ratio of 40:17:43 [8]. The material was mixed and then dried in an oven at 100°C for 24 h. The mix was melted at a maximum temperature of 1,020°C, stopping and holding at various temperature points as described in Fig. 1. The molten material was cast in metal moulds, and annealed at 550°C for 4 hours to yield a green Chrompik III simulant wasteform; the glass transition temperature was previously determined to be 490–515°C [8].

2.2 Analysis Methods

X-ray diffraction data were collected using a Bruker D2 PHASER diffractometer (Cu Kα, 1.5418 Å), with a Ni foil to filter Kβ radiation. Diffraction patterns were collected between 5−70° 2θ, with a step size of 0.02° and a dwell of 1 s per step, with powder samples crushed in an agate mortar prior to analysis.

Scanning electron microscopy (SEM) and elemental mapping utilised a Hitachi TM3030 scanning electron microscope (backscattered electron mode, 15 kV accelerating voltage), coupled with a Bruker Quantax 70 Energy Dispersive X-ray Spectrophotometer (EDX). Monolith samples were either mounted on carbon tabs for surface analysis as-is, or mounted in epoxy resin and ground using progressively finer SiC grit paper, and ultimately polished to a 1 μm finish using diamond suspension, then carbon coated for analysis.

The durability assessment for Chrompik III was undertaken on both crushed (using both the ASTM C1285 PCT-B (Product Consistency Test) methodology, and a non-standard modified PCT-B methodology utilising a lower surface area and larger particle size), and monolithic materials (using ASTM C1220 MCC-1 (Materials Characterization Center) methodology). For the ASTM PCT-B protocol, material was crushed and sieved to between 75–150 μm, then washed with isopropyl alcohol (IPA) to remove fines. The required quantity of sieved and washed material was added to cleaned PFA (PerFluoroAlkoxy) vessels with ASTM Type 1 water to achieve a surface area to volume (SA/V) ratio of 2,000 m^{-1}. The SA/V was calculated assuming geometric surface area (density acquired via helium pycnometry using a Micrometrics Accupyc II). Static leaching was undertaken at 90 ± 3°C for up to 112 days, with triplicate sampling at regular intervals. As part of a multi-partner testing programme under the EC THERAMIN project (European Commission – THErmal treatment for RAdioactive waste MINimisation and hazard reduction), comparing this to other thermally treated wasteforms [9], a second PCT-B test was performed using a size fraction of 125–250 μm, at a SA/V of 10 m^{-1} (conditions which required less material for testing, and may be more suitable for heterogeneous materials). In this test, leaching was undertaken at 90 ± 2°C for

up to 28 days, with duplicate sampling at regular intervals.

Monolith Chrompik III specimens were tested according to ASTM C1220 (MCC-1), with monoliths sectioned using a Buhler Isomet Slow Saw and a diamond wafering blade, then ground down with progressively finer SiC grit paper, and polished to a 1 μm finish using diamond suspension. Monolith samples were placed in PFA baskets inside cleaned PFA vessels, filled with 40 mL ASTM type 1 water, and subject to static leaching at 90 ± 3°C for up to 112 days, with duplicate sampling at regular intervals. The target SA/V ratio was ~10 m^{-1}, but varied slightly depending on the actual monolith dimensions.

At each sampling time point, vessels were removed from the oven and allowed to cool to room temperature. Aliquots of leaching solution were extracted from each vessel and filtered using 0.45 μm cellulose acetate filters. The pH was measured using a 3-point calibrated pH probe, then each aliquot was acidified with ultrapure nitric acid (VWR, ultrapure NORMATOM, 67–69% HNO$_3$), and analysed by inductively coupled plasma – optical emission spectrometry (ICP-OES, Thermo Fisher iCAP Duo 6300). The normalised mass loss was calculated using elemental data obtained via X-Ray fluorescence analysis (XRF), relative to the calculated SA/V, as calculated via equation 1:

$$NL_i = \frac{C_i \, (sample)}{(f_i) \cdot (\frac{SA}{V})} \qquad (1)$$

Where NL_i is the normalised elemental mass loss (g$_{wasteform}$/m^2); C_i(sample) is the concentration of element i in the solution (g$_i$/m^3); f_i is the mass fraction of the element i in the unleached waste form (g/g$_{glass}$); and SA/V is the surface area divided by the leachate volume (m^2/m^3).

3. Results

3.1 Glass Characterisation

The Chrompik III glass used in this study comprised

1 cm

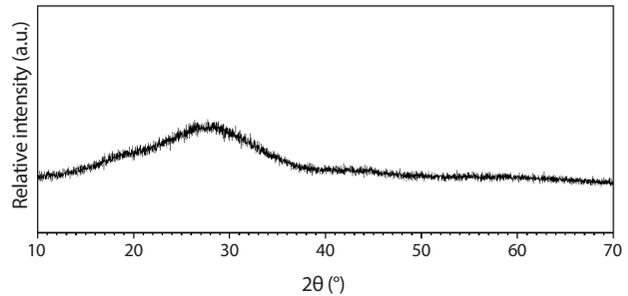Fig. 2. Photograph of Chrompik III simulant glass cast block.

Fig. 3. X-ray diffraction pattern of Chrompik III simulant glass monolith.

several cast bars, green in colour with the presence of some fine bubbles throughout (Fig. 2). X-ray diffraction (Fig. 3) and SEM/EDX of the glass (Fig. 4) did not reveal any significant crystalline component or phase separation, just a singular amorphous product with diffuse scattering evident in XRD data between 15° ≤ 2θ ≤ 40° and a uniform elemental distribution at the micro scale in SEM/EDX.

