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Preliminary surface study of short term dissolution of UK high level waste glass

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Abstract

A simulated Magnox glass which is Mg- and Al- rich was subjected to aqueous corrosion in static mode with deionised water at 90 °C for 7 days and assessed using Cameca and Ion-ToF Secondary Ion Mass Spectrometry (SIMS). Depth profiling and ion imaging were done for both unleached and leached samples to reveal elemental distributions from the glass surface into the bulk. All the elements were distributed evenly for unleached glass. After leaching, depletion of alkali ions i.e. Na and Li was observed indicating the interdiffusion (ion exchange) process of the initial stage of leaching. Enrichment of Mg near the surface layer indicated precipitation of Mg-rich crystals at the near surface region.

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1. Introduction

Dissolution studies of nuclear high level waste (HLW) glass are of great interest due to the potential long term affects of HLW on the environment. In the future, HLW will be disposed of below ground at approximately 1000m depth. A potential strategy for immobilisation of HLW is vitrification. However, interactions may occur between the waste and underground water which will potentially compromise the glass durability (Jain and Pan, 2000).

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Many studies have been done to understand the release of radionuclides from glass wastefoms over time. For HLW glasses, the release is usually assessed through studies of kinetic dissolution behaviour. A large body of data exists from international waste programmes such as those based on COGEMA's R7T7 vitrified product and simulant SON68 (Frugier et al., 2008). In the UK, most of the data that exists are from Soxhlet tests on simulant glasses, in deionised water at $\geq 90^\circ\text{C}$. However, there are significant differences between the compositions of UK glasses and those in other programmes. There are two UK HLW glass compositions: (a) Magnox which arises from reprocessing of Magnox fuel (Mg- and Al- rich); and (b) Blend that arises from other reprocessing activities within the Thermal Oxide Reprocessing Plant (THORP) at Sellafield (Cassingham et al., 2008). The major difference of UK HLW glasses compared to other countries is the high Mg and Al content making the properties of this glass different especially in terms of durability (Swanton, 2012a). Thus, there are significant uncertainties associated with extrapolating data from international programmes to represent the behaviour of UK glass products (Swanton, 2012). The aim of this project is to characterize the surfaces of UK HLW glass leached for a week to help interpret the corrosion mechanism of simulated waste glass in aqueous environments.

Leaching of glass occurs through several different mechanisms when it is in contact with water. The process starts with ion exchange of H_3O^+ or H^+ with available network modifier by the leaching of free aqueous ions in the glass e.g. Na^+ and Ca^{2+} (Ojovan et al., 2006). In parallel, hydrolysis of the network former of the glass structure occurs with the previous stage leaving behind Si-OH bonds. At this point a gel or diffusion layer forms which acts as a barrier for dissolution to progress (Swanton et al., 2012b). At some point, saturation may occur which will reduce the glass dissolution rate (Swanton, 2011) and in some cases at saturation, precipitation of secondary phases on the glass surface may occur (Hyatt et al., 2003). The leaching rate depends on the composition of the glass, pH of the solution and the temperature of the environment (Jain and Pan, 2000). The details of glass corrosion mechanisms have also been discussed extensively by Jain and Pan (2000), Jones (2013), and Donald (2010).

In this paper, surfaces are studied using Secondary Ion Mass Spectrometry (SIMS) to examine details of changes of glass surfaces after leaching. SIMS is a unique technique as it can detect small changes in composition at the surface compared to bulk material. Many authors have applied this technique to examine distributions of corroded glass composition in terms of depth. Lodding and Van Iseghem (2001), for example, looked at elemental distributions in terms of depth for SON68 and SM513 glasses that had been leached for 5 years. Chave et al. (2007) used ToF-SIMS to carry out depth profile analysis on understanding the solid state diffusion of SON68 glass. Gin et al. (2011) examined alteration glass properties of borosilicate glass after 26 years leaching by using NanoSIMS. Others have used SIMS to study different types of glass, for example, to characterise the surface of corroding museum glass (Fearn et al., 2006).

