Chemical durability of vitrified wasteforms: effects of pH and solution composition

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ABSTRACT

Vitrification is used for the immobilization and conditioning of high-level waste (HLW) arising from the reprocessing of spent nuclear fuel in the UK. Vitrification is also under consideration for the immobilization of certain intermediate-level wastes (ILW), where there may be advantages of volume reduction and removal of uncertainties in long-term waste behaviour, compared to encapsulation in a cement grout. This paper gives an overview of recent work into the chemical durability of UK vitrified wasteforms to inform the technical specification for the disposal facilities for these waste products and the treatment of their long-term behaviour in post-closure performance assessment. This has included: (1) measurements of the initial glass dissolution rates of a simulated HLW Magnox waste glass in a range of groundwater types representative of potential UK host geologies and in simulated high pH near-field porewaters relevant to potential disposal concepts, using Product Consistency Test type-B (PCT-B) at 40ºC; and (2) durability testing of three simulant ILW glasses in a saturated calcium hydroxide buffered solution to simulate conditions in cement-based disposal vaults, using PCT-B tests at 50ºC.

The experimentally defined initial rate of HLW Magnox waste glass dissolution in a range of simulated groundwater compositions appears to be similar regardless of the ionic strength and major element composition of the solution. The release of caesium from HLW Magnox waste glass appears to be sensitive to solution composition. Caesium is selectively retained in the glass compared to other soluble components in the two low ionic strength solutions, but is released at similar rates to other soluble components in the three groundwaters and $Ca(OH)_2$ solution. Whether this change in caesium retention is an ionic strength effect or is related to changes in the nature of the surface alteration layer formed on the glass, has yet to be established. For HLW Magnox waste glass, dissolution is accelerated at high pH in NaOH solution, however, the presence of calcium acts to mitigate the effects of high pH, at least initially. In $Ca(OH)_2$ solution, calcium is found to react with all the glasses studied leading to the formation of calcium-containing alteration products. The initial dissolution behaviour in $Ca(OH)_2$ solution varies with glass composition and in particular appears to be sensitive to the boron content.

KEYWORDS: high-level waste glass, intermediate-level waste glass, chemical durability.

Introduction

VITRIFICATION is used for the immobilization and conditioning of high-level waste (HLW) arising

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from the reprocessing of spent nuclear fuel in the UK. By 1 April 2010 (Nuclear Decommissioning Authority and Department of Energy and Climate Change, 2011), 766 m^3 of vitrified high-level waste (HLW glass) had been produced. Vitrification is also under consideration for the immobilization of certain intermediate level wastes (ILW), where there may be advantages of

volume reduction and removal of uncertainties in long-term waste behaviour, compared to encapsulation in a cement grout (e.g. removal of organic waste materials that may degrade to complexants, non-aqueous phase liquids and/or gas).

An important criterion for the disposability of vitrified wastes in a geological disposal facility (GDF) concerns their long-term durability under near-field conditions. However, there has been a relative lack of information concerning the durability of UK vitrified waste products under disposal conditions. For example, one option for the disposal of some vitrified ILW would be co-disposal with cemented wastes in vaults backfilled with a cement-based backfill. However, the effects of alkaline cementitious porewaters on the aqueous durability of vitrified wasteforms are not well understood.

There is also a relative lack of glass durability data suitable for use in post-closure performance assessment of UK vitrified waste products. In the recent NDA generic assessment of an illustrative HLW disposal concept (Nuclear Decommissioning Authority, 2010), historic dissolution rate data for borosilicate glasses derived for a Belgian HLW disposal concept in a clay geology prior to 2001 were used (Marivoet *et al*., 1999). The UK HLW glasses have higher magnesium contents than most glasses developed internationally, which is known to have a significant effect on the alteration products formed and appears to increase the dissolution rate both initially and in the longer term (Curti *et al*., 2006), the so-called residual rate.

This paper gives an overview of recent work concerning the chemical durability of simulant UK vitrified products. This work is being undertaken to inform the disposal concept design for vitrified wastes, both HLW and ILW, and the treatment of their long-term behaviour in the safety case for a UK GDF. This paper describes the results of relatively short-term glass dissolution experiments undertaken using variants of the Product Consistency Test type B (PCT-B) to investigate the early stages of dissolution when an initially pristine glass comes into contact with water. The tests were designed to compare the initial rates of glass dissolution and the progression of dissolution into the so-called rate drop regime. The latter is when the rate of glass dissolution drops due to the formation of a gel layer on the glass surface, which may act as a diffusion barrier to solute exchange (Frugier *et al*., 2008). In the longer

term, glass dissolution is expected to progress to a residual rate regime, where glass dissolution continues at a slow but non-zero rate (Frugier *et al*., 2008). It should be noted that owing to the relatively high glass surface area to solution volume ratio (SA/V) used in these tests, the experimentally determined initial dissolution rate will be lower than the rate of congruent dissolution at time equals zero, which may be approached under very dilute conditions.