The elemental composition of the Chrompik III glass was determined by XRF spectroscopy to be a sodium-potassium aluminoborosilicate glass, with notable concentrations of Fe$_2$O$_3$ (3.08wt%), Li$_2$O (2.40wt%), PbO (1.35wt%) and TiO$_2$ (3.32wt%), amongst some other minor elements (Table 2). This composition is comparable to established borosilicate radioactive waste glass analogues SON68 and MW25, though with some key differences. The Chrompik III glass contains a lower proportion of B$_2$O$_3$ and more Al$_2$O$_3$ compared to SON68 and MW25 (French and UK nuclear waste glasses, respectively), along with an overall low level < 1wt% of divalent alkaline earth elements, and a higher proportion of monovalent alkaline
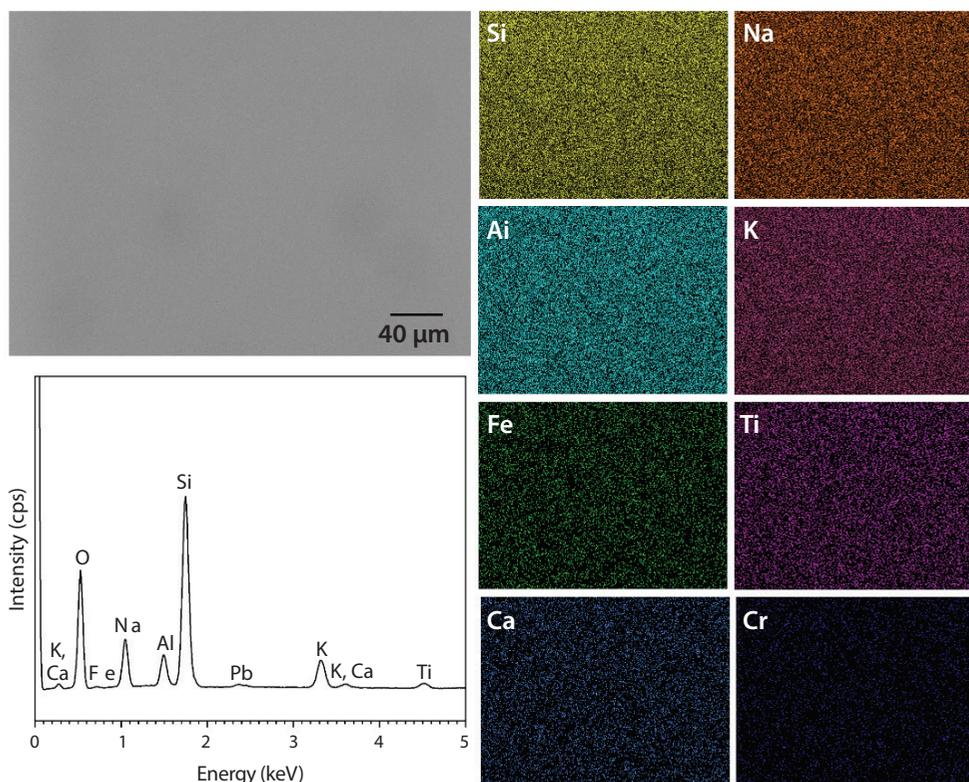
Fig. 4. Scanning electron micrograph, and elemental maps and EDX spectra of the bulk Chrompik III simulant glass monolith.

Table 2. XRF composition for Chrompik III simulant glass (error ± 5% of stated value)

Oxide	(wt%)	Oxide	(wt%)
Al_2O_3	7.20	Na_2O	11.16
B_2O_3	7.71	P_2O_5	< 0.10
BaO	0.26	PbO	1.35
CaO	0.30	SiO_2	52.06
Cr_2O_3	< 0.10	SrO	< 0.10
Fe_2O_3	3.08	TiO_2	3.32
K_2O	7.78	V_2O_5	< 0.10
Li_2O	2.40	ZnO	0.20
MgO	0.10	ZrO_2	< 0.10
Mn_3O_4	< 0.10		

elements (Li_2O + Na_2O + K_2O = 21.34wt%) [10, 11]. An additional difference in this glass is the presence of PbO, at 1.35wt%.

3.2 Durability Assessment

The aqueous durability of the simulant Chrompik glass was assessed by three separate leaching methods to build a comprehensive assessment of its overall durability. Two of these methods (MCC-1 and PCT-B) were conducted up to 112 days and according to ASTM standards, while the modified PCT (THERAMIN variant) test was only conducted up to 28 days. The latter was run in-parallel to other experiments performed on simulant nuclear waste glass formulations, enabling direct comparison to other vitreous products.

3.2.1 Powdered Material Durability (PCT-B)

PCT-B dissolution testing resulted in a rapid increase in the leaching medium pH, reaching pH 10.4 ± 0.0 within the first day, before rising to pH 11.4 ± 0.0 after 28 days, and remaining at pH > 11 for the duration of the test, as shown