2. Methodology

Samples of simulated Magnox waste glass with incorporation of 25wt% waste loading and 75wt% baseline glass were provided by the UK's National Nuclear Laboratory (courtesy of C. R. Scales). The glass was produced in February 2010 as Pour 36 during VTR (Vitrification Test Rig) campaign 10 at Sellafield. Oxides were mixed and melted at 1050°C and poured into a storage canister (Scales, 2011). The glass composition is given in Table 1.

7 days dissolution test was performed using the MCC-1 method at a temperature of 90°C (ASTM Intl., 2004). The sample surface area to water volume ratio (SA/V) is approximately 10m^{-1} (Lee et al., 2006). The samples were sectioned to about $1 \times 1 \times 0.2 \text{ cm}$, ground and polished to a $1\mu\text{m}$ surface finish and cleaned prior to leaching in deionised water (dH_2O).

SIMS depth profiling was carried out using Cameca ims 3f instrument. The primary ion beam used was O^- ions with positive secondary ion detection. The beam energy was 10 keV. Since the samples were electrically insulating, a novel low energy electron gun would normally be used to reduce charge compensation effects. However, as a negative ion beam was used with this instrument, there was no need to use any compensating electrons.

Ion mapping of sample surfaces was done using time-of-flight secondary ion mass spectrometry (ToF-SIMS) using an IONTOF SIMS V instrument. The instrument is equipped with a bismuth (Bi) liquid metal ion gun. A 25keV primary ion beam of 1pA current was used in the sawtooth mode to obtain high lateral resolution during the analyses. The lateral distribution of elements and organic species was analysed for fields of view (FoV) of $37 \mu\text{m} \times 37 \mu\text{m}$ and $150 \mu\text{m} \times 150 \mu\text{m}$ for unleached and leached surfaces respectively. A wedge, as shown in Fig. 1, was made beforehand using an FEI Focussed Ion Beam (FIB) 200-SIMS instrument so that the ion distributions in terms of depth could be observed. The wedge depth was measured using a Zygo white light optical interferometer.

Table 1: List of glass compositions

Oxide	Wt. %	Oxide	Wt. %	Oxide	Wt. %
<i>SiO₂</i>	46.83	<i>BaO</i>	0.48	<i>Pr₂O₃</i>	0.56
<i>B₂O₃</i>	17.04	<i>La₂O₃</i>	0.58	<i>RuO₂</i>	0.77
<i>Na₂O</i>	8.46	<i>Al₂O₃</i>	4.41	<i>Sm₂O₃</i>	0.38
<i>Li₂O</i>	4.12	<i>MgO</i>	4.68	<i>SrO</i>	0.28
<i>CeO₂</i>	1.13	<i>MoO₃</i>	1.44	<i>TeO₂</i>	0.17
<i>Cr₂O₃</i>	0.6	<i>Nd₂O₃</i>	1.86	<i>ZrO₂</i>	1.41
<i>Cs₂O</i>	1.07	<i>NiO</i>	0.37		
<i>Fe₂O₃</i>	2.93	<i>Y₂O₃</i>	0.18	Total	100

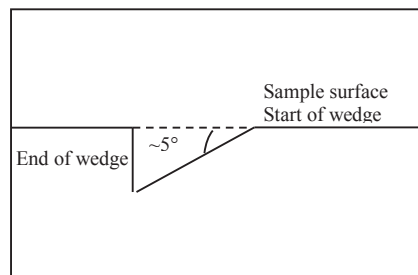


Fig. 1 Side view image of wedges made. By knowing the wedge angle, assumptions of ion distributions in terms of depth could be made.

3. Results and discussion

SIMS depth profiles for 7 days leached samples is shown in Fig. 2. Regions depleted compared to the bulk values were observed near the sample surface to a depth of approximately $0.4\mu\text{m}$ indicating some elements have been removed from the surface region. Fig. 2 reveals that network modifier cations e.g. Na, Li were leached from the surface which indicates stage I corrosion (ion exchange process) where alkali ions were removed from the surface and replaced by H^+ (Jones, 2013; Lucksheiter and Nesovic, 2004). The profile in Fig. 2 also shows apparent enrichment of ions e.g. Mg near the surface which might indicate formation of an ‘alteration’ layer near the surface region. Note that the signals reached their bulk levels at different depths and that the marker at $0.4\mu\text{m}$ is a rough guide of end of depletion region.