The work described here on HLW glass has focussed on the chemical durability of an inactive simulant Magnox waste glass in illustrative UK groundwaters that may be representative of different geological settings for a UK GDF (Nuclear Decommissioning Authority, 2010), and the potential effects of an alkaline plume from co-located cement-backfilled ILW vaults. These studies are being undertaken to understand whether solution pH and composition have an impact on the dissolution rate of this HLW glass. The work described here on inactive simulant ILW products has focussed on the interaction of illustrative vitrified wasteforms with a cementitious backfill and in particular has sought to understand the effect of high-pH, cementitious near-field conditions on the durability of vitrified products.

Experimental

Materials

One simulant HLW glass and three simulant ILW glass compositions were used in these experiments. The simulant HLW glass was a 25 wt.% waste-loaded Magnox waste glass fabricated at full scale on the Vitrification Test Rig at Sellafield (Scales, 2011). This glass is regarded as providing a baseline composition representative of a significant proportion of existing active Magnox waste glass.

The three simulant ILW glasses were as follows: two full-scale simulant vitrified ILWs, a clinoptilolite-sand glass, 'clino glass', and a plutonium-contaminated material (PCM)/ Magnox waste slag, 'PCM/Mx slag'; and a simulant laboratory-produced borosilicate glass, 'LBS ILW glass'. The clino glass was produced by plasma vitrification in a cold crucible by Tetronics Limited (Deegan, 2007). The PCM/Mx slag was produced via the Geomelt process by Impact Services Inc. Both full-scale glasses were trial products with compositions that had not been optimized with respect to their waste loading,

homogeneity or durability. The composition of the LBS ILW glass was based on compositions developed by Bingham *et al.* (2009) for immobilization of ILW. This glass was well-characterized and homogenous, compared to the trial full-scale products, and contained boron, which is commonly used as a tracer to follow glass dissolution.

The compositions of the four glasses in terms of the major oxide components are presented in Table 1. Further details are provided in Scales (2011), Schofield *et al.* (2012) and Utton *et al.* (2012).

Experiments

Glass durability has been studied using variants of the PCT−B method. All four glasses were crushed and sieved to a 75−150 μm size fraction according to the ASTM standard test method (ASTM, 2008). The powders were washed ultrasonically with ASTM Type 1 water and ethanol to remove fines and dried at 90ºC. The geometric surface area of the powders was calculated to be 0.02 $m^2 g^{-1}$, assuming spherical particles with a mean diameter of 112.5 μm. The surface area of the HLW glass powder was measured to be 0.057±0.002 m^2g^{-1} by the BET method based on krypton gas adsorption. The ratio of BET to geometric surface area of 2.82 falls within the range 2−3.5 that is characteristic of non-porous materials that have been crushed, sieved and washed (Gin and Jégou, 2001).

All PCT-B tests were undertaken at an initial geometric SA/V of 1200 m^{-1} (except for the clino glass which used a ratio of 1300 m^{-1}). All preparation and handling of solutions was under-taken in a nitrogen atmosphere glove box to exclude carbon dioxide.

Different test protocols were used for the tests on HLW and ILW glasses. For the HLW glass, individual experiments were terminated at each sampling time for greater ease of sampling and pH measurement at the experimental temperature. For the ILW products, periodic sampling was undertaken from larger volume tests; these tests were designed to allow buffering of the solutions to high pH with calcium hydroxide solid.

High level waste glass

The PCT-B tests on the HLW glass were undertaken in triplicate in 50 cm^3 screw-capped polypropylene centrifuge tubes containing 2.4 g of glass and 40 cm^3 of solution, with either one or two blank (glass-free) experiments in parallel. A leaching temperature of 40ºC was chosen as an upper limit for the temperature within a GDF at the time when vitrified products may come into contact with groundwater following canister failure. Canister failure is not expected to occur until after the heat-emitting period (i.e. after shorter-lived radionuclides present in the waste have decayed away). Leaching was undertaken in one of six solutions: (1) demineralized water (DM); (2) an illustrative lower strength sedimentary rock groundwater (LSSR), based on a Callovo-Oxfordian argillite groundwater composition from Bure in France (Gaucher *et al.*, 2006); (3) an illustrative higher strength rock groundwater (HSR), based on a saline groundwater composition RCF3 DET5 from Borrowdale Volcanic Group rocks near Sellafield (Bond and Tweed, 1995); (4) an illustrative groundwater associated with evaporite deposits (brine), based on a brine

TABLE 1. Glass compositions (wt.%).

Oxide	Magnox HLW	LBS ILW	Clino ILW	PCM/Mx ILW
SiO_2	47.1	48.9	66.0	58.8
Na_2O	8.5	13.6	14.9	6.2
B_2O_3	16.7	9.0	0.1	0.1
MgO	4.5	4.8	5.6	12.8
Al_2O_3	4.3	3.7	9.3	13.1
Fe_2O_3	3.0	11.1	0.8	0.7
Li_2O	4.0	4.1	−	−
CaO	−	0.4	1.6	5.7
Cs_2O	1.0	0.3	−	−
Others	10.9	4.1	1.7	2.6

composition from Gorleben in Germany (Artinger *et al.*, 2000); (5) a saturated calcium hydroxide solution (Ca(OH)$_2$); and (6) a 0.03 mol dm^{-3} sodium hydroxide solution (NaOH). The last two solutions have the same pH value, 12.0, at 40ºC.