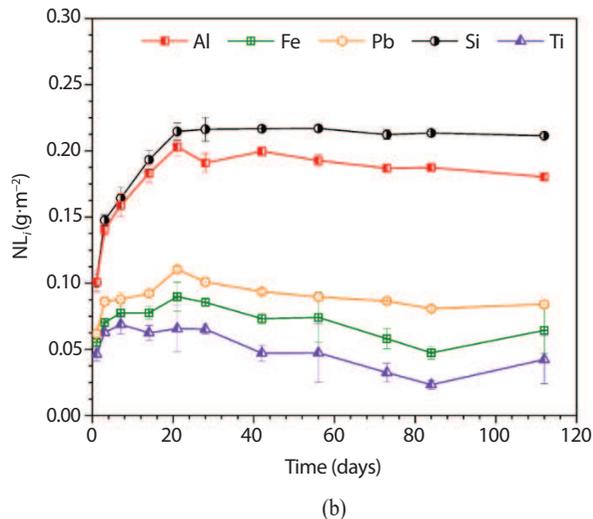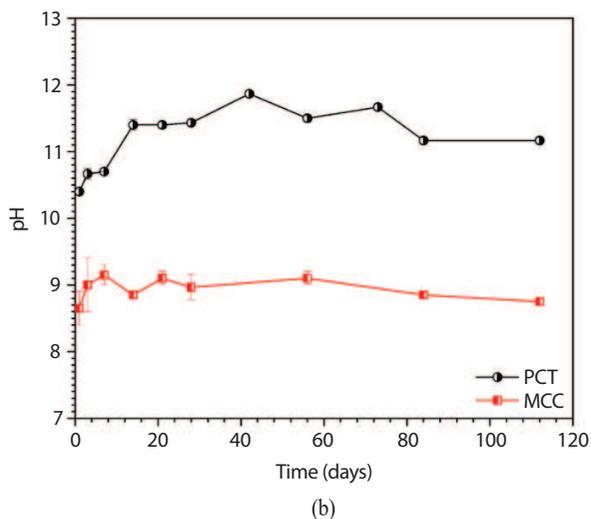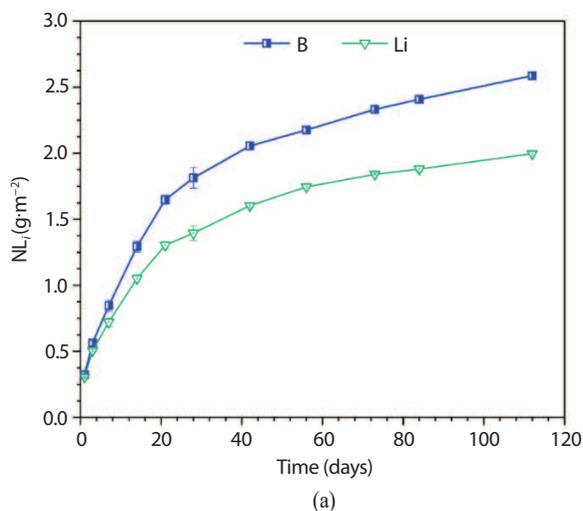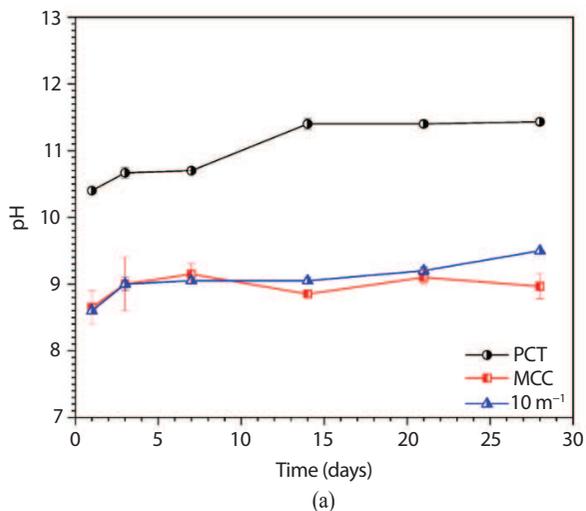Fig. 5. pH values from Chrompik III glass dissolution (PCT, MCC-1 and 10 m^{-1}) between durations of (a) 1–28 days and (b) 1–112 days. Errors represent the standard deviation of replicate measurements.

Fig. 6. Normalised elemental mass losses (NL$_i$) for (a) B and Li and, (b) Si, Al, Ti, Fe and Pb from PCT-B testing up to 112 days.

in Fig. 5. The relatively high surface area of the PCT-B testing (2,000 m^{-1}) contributed to this increased pH.

The normalised elemental mass loss (NL$_i$) can be split into two periods for the Chrompik III glass: 1) 1–21 days, and 2) 21–112 days, as shown in Fig. 6. The initial period of up to 21 days was characterised by a rapid release of elements into solution, with B and Li being the most readily released. B is a useful indicator of glass dissolution, as it is not considered to form precipitates or be retained within an alteration layer [10, 12], therefore, B can be used as a proxy for overall glass dissolution. The NL$_{Si}$ and NL$_{Al}$ at 21 days of 0.21 ± 0.01 and 0.20 ± 0.01 g·m^{-2} respectively, were lower than NL$_B$ of 1.65 ± 0.03 g·m^{-2}. This implies incongruent dissolution and the existence of an aluminosilicate alteration layer, which retains the Si and Al close at the glass / solution interface. Even lower elemental release was observed for NL$_{Fe}$, NL$_{Pb}$ and NL$_{Ti}$ (0.09 ± 0.01 g·m^{-2}, 0.110 ± 0.002 g·m^{-2}, and 0.07 ± 0.02 g·m^{-2} respectively), which is likely due to their relatively low aqueous solubility at this pH [13]. After 112 days, NL$_B$ and NL$_{Li}$ reached 2.59 ± 0.01 and 2.00

Table 3. Elemental release rate data for the PCT, MCC-1 and modified PCT (10 m^{-1}) dissolution

(g·m^{-2}·d^{-1})	PCT	MCC-1	Modified PCT (10 m^{-1})
	1–21 days	2–21 days	1–21 days
B	0.0648 ± 0.0050	0.2067 ± 0.0244	0.2629 ± 0.0222
Li	0.0493 ± 0.0050	0.4031 ± 0.0454	0.2589 ± 0.0256
Si	0.0047 ± 0.0011	0.0986 ± 0.0127	0.1498 ± 0.0079
	21–112 days	21–112 days	
B	0.0084 ± 0.0009	0.0744 ± 0.0105	
Li	0.0065 ± 0.0010	0.0759 ± 0.0065	
Si	−0.0001 ± 0.0000	0.0475 ± 0.0061	

± 0.02 g·m^{-2} respectively, while the normalised mass loss for Si and Al (along with Fe, Pb and Ti) remained the same (or slightly lower than) than that recorded at 21 days (NL$_{Si}$ 0.211 ± 0.001 and NL$_{Al}$ 0.180 ± 0.001 g·m^{-2}). These two different regions are clearly demonstrated by the variation in normalised elemental release rates (NR$_i$) for B and Si (Table 3), which changed between days 1–21 and days 21–112. The NR$_{Si}$ became effectively zero from (0.0047 ± 0.0011) to (−0.0001 ± 0.0000) g·m^{-2}·d^{-1}, with an associated reduction in B release from (0.0648 ± 0.0050) to (0.0084 ± 0.0009) g·m^{-2}·d^{-1}. This rate turnover is indicative of solution saturation and the formation of a semi-protective alteration layer, which mitigates the transfer of ions to and from the pristine glass surface – further evidenced by a reduction in NR$_{Li}$, which follows the same trend as B (Table 3).