To understand this in detail, ion mapping was done for both samples on the wedges made as shown in Fig. 3. The wedges started from the right side and go deeper into the sample bulk going to the left. The field of view chosen and polarity are shown on the figure.

For unleached samples, the distribution of all ions throughout the wedge was the same as shown in Fig. 3(a). There were no changes of composition indicating all elements were distributed evenly through the bulk. However, after being leached for 7 days, complex layers were observed as shown in Fig. 3(b). The mapping was done using colours for easy comparison revealing that most of the elements were depleted and there was enrichment of Mg near the surface. The colour scale bar at each ion mapping image represents the intensity of ions that was detected by the instrument and the maps were normalized to the total ion count. Colour scale runs from black being 0 and white being the maximum normalized ion counts.

The depleted regions explained the early stage of the interdiffusion (ion exchange) process that happens when glass is in contact with water (Jones, 2013). Most of the alkali ions i.e Na, Li, Cs leached out from the surface leaving behind silanol bonds. However, from Fig 3 (b) it can be observed that these ions were precipitated onto the glass surface forming another layer which was brittle and cracked. Chêne and Trocellier (2004) also observed the formation of this layer with microcracking when an alkali-borosilicate glass was exposed to water at 90 °C for 7 days but the layer was rich in Si and O.

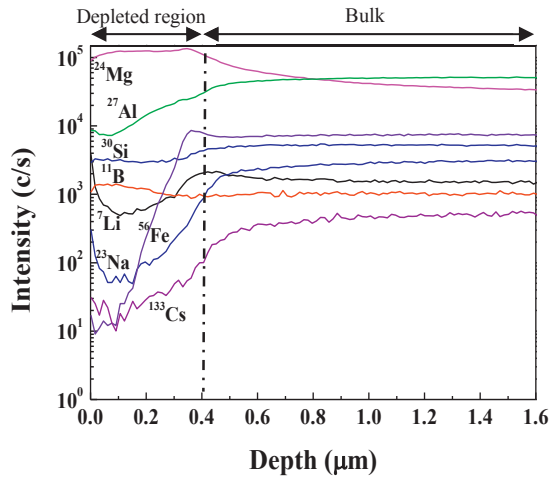


Fig. 2 SIMS depth profiles of 7 days leached samples. c/s = counts per second

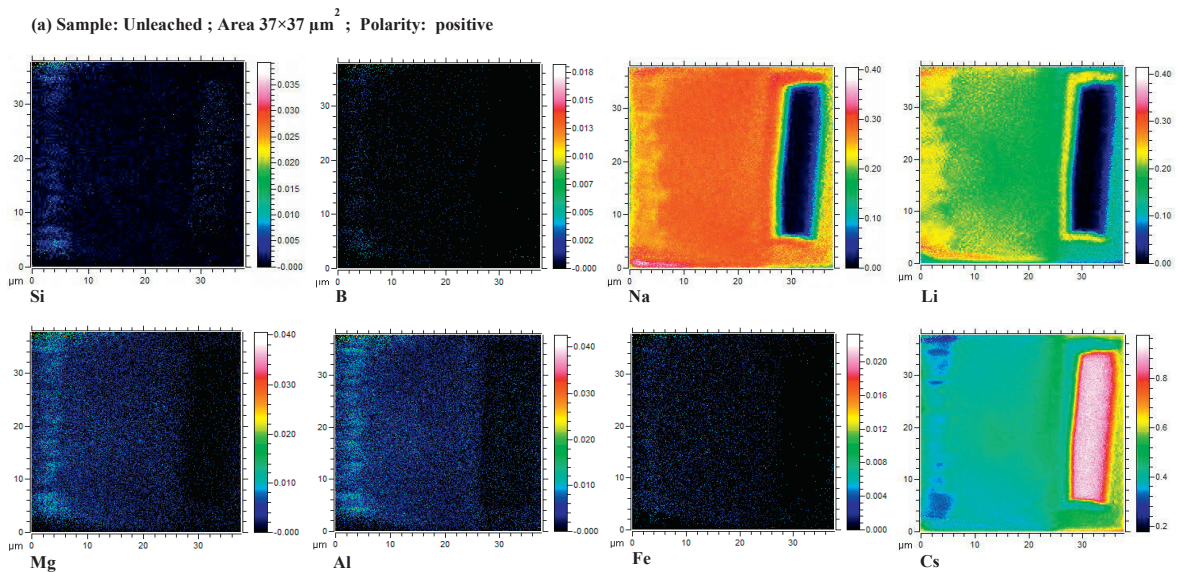


Fig. 3(a): Normalized ion images of unleached glass

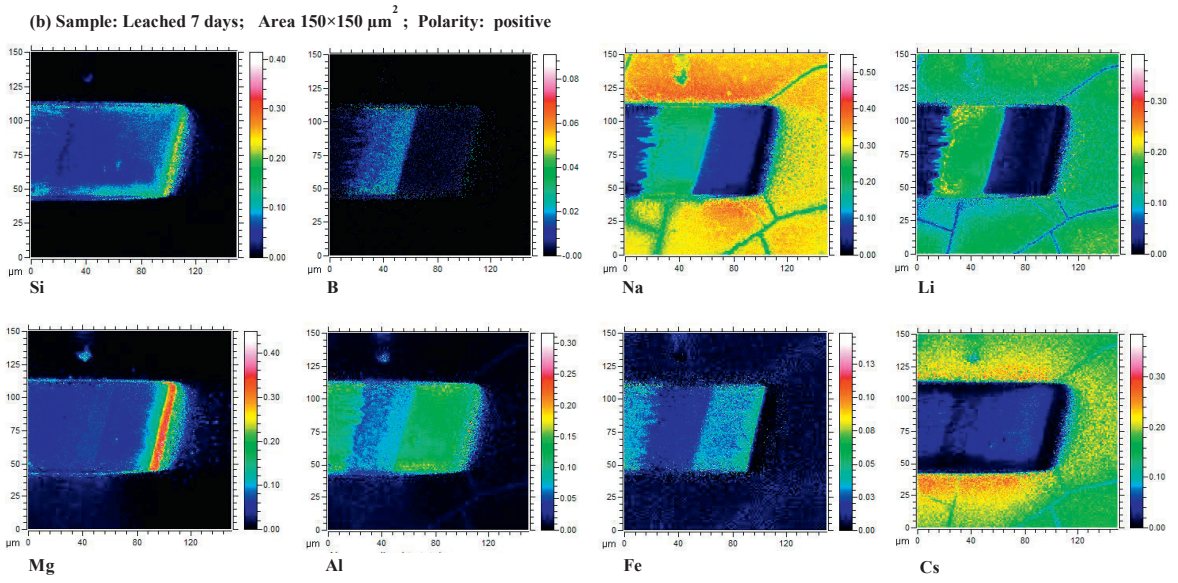


Fig. 3(b): Normalized ion images of 7 days leached glass