The target compositions of the three illustrative groundwaters are presented in Table 2. Recipes were designed to achieve these target compositions; a number of minor components were excluded in each case. In practice, concentrations of strontium in the LSSR solution and carbonate in all three groundwaters were lower than target due to solubility limitations. Although, based on thermodynamic modelling, the solutions prepared were close to saturation with respect to a number of mineral phases, there was no evidence from analysis of blank solutions for precipitation of groundwater components over the duration of the tests. The calcium hydroxide solution was prepared by equilibrating a saturated solution with solid overnight at 40ºC.

After addition of the leachant to the tubes containing glass, each tube was gently rotated at an angle to ensure wetting of the glass particles. One set of tubes including blanks was terminated after 3, 7, 14, 21, 28, 35, 42 and 89 days leaching in an oven at 40ºC. After reweighing, the tubes were placed in a purpose-built heater block at 40ºC. A 15 cm^3 aliquot was removed, filtered (pre-conditioned 0.45 μm Millex HV) and acidified with 1 cm^3 of 50% nitric acid for inductively coupled plasma-optical emission spectroscopy or inductively coupled plasma-mass spectrometry (ICP−OES or ICP−MS). The pH measurements were made on the residual solution at 40ºC.

Intermediate level waste glasses

The PCT-B tests on the ILW glasses were undertaken in duplicate in 500 cm^3 high-density polythene containers with 24 g of glass and 400 cm^3 of 'buffered' saturated Ca(OH)$_2$ solution (prepared as above at the required temperature), with an additional blank experiment (glass-free) run in parallel. To buffer the solutions, excess Ca(OH)$_2$ solid was placed in a 10,000 nominal molecular weight cut-off ultrafiltration unit, which was placed in contact with the solution. Tests on all three ILW glasses were undertaken at 50ºC with periodic sampling of the test solution after 1, 3, 7, 14, 21, 28, 35 and 42 days leaching: 5 cm^3 of solution was removed and filtered through a 0.2 μm polyethersulphone filter and 4 cm^3 of the solution was acidified with nitric acid and sent for elemental analysis by ICP-OES/ −MS. The pH of the remaining solution was measured at ambient temperature.

TABLE 2. Compositions of illustrative groundwaters selected for use in durability tests of HLW Magnox waste glass.

Element	LSSR water (mol kg^{-1})	HSR water (mol dm^{-3})	Brine (mol dm^{-3})
Na	3.20×10^{-2}	3.70×10^{-1}	4.87×10^{0}
K	7.10×10^{-3}	4.40×10^{-3}	2.03×10^{-2}
Mg	1.40×10^{-2}	5.70×10^{-3}	8.23×10^{-2}
Ca	1.50×10^{-2}	2.90×10^{-2}	2.65×10^{-2}
Sr†	$\underline{1.10 \times 10^{-3}}$	2.00×10^{-3}	–
Ba*	–	*1.30×10^{-6}*	–
Al*	6.90×10^{-9}	1.70×10^{-6}	–
C† as CO$_3^{2-}$	$\underline{3.00 \times 10^{-3}}$	$\underline{1.00 \times 10^{-3}}$	$\underline{2.09 \times 10^{-3}}$
Si	9.40×10^{-5}	2.50×10^{-4}	–
SO$_4^{2-}$	3.40×10^{-2}	1.20×10^{-2}	5.30×10^{-2}
F	–	1.20×10^{-4}	–
Cl	3.00×10^{-2}	4.20×10^{-1}	4.77×10^{0}
Br	–	3.20×10^{-4}	–
I*	–	*1.00×10^{-6}*	–
pH	7.0	7.2	7.0

* Component concentrations in italics were not included in the simulant groundwater.
† Component concentrations underlined were not achieved in the simulant groundwater solutions used in the experiments.

Scanning electron microscopy/energy disperive X-ray spectrometry

To observe the glass surfaces after leaching, scanning electron microscopy (SEM) was undertaken on carbon-coated samples of leached glasses using a JEOL 6400 SEM equipped with an Oxford Instruments INCAx-sight energy dispersive X-ray (EDX) spectrometer.

Treatment of results

The concentration of elements in solution for each static test is used to calculate the normalized release of elements from the glass. The normalized mass loss of element i from the glass, is calculated as: $NL_i = C_i/(f_i.(SA/V))$, where f_i is the mass fraction of element i in the glass and C_i is the blank-corrected solution concentration, which is also corrected for any change in solution volume. Results presented in this paper are based on the geometric surface area of the crushed glass, recognizing that this may lead to an overestimation of glass dissolution rate by a factor of about 2.82 (based on the crushed HLW glass BET surface area).