Durability comparisons with other glass wasteforms are challenging due to the varied glass compositions and leaching conditions investigated in the literature. UK simulant MW-blend HLW glasses tested under similar conditions typically released NL$_B$ = 1−8 g·m^{-2} after 28 days and up to NL$_B$ = 10 g·m^{-2} after 110 days, with NL$_{Si}$ < 1 g·m^{-2} for the duration, though with large variation depending on glass formulation and waste loading [14]. Simulant full Magnox (non-blended) glasses released up to NL$_B$ = 20 g·m^{-2} after 28 days, with NL$_B$ = 45 g·m^{-2} after 110 days (though the high magnesium content is considered to enhance dissolution, and variations in Li$_2$O and waste content may result in reduced extent of dissolution) [14]. Recently, Barlow et al. compiled literature

from a range of sources where UK and French nuclear waste glass simulants were tested under similar conditions (90°C, ASTM Type 1 water), finding NL$_B$ release ranging from ~1 g·m^{-2} to ~10–20 g·m^{-2} after reaching pseudo-equilibrium [15]. All of the normalised mass loss data available in the literature place Chrompik III elemental release firmly within the lower end of the expected range of a nuclear waste glasses that are considered acceptable for geological disposal.

3.2.2 Monolith Material Durability (MCC-1)

Dissolution of monolith material using the MCC-1 methodology typically results in very different leaching rates compared to powdered PCT-B samples, due to the much lower surface area and more dilute leaching medium which keeps the solution under saturated with regards to silica for a longer period of time. As with the PCT-B testing, Li and B are most readily released into solution, indicative of continued glass dissolution up to 112 days. As shown in Fig. 5, the release of alkalis into solution resulted in the increase of solution pH to pH 9. In Fig. 7, Si and Al continued to be released uniformly during the dissolution test, albeit at a lower rate than B and Li, up to 84 days. Unlike the PCT-B testing, the B release rate do not reduce to a slow residual rate (Table 3), indicating the leaching solution remains sufficiently dilute enough to maintain dissolution though at a reduced rate (NR$_B$ 0.2067 ± 0.0244 g·m^{-2}·d^{-1} for 2–21 days, compared to NR$_B$ 0.0744 ± 0.0105 g·m^{-2}·d^{-1} for 21–112 days). Si elemental concentration (along with Al) does remain
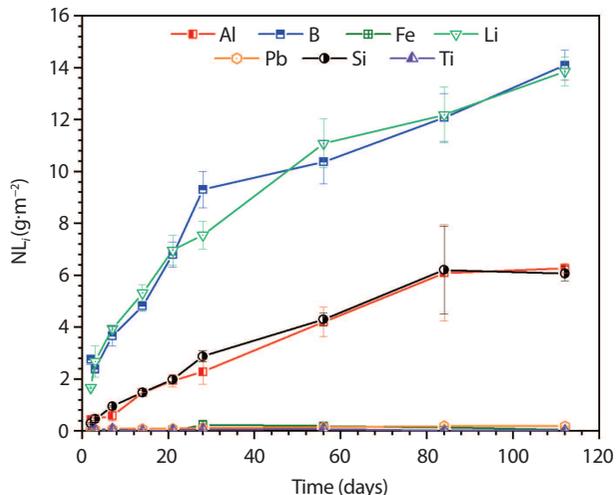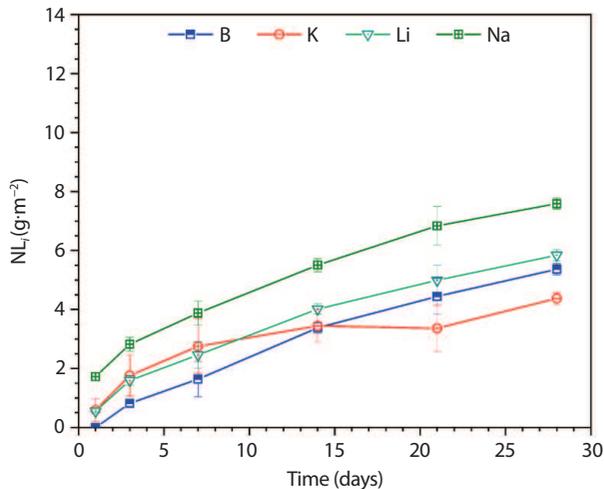
Fig. 7. Normalised elemental mass losses (NL_i) for Al, B, Li and Si from MCC-1 testing up to 112 days.

similar between 84 and 112 days, however PHREEQC modelling of the solution at 112 days suggests it remains under saturated in silica, therefore further sampling time points would be required to determine if release continues.

Release of the other less soluble elements was substantially lower, with Pb, Fe, and Ti all recording very low release into solution throughout the duration of the test, reaching a normalised mass loss at 112 days of NL_{Pb} 0.188 ± 0.001 g·m^{-2}, NL_{Fe} 0.06 ± 0.06 g·m^{-2}, and NL_{Ti} 0.02 ± 0.02 g·m^{-2}. This was expected due to their low solubility within this pH range [13]. Simulant UK HLW glasses undergoing MCC-1 testing under similar conditions have shown NL_B release of between ~17 to 100 g·m^{-2} after 42 days, but was very dependent on chemical composition, with one formulation substantially reducing the dissolution rate after 21 days, with the other continuing dissolution (albeit at a slightly slower rate) [14]. Chrompik III elemental release values appear at the lower end of this comparative range.