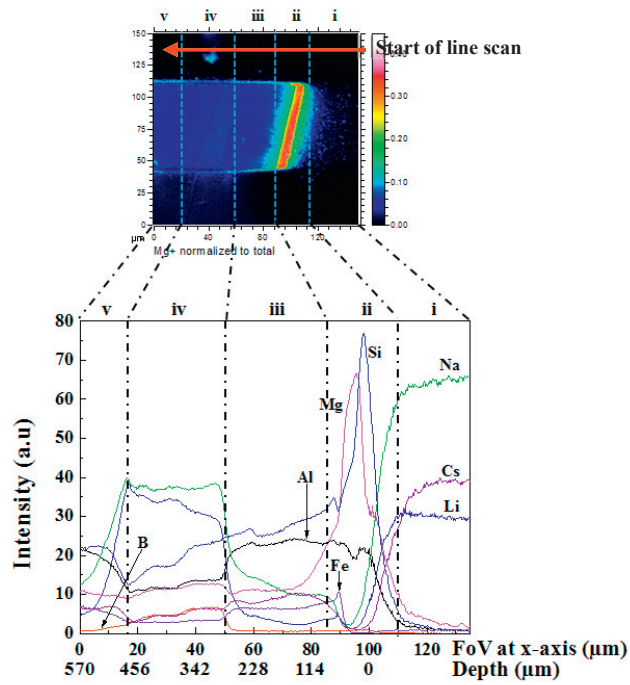


Fig. 4: Line scans showing intensity vs depth for the ion mapping. Field of view (FoV) as reference for regions mentioned.

Line scans were then taken from the ion image of glass leached for 7 days to obtain depth profiles. This can be seen in Fig. 4 where region; (i) shows the glass surface ‘alteration layer’ formed, (ii) beginning of wedge, (iii) and (iv) along the surface of the wedge, and (v) the end of wedge (this is called the ‘wall’ due to skirting effects during FIBbing). An ion map image is also shown in Fig. 4 to illustrate the positions of the regions mentioned earlier for the line scan. Depth profiling was deeper into the bulk that is to approximately 570µm. This is one of the advantages of performing wedge milling compared to normal depth profiling method.

From the line scan, it can be assumed that region (iv) is the bulk region (pristine glass). Most of the elements were well distributed in the bulk. As the scan reaches near the sample surface, two observations are: (1) depletion of alkali ions and (2) enrichment of other mobile ions eg. Na, Li and Mg. Depletion of alkali ions arises from the ion exchange process where these ions were leached out from the bulk. This process can be observed at region (iii) where the intensity level of most ions was reduced compared to the bulk region. As these ions leached out, silanol (Si-OH) bonds remain near the surface (Jones, 2013). This is clearly shown at region (ii) in Fig. 4 where there is an enrichment of Si ions. However, since the scan was done for positive polarity ions, negative ions i.e. OH are not shown here. At this region, enrichment of Mg ions was also observed. Two assumptions could be made on reactions occurring in this region. First, hydrolysis reaction occurs in which Si-O-Si bonds broke and formed the silanol bonds (Jones, 2013; Menard