The rate of glass dissolution is obtained from the gradient of the normalized release *versus* time curve and has been calculated using a linear least-squares fit to selected portions of the curve. Errors in the fitted gradient were evaluated using the method of Press *et al.* (1986). Dissolution rates during the early stages of glass dissolution were calculated by fitting to the initial linear portion of the normalized release *versus* time curves for each soluble element (B, Li, Na, Cs, Mo). In cases where the normalized release appeared to reach a plateau, a residual rate at the end of the tests was calculated by fitting in the plateau region.

Results

High level waste glass
Effects of solution composition

Glass dissolution experiments in DM water and the three illustrative groundwaters that varied in their ionic strength and major-element composition were undertaken to investigate whether there were any significant differences in HLW glass dissolution behaviour with solution composition. Although the four solutions had initial pH values close to neutral, each solution was found to equilibrate rapidly (3 days) to maintain a different pH in contact with the glass: DM water pH 9.8; LSSR and HSR solution pH 8.7; and brine pH 7.6 (little change). In terms of reaction of groundwater ions with the glass, only a small decrease in magnesium concentration in the LSSR solution could be clearly distinguished. In the case of the LSSR and HSR solutions, which contain added silicate, further silicon was leached from the glass during the tests.

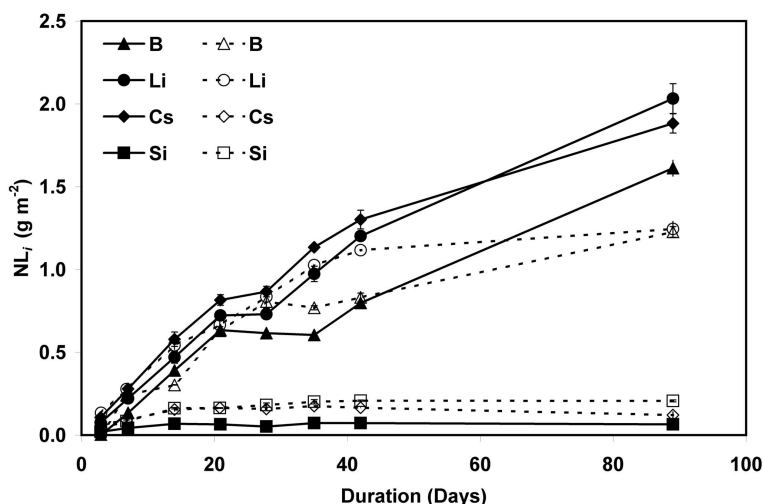Figure 1 compares the dissolution behaviour of the HLW glass in DM water and LSSR solution.

FIG. 1. Normalized releases for selected elements from HLW glass at 40ºC in LSSR solution (closed symbols) and DM water (open symbols).

(Here, the mean values of NLi for each element are plotted at each duration; the error bar represents one standard deviation of the triplicate results. The lines between points are added to aid the eye.) In both cases, soluble elements are released at similar rates initially, but whereas the dissolution rate of the glass in DM water appears to be decreasing towards a residual rate at 89 days of tests, dissolution in LSSR solution appears to be continuing at a rate close to the initial rate. In both solutions, silicon appears to reach saturation after about 14 days leaching, but at a significantly higher concentration in DM water (~43 mg dm^{-3}) compared to the LSSR solution (~20 mg dm^{-3}); this is likely to be due to the higher solubility of silicon at the higher pH of the DM water system. In contrast to other soluble elements, the release of caesium appeared to be sensitive to the solution composition. Whereas in LSSR solution caesium was released in a similar manner to the other soluble elements (B, Li, Na), in DM water, caesium release was limited and similar to silicon. This suggests that caesium may sorb to glass alteration products, but that the extent of sorption is sensitive to solution composition.

The rates of glass dissolution in the HSR solution and brine are similar to those in the LSSR solution (Table 3). In particular, the releases of caesium in these higher ionic strength solutions were similar to that in the LSSR solution.

Effects of high pH

In contact with the HLW glass, calcium was removed from the Ca(OH)$_2$ solution due to reaction with the glass (Fig. 2). A small decrease in pH was also observed from pH 12.0 to pH 11.7 over the duration of the tests (Fig. 3). In the case of NaOH solution, however, a much more significant drop in pH from 12.0 to 10.75 was observed (Fig. 3) indicating the consumption of hydroxide ions; sodium was leached from the glass (Fig. 2).

Figure 4 compares the normalized releases for B, Li, Cs and Si from the HLW glass in contact with the high pH solutions. The rate of Li release (and also B, Mo) is observed to be faster initially in the 0.03 M NaOH solution by a factor of 4−5 compared to the Ca(OH)$_2$ solution and the soluble elements continue to be released at the initial rate at the end of the tests. Silicon appears to reach saturation after 21 days. In contrast, in Ca(OH)$_2$ solution, the rate of alkali metal release (i.e. Li, Na and Cs) is fastest initially and appears to be decreasing with time, suggesting that glass dissolution may be approaching a residual regime at the end of the tests. There was no detectable release of silicon over the test duration. The release of boron appeared to be reduced compared to the alkali metals and no boron release was detectable until 14 days leaching. Thereafter the release of boron increased but the rate of release appeared to decrease after 21 days.