3.2.3 Modified PCT (THERAMIN Dissolution Test)

This modified-PCT dissolution test was part of a wider suite of characterisation applied under the THERAMIN project, assessing the durability of thermally treated wastes across Europe. This utilised a PCT-B methodology, but with
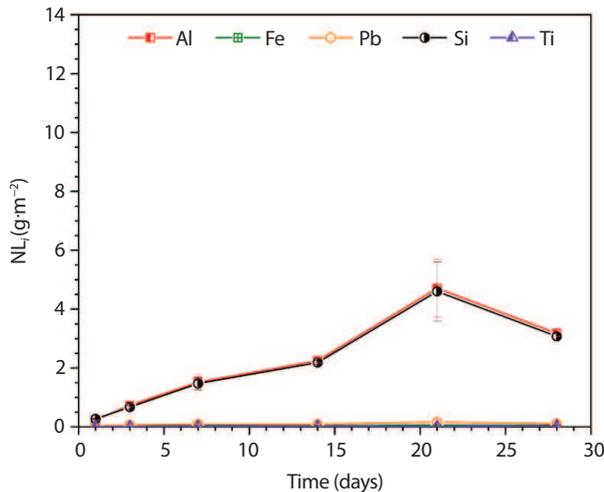
Fig. 8. Chrompik III normalised elemental mass losses (NL_i) for (a) B, K, Li and Na and, (b) Al, Fe, Pb, Si and Ti at 10 m^{-1} for 28 days.

a larger particle size, potentially more appropriate for heterogeneous materials, and a SA/V similar to the MCC-1 method.

These data were only acquired up to 28 days (Fig. 8), however, to aid comparison data from other vitrified wasteforms tested under identical conditions are included for comparison (Fig. 9). These other wasteforms include the International Simple Glass (ISG, a simplified borosilicate glass [16, 17]), In Container Vitrified material (ICV, vitrified soil, glass frit, and simulant intermediate level waste [18]), and plasma vitrified simulant Plutonium Contaminated
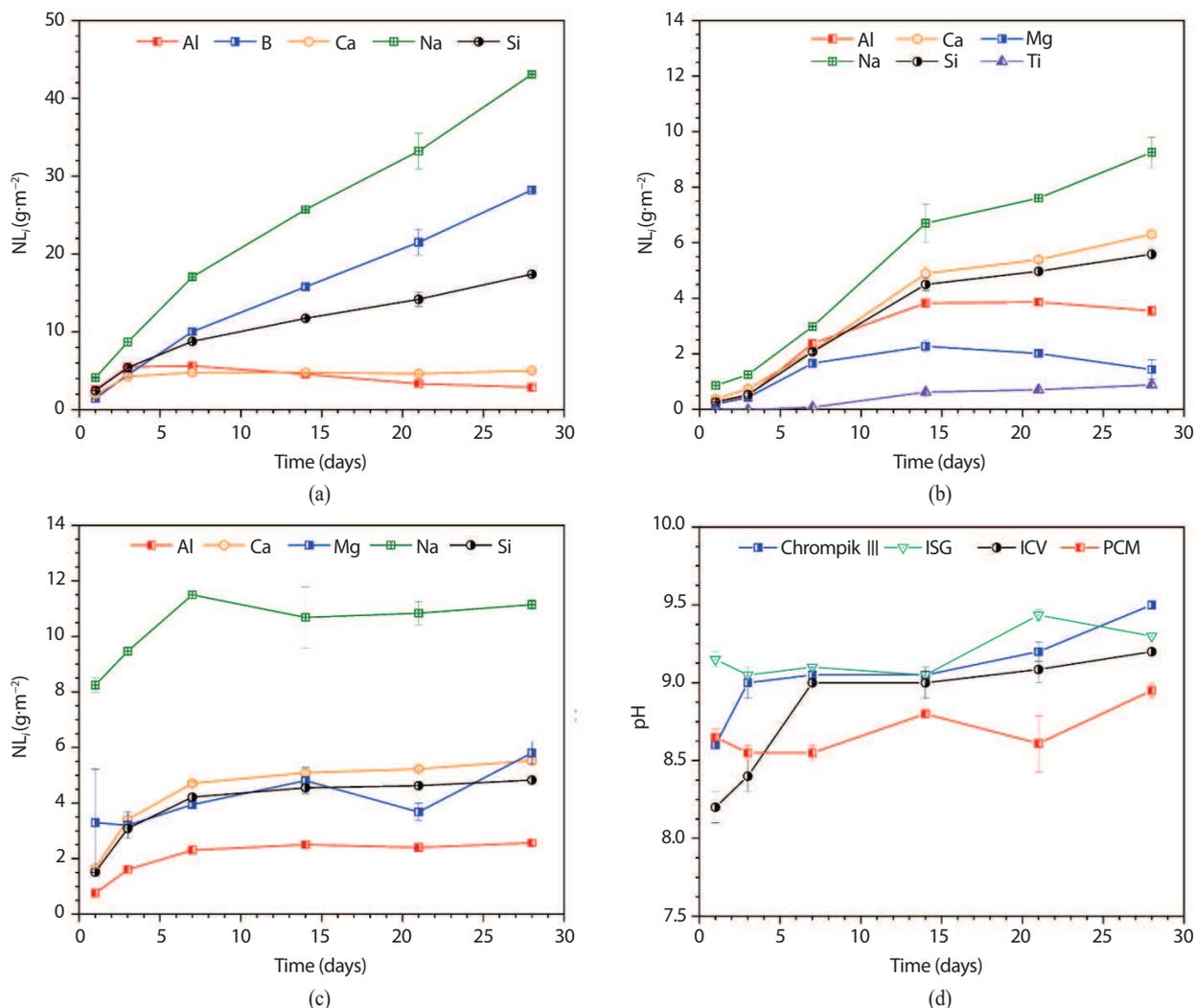
Fig. 9. Comparison of normalised elemental mass losses (NL_i) at 10 m^{-1} for simulant wasteforms (a) ISG, (b) ICV, (c) PCM with (d) pH, up to 28 days.

Material (PCM, a low alkali aluminosilicate glass [19]).

In Fig. 8, the elemental release from the Chrompik III glass using this testing method was similar to that from the MCC-1 method, albeit with lower overall normalised elemental mass loss. B release occurred at a rate of 0.2629 ± 0.0222 g·m^{-2}·d^{-1}, similar to that of K, Li and Na (Fig. 8), although K release deviated after 14 days. These elemental releases resulted in a pH of around pH 9.0 for the duration of the experiment (Fig. 5(a)). The elemental release of Al and Si largely followed a continuous increasing trend (NR_{Si} 0.1498 ± 0.0079 g·m^{-2}·d^{-1}), with the obvious excep-

tion of 28-day test data. Whether this is indicative of a rate turnover, would require further time points to ascertain. In agreement with the MCC-1 test (Fig. 7), the NL_{Fe}, NL_{Pb}, and NL_{Ti} were extremely low throughout the test duration, with 28 day values at 0.06 ± 0.01, 0.110 ± 0.002, and 0.038 ± 0.004 g·m^{-2}, respectively.

A direct comparison between the durability characteristics of the Chrompik III glass and other vitreous wasteform simulants is obtained by comparison between the elemental release values in Fig. 8 and Fig. 9. The elemental release was observed to vary greatly depending on the glass

formulation, as is to be expected. For example, the B, Na and Si normalised mass loss from Chrompik III were all substantially lower than those for ISG after 28 days at; NL_B 5.4 ± 0.2 $g \cdot m^{-2}$, NL_{Na} 7.6 ± 0.2 $g \cdot m^{-2}$, NL_{Si} 3.1 ± 0.1 $g \cdot m^{-2}$ (Chrompik III) compared to NL_B 28.2 ± 0.1 $g \cdot m^{-2}$, NL_{Na} 43.1 ± 0.3 $g \cdot m^{-2}$, and NL_{Si} 17.41 ± 0.01 $g \cdot m^{-2}$ for ISG. It should be noted ISG is not designed as a final wasteform, rather as a simplified borosilicate nuclear glass for study of dissolution mechanisms.

The release of elements from Chrompik III was similar to that observed for the ICV and PCM samples, particularly for Si release (both ICV and PCM have higher NL_{Na}, though a broadly similar pH (Fig. 9(d)) for much of the test period). The ISG, ICV and PCM samples exhibited a lower Al release than their corresponding Si release, unlike Chrompik III, where the elemental release for Si and Al were in tandem. This may be due to the lack of appreciable Ca or Mg within the Chrompik III (unlike ISG, ICV and PCM), which would otherwise encourage the formation of aluminium-rich siliceous alteration layers, reducing the release of Al into solution [14, 20].

The normalised elemental mass losses for this modified-PCT test were somewhat lower than those from the MCC-1 test, despite similar nominal surface area to volume ratio (10 m^{-1} SA/V, assuming a geometric surface area), although the same trends in elemental release are followed. The reason for these differences in the absolute values is likely due to differences in the geometric surface area estimation, and changes in the SA/V ratio during the dissolution test.

3.3 Post Dissolution Characterisation

At each sampling time point, powders (PCT-B) and monolithic samples (MCC-1) were removed from solution, providing the opportunity for post-dissolution characterisation of the altered glasses. X-ray diffraction was undertaken on both types of materials, as shown in Figs. 10−11. All altered Chrompik III presented only diffuse scattering between $15° \leq 2\theta \leq 40°$, characteristic of an amorphous
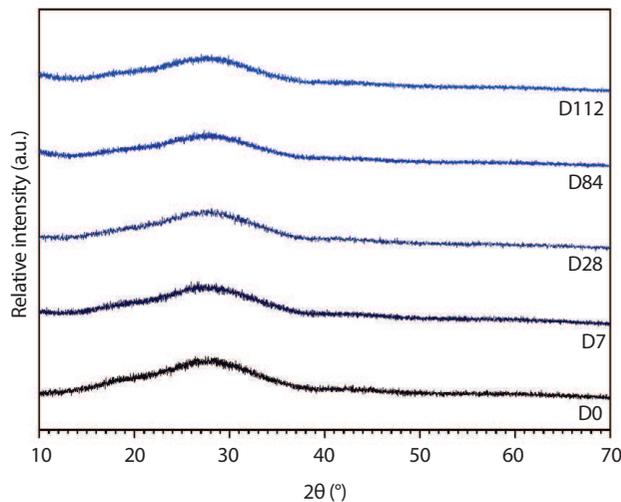

Fig. 10. X-ray diffraction patterns of Chrompik III simulant glass, post dissolution, up to 112 days PCT testing.
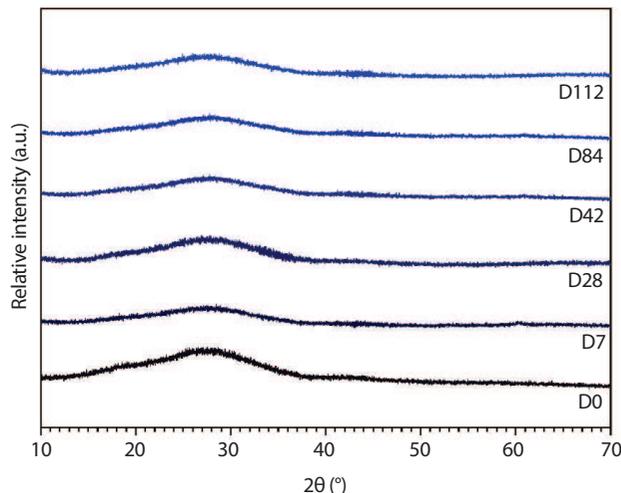

Fig. 11. X-ray diffraction patterns of Chrompik III simulant glass monolith up to 112 days MCC-1 testing.

material. In Figs. 10–11, there were no Bragg reflections indicative of the presence of significant crystalline alteration products.