TABLE 3. Initial dissolution rates, based on soluble element releases, for HLW Magnox waste glass in groundwaters and high pH solutions at 40ºC compared with the LBS ILW glass maximum dissolution rate extrapolated to 40ºC (g m^{-2} d^{-1}).

Solution	B	Li	Na	Cs	Mo
HLW Magnox waste glass					
DM	0.024±0.004	0.030±0.003	0.025±0.003	0.007±0.001	0.030±0.002
LSSR	0.026±0.003	0.030±0.002	–	0.030±0.002	0.028±0.003
HSR	0.030±0.004	0.026±0.002	–	0.025±0.002	0.023±0.002
Brine	0.027±0.002	0.024±0.002	–	0.022±0.002	0.018±0.002
0.03M NaOH	0.156±0.010	0.126±0.010	–	0.05±0.01	0.095±0.008
Sat. Ca(OH)$_2$	0.029±0.003	0.038±0.003	0.038±0.004	0.036±0.003	0.029±0.002
LBS ILW glass*					
Sat. Ca(OH)$_2^{†}$	0.024 (0.011−0.052)	0.035 (0.015−0.083)	0.015 (0.006−0.034)	–	–

* Maximum rate, extrapolated to 40ºC
[†] Best estimate value; the range of extrapolated values accounting for uncertainties in the extrapolation is given in brackets.
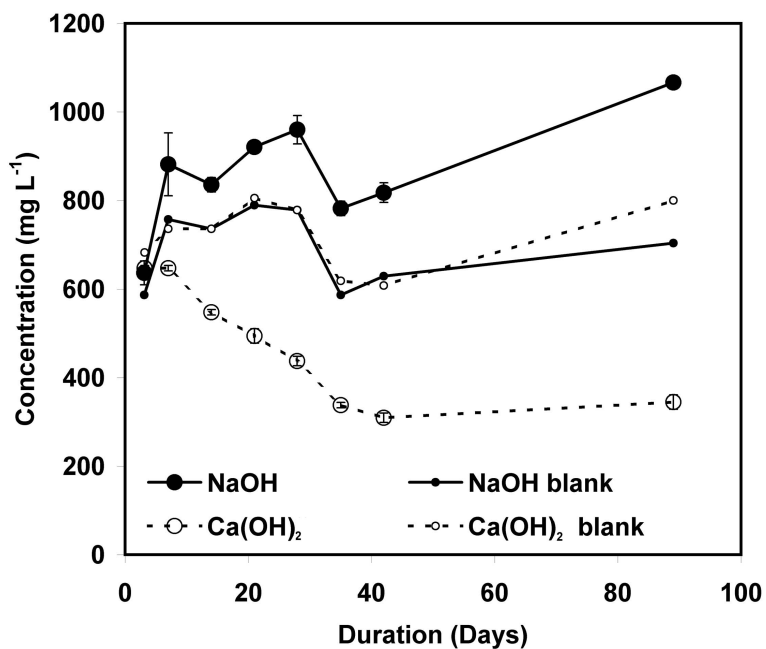
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FIG. 2. Variation of calcium concentration in Ca(OH)$_2$ solution (open symbols) and sodium concentration in NaOH solution (closed symbols) with duration of HLW glass leaching at 40ºC compared to respective glass-free blank solutions.
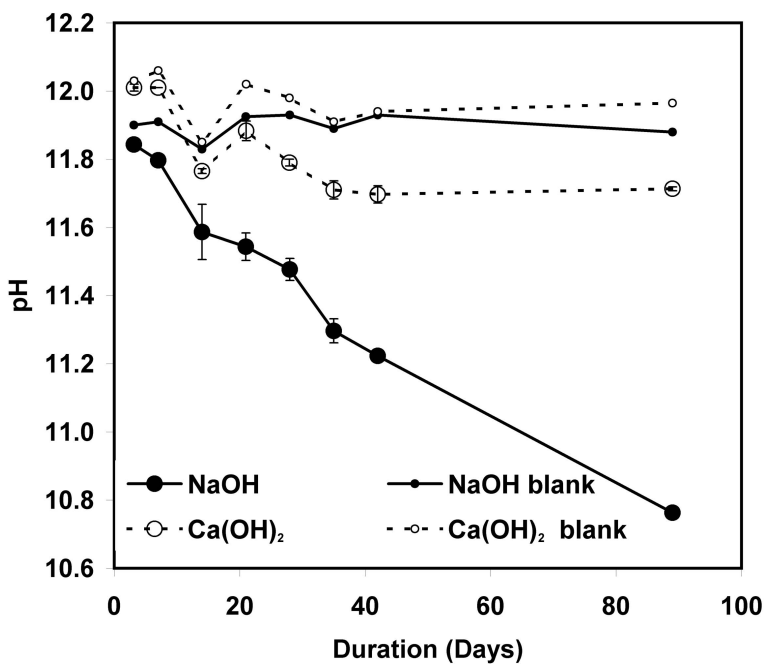