A more detailed analysis of any alteration characteristi cs can be obtained via electron microscopy analysis of cross-sectioned monolithic samples. Electron micrographs, and accompanying elemental X-ray maps shown in Fig. 12 revealed that surface alteration was present from 7 days onwards. At 7 days (Fig. 12(a)), only minor
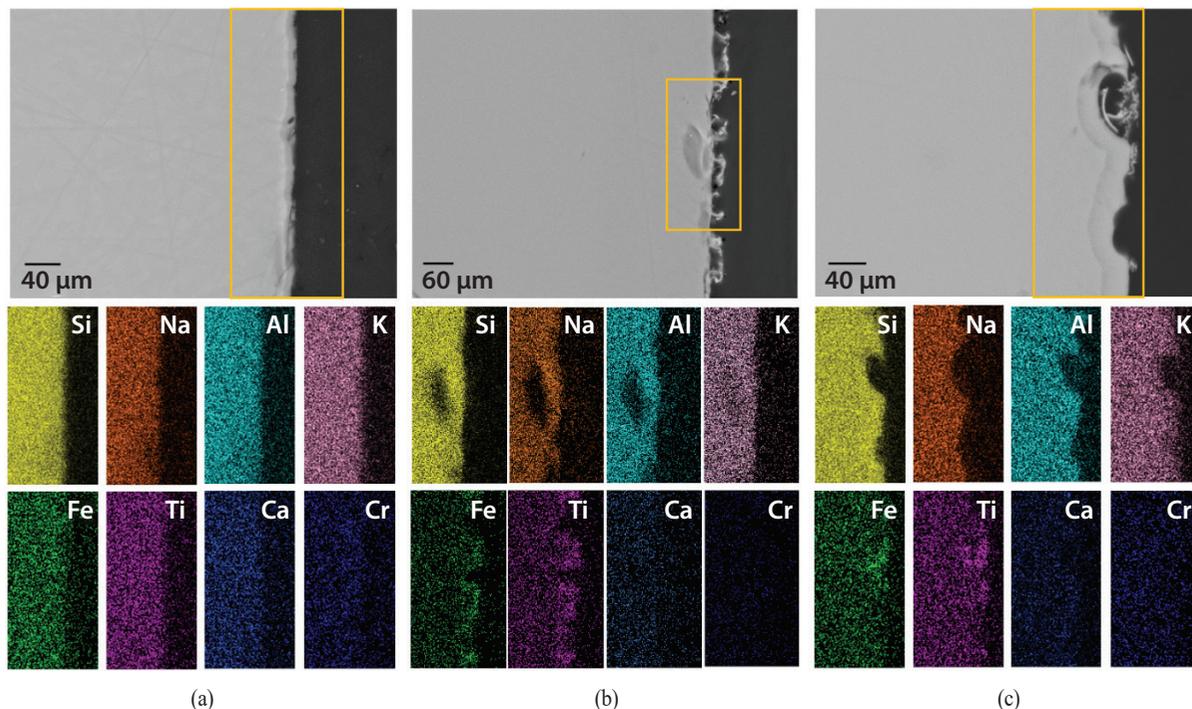
Fig. 12. Scanning electron micrographs and elemental maps of Chrompik III simulant glass after MCC-1 dissolution testing at (a) 7 days, (b) 84 days and, (c) 112 days.
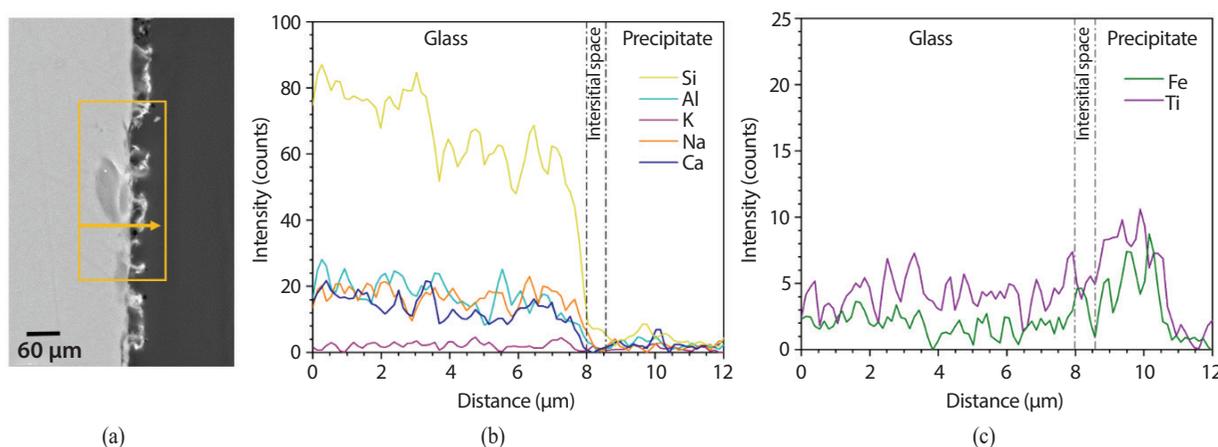

Fig. 13. (a) Scanning electron micrograph of Chrompik III simulant glass after MCC-1 dissolution testing at 84 days, with elemental line scan data in (b) and (c). The scan area is noted by the arrow in (a).