FIG. 3. Variation of solution pH with leaching time for HLW glass at 40ºC in NaOH and Ca(OH)$_2$ solutions.
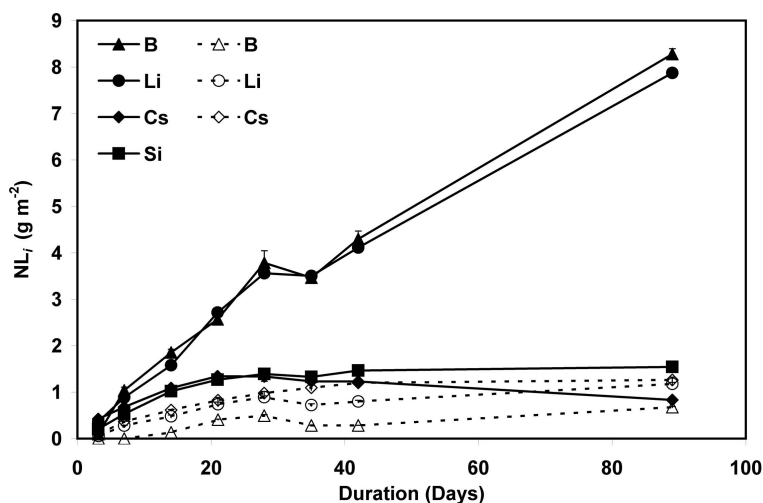
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FIG. 4. Normalized releases for selected elements from HLW glass at 40ºC in NaOH (closed symbols) and Ca(OH)$_2$ solutions (open symbols). Note that no release of silicon was observed in Ca(OH)$_2$ solution over experimental timescales.

Caesium release behaviour is also different between the two solutions; in Ca(OH)$_2$ solution, caesium release is comparable with other soluble elements but in the NaOH solution it is limited and reaches a plateau after 21 days, in common with silicon.

The calculated initial dissolution rates for the HLW glass in groundwater and high pH solutions are presented in Table 3, based on the release of a number of soluble elements between 3 and 28 days.

Intermediate level waste glasses

PCT-B Tests

The change in mean calcium concentrations with time in solutions in contact with the three ILW glasses at 50ºC is shown in Fig. 5. In common with the HLW glass, calcium was removed from the Ca(OH)$_2$ solution indicating reaction with the glass. This was despite the buffering of the solution with solid Ca(OH)$_2$. Similarly there was no significant variation in the measured pH of the solutions over the test period. The pH values were in all cases 0.1 to 0.2 pH units lower than the glass-free blanks. The mean pH values were: clino glass pH 12.3, PCM/Mx slag pH 12.4 and LSB ILW glass pH 12.36.

The full-scale simulant glasses contained virtually no boron and so their dissolution behaviour at 50ºC is compared with the LBS

ILW glass in terms of normalized sodium release in Fig. 6. Contrasting dissolution behaviour is observed for the three glasses. The two full-scale simulant glasses show an initial fast rate of sodium release, which after 3 days rapidly declines to a slower residual rate after 14 days. In contrast, during the initial stages of the tests, dissolution of the LBS ILW glass appears to be inhibited and an induction period of slow dissolution is observed before the rate of glass dissolution increases. This delay is comparable to that observed for NL$_B$ for the simulant Magnox HLW glass in Ca(OH)$_2$, (but not observed for NL$_{Na}$). This suggests that the composition of the glass, in particular the boron content, is important for the initial dissolution behaviour in the presence of calcium at high pH.