surface alteration was visible, with all elements uniformly distributed within the sample. A thin alteration band (up to 1 μm) may be observed between the pristine glass (light grey, left hand side) and the epoxy resin (dark grey, right hand side). After 84 days leaching (Fig. 12(b)), there was

evidence of surface precipitates on the outer surface of the altered glass, along with a disc-shaped feature. This feature may be the edge of a bubble formed within the glass, or a region which has undergone preferential dissolution, being deficient in Si, Al, Na and K (though still retaining Fe, Ti
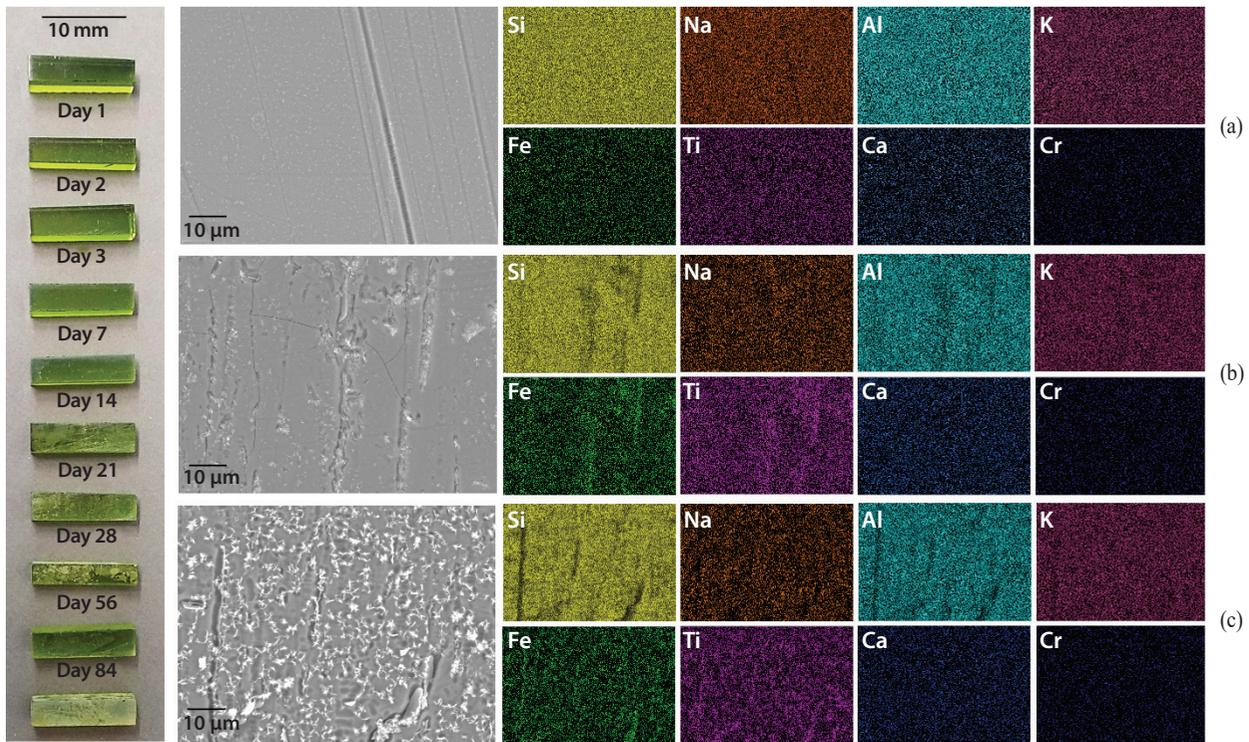
Fig. 14. Photographs of Chrompik III simulant glass monoliths after MCC-1 leach testing up to 112 days and
SEM-EDX at the monolith surface (unpolished) at (a) 1 day, (b) 28 days and, (c) 84 days.

and Ca), which can be observed by the relevant elemental maps in Fig. 12(b). The precipitates forming at the glass face are clearly enriched in Fe and Ti, without appearing to be associated with any other elements – clearly demonstrated by elemental line scan data in Fig. 13(b), (c). These may be iron and titanium oxides/oxy-hydroxides that have precipitated after glass dissolution, which has been noted in some basaltic glass and nuclear glass dissolutions [21, 22]. These elements have a very low aqueous solubility and were only found at low concentrations in the leachate despite continued glass dissolution evidenced by boron release (Fig. 7).

By 112 days leaching (Fig. 12(c)) a thick alteration layer, 30 µm thick, had formed at the glass surface, along with Fe/Ti precipitates. This alteration layer appears deficient in Na, but remained relatively rich in Si, Al, Fe and Ti. This correlates well with the dissolution data, where Si and Al release was slower (though still increasing) than B and Li, leaving an alteration layer rich in Si and Al (note, however,

B and Li are unable to be detected via conventional desktop SEM-EDX analysis). The continued presence of enriched Fe/Ti precipitates was also consistent with their very low level of detection within the bulk dissolution liquid.

In Fig. 14, photographs of the monoliths after removal from the dissolution medium reveal a progressively deteriorating glass surface (with day 84 an obvious exception), becoming opaque or tarnished as more glass is dissolved. This is indicative of the formation of an alteration layer. Unpolished SEM-EDX analysis of the surfaces at 1, 28, and 84 days shows clear evidence of precipitates forming at the glass surface. Grooves visible from 1 day are artefacts from grinding/polishing surfaces prior to leaching. The precipitates were observed to form by 7 days as minor clusters, and were widespread by 84 days, and appeared clearly enriched in Fe and Ti, in agreement with the SEM-EDX of the mounted and polished monolith samples in cross section (Fig. 12).

4. Conclusions

The characteristics and aqueous durability of a Chrompik III glass was assessed via three different leaching methodologies, two with powdered material, one using monolithic samples. Dissolution results in the release of more mobile elements (B, Na, K, Li) into solution, along with a slower release of Si and Al, with only minor release of less soluble elements (Fe, Ti, Pb). These dissolution mechanisms were broadly similar to those expected for an alkali borosilicate glass wasteform, and have been shown to compare favourably to several other vitreous simulant wasteforms and simulant nuclear glasses. The dissolution of this glass results in the formation of an interfacial alteration layer by 112 days of leaching, with the presence of fine Fe/Ti rich precipitates appearing from at least 28 days onwards, progressively coating the surface of the glass. No large crystallites, or presence of any other crystalline products (zeolites, etc.) were detected. Overall the conventional dissolution mechanisms observed in this study should bring confidence in the durability of this simulant glass wasteform, however with the understanding that longer term durability assessments are required to understand the full long-term performance of this material.

Acknowledgements

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