Initial dissolution rates for the full-scale simulant glasses were calculated between 1−3 days and residual rates between 7 and 42 days. Owing to the slow initial dissolution of the LBS ILW glass, the most appropriate dissolution rate to use for comparison purposes is the rate after the induction period, calculated between 7 and 42 days. Calculated dissolution rates for the 3 ILW glasses based on sodium release are presented in Table 4. Despite their initially faster dissolution rate, the clino glass and PCM/Mx slag appear to be chemically more durable than the LBS ILW glass over the duration of the tests.
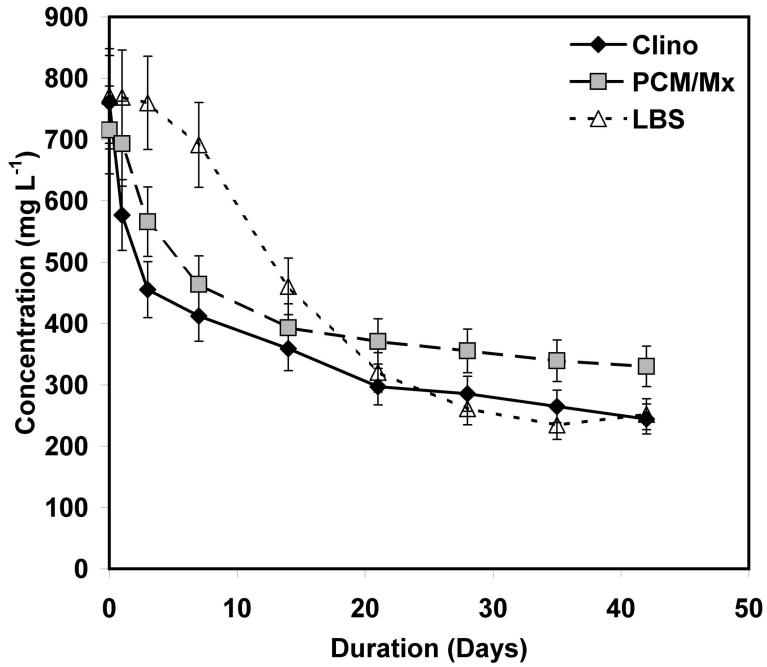
FIG. 5. Calcium removal from Ca(OH)$_2$ solution with leaching time for the three ILW glasses at 50ºC.
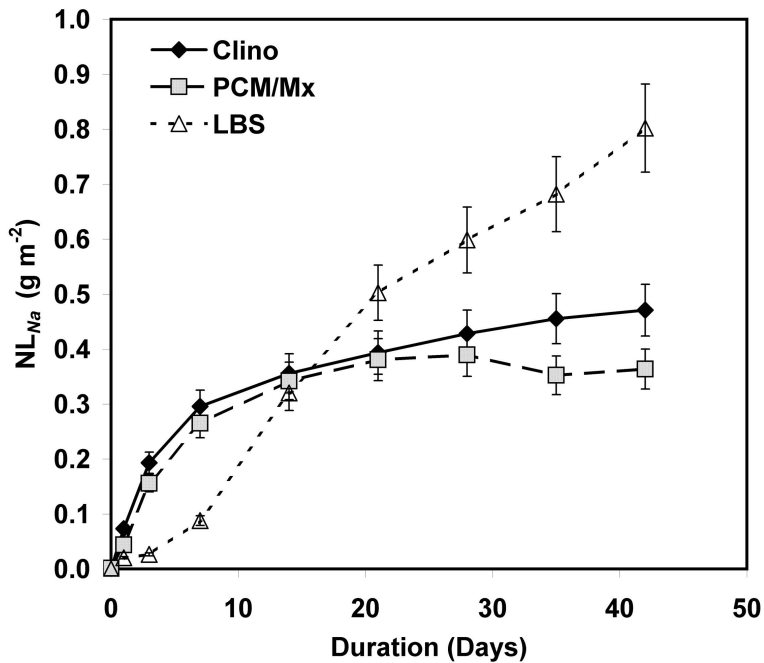

FIG. 6. Normalized releases for sodium from the three ILW glasses on leaching at 50ºC in Ca(OH)$_2$ solution.

TABLE 4. Measured dissolution rates based on sodium release for simulant ILW glasses in saturated calcium hydroxide solution at 50ºC (g m^{-2} d^{-1}).

Glass	Initial rate 1−3 days	Residual rate 7−42 days	Maximum rate 7−42 days
LBS	–	–	0.023±0.001
Clino	0.041±0.005	0.0052±0.0013	–
PCM/Mx	0.041±0.004	0.0027±0.0011	–

Examination of alteration products

At the end of the tests, it was noted that in Ca(OH)$_2$ solution all the glass powders had cemented together and a white crust had formed on the surface. The SEM/EDX examination of selected HLW and ILW glass particles revealed the effects of leaching on the glass surfaces and the presence of precipitates. This is illustrated in Fig. 7 for the LBS ILW glass where the appearance of a pristine glass particle is compared with a particle leached for 42 days at 50ºC. The EDX analysis showed that irregular white precipitates contain significant calcium; however, no crystalline phases could be identified by X-ray diffraction.

FIG. 7. Surface alteration of LBS ILW glass with leaching in Ca(OH)$_2$ solution: (*a*) unleached glass; (*b*) after leaching at 50ºC for 42 days.

Discussion

The initial glass-dissolution behaviour of a simulant HLW Magnox waste glass has been studied in a range of illustrative groundwaters and high-pH near-field porewaters at 40ºC to understand the effects of pH and groundwater composition on glass-dissolution rate. The initial dissolution behaviour is similar in three groundwaters (that differ significantly in ionic strength) and in DM water (Table 3). The dissolution rate is accelerated by about a factor of 4−5 in 0.03 mol dm^{-3} NaOH solution (pH 12 initially), with no significant decrease in alteration rate over the experiment duration. A drop in pH from 12 to 10.8 over 89 days is observed, indicating the consumption of hydroxide ions. It is considered likely that the alteration rate may decrease once the excess hydroxide has been consumed. In contrast, the presence of calcium was found to be important in mitigating the effects of high pH, at least initially. In contact with initially saturated Ca(OH)$_2$ solution, for all four glasses, calcium reacted with the glass and was removed from solution but with little significant change in solution pH. The presence of calcium-containing alteration products is observed on the surfaces of the HLW and ILW glasses. These may be responsible for maintaining a higher pH in the HLW glass leachate compared to the NaOH solution.

Further tests on the LBS ILW glass were performed at temperatures up to 90ºC (Utton *et al.* 2012). Based on the activation energy for LBS ILW glass dissolution in Ca(OH)$_2$ solution, the maximum dissolution rates for the ILW glass based on boron, lithium and sodium have been extrapolated, using the Arrhenius expression, to
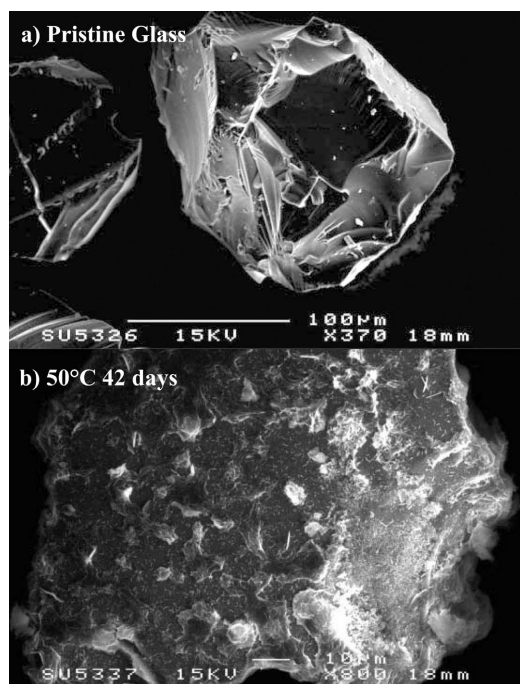
40ºC. These extrapolated rates are also included in Table 3 for comparison with the HLW glass. Maximum rates for the ILW glass in Ca(OH)$_2$ solution are similar to the measured initial dissolution rates for the HLW glass in groundwaters and Ca(OH)$_2$ solution. The LBS ILW and simulant HLW Magnox waste glass have similar compositions with respect to a number of the major cations (Si, Al and Mg). This may account for the comparable rates obtained (same order of magnitude), suggesting similar mechanisms of dissolution/reaction in Ca(OH)$_2$ solution.

Abraitis *et al.* (2000) studied the initial dissolution behaviour of a simulant Magnox waste glass similar to the HLW glass composition used in this study. Abraitis *et al.* (2000) used single pass flow through tests at 40ºC in a pH 9.8 KOH/KCl solution. The rates of boron release varied from 0.17 to 0.035 g m^2 d^{-1} with decreasing flow rate as the concentration of boron in solution increased from 0 to 30 mg dm^{-3}. The rates, at the lower flow rates, are considered most comparable with the results of the current study, and are consistent with the initial dissolution rates measured here.

The selective retention of caesium in the surface layer of Magnox waste glass on leaching in pure water at elevated temperatures (70−110ºC) has been reported previously by Zwicky *et al.* (1989). Limited release of caesium compared to other soluble species has been observed here at 40ºC in the two solutions of lowest ionic strength (DM water and NaOH solution) consistent with selective caesium retention. However, in the other four solutions, which are of significantly higher ionic strength, caesium release is similar to that of other soluble elements. This suggests either that the nature of the surface layer is different in the presence of these solutions such that caesium retention is no longer favourable, or that caesium retention is sensitive to ion exchange and hence to solution ionic strength. Further work is required to understand the processes underlying caesium retention and release.

Conclusions

The principal findings of this work can be summarized as follows.

(1) The initial rate of HLW Magnox waste glass dissolution in a range of simulant groundwater compositions appears to be similar regardless of the ionic strength and major element composition of the solution.

(2) The release of caesium from HLW Magnox waste glass appears to be sensitive to solution composition. Caesium is selectively retained in the glass compared to other soluble components in the two low ionic strength solutions, but is released at similar rates to other soluble components in the three groundwaters and calcium hydroxide solution. Whether this change in caesium retention is an ionic strength effect or is related to changes in the nature of the surface alteration layer formed on the glass, has yet to be established.

(3) For HLW Magnox waste glass, dissolution is accelerated at high pH in NaOH solution, however, the presence of calcium acts to mitigate the effects of high pH, at least initially.

(4) In Ca(OH)$_2$ solution, calcium is found to react with all the glasses studied leading to the formation of calcium-containing alteration products.

(5) The initial dissolution behaviour of the four glasses studied in Ca(OH)$_2$ solution varies with glass composition and in particular appears to be sensitive to the boron content.

Further work is planned to study the longer term dissolution behaviour of the HLW Magnox waste glass in the illustrative groundwaters and high pH solutions and examine the alteration products formed. Further studies of the ILW glasses are planned to compare the effects of saturated Ca(OH)$_2$ solutions with high pH NaOH solutions and solutions of lower pH. Further work will be reported on the formation of alteration products and effect of composition (in particular boron) on the initial dissolution rate of the three ILW glasses in Ca(OH)$_2$ solution.

Acknowledgements

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