et al. 1997). Second, some of the Mg acts as a network intermediate which created Mg-Si bonds hence forming a diffusion or gel layer (Menard et al., 1997; Watts et al., 2010). While Corkhill et al. (2013) claim that the release of Si ions into solution forms an Mg-Si crystalline phase that precipitates near the glass surface. As the alkali ions are depleted e.g. Na, Li, Cs, they precipitate back on the glass surface forming another layer the so called ‘alteration layer’ on top of the glass surface as shown at region (i). Since the test was done in deionised water, there are no competing ions in solution so these ions were sorbed onto the glass surface (Swanton et al., 2012b; Lucksheiter and Nesovic, 2004). Further analysis will be done to confirm the formation of these layers.

Gin et al. (2011 & 2013) and Lodding and Van Isegham (2001) also found these various zones of layers for French nuclear waste glass that had been leached for longer times i.e. 26 years and 5 years. Estimation of diffusion coefficient for Na and Li is done by using a Brownian Motion equation (Hiemenz and Rajagopalan, 1997):

$$x = 2\sqrt{(D.t)}$$

where x is the diffusion length (m), t is leaching time (s) and D is the diffusion coefficient. D_{Li} and D_{Na} calculated in this work is $1.7 \times 10^{-19} \text{ m}^2\text{s}^{-1}$ and $2.6 \times 10^{-19} \text{ m}^2\text{s}^{-1}$ respectively. Nonaka et al. (2002) found the D_{Na} to be $1.5 \times 10^{-22} \text{ m}^2\text{s}^{-1}$ and Gin et al. (2013) found D_{Li} to be $1.5 \times 10^{-22} \text{ m}^2\text{s}^{-1}$. The difference in the values compared to previous work is three orders of magnitude which may be due to the period of corrosion as for this work it was done for a short term test i.e. 7 days. It can be assumed that at this particular leaching time ion exchange and hydrolysis processes are still active making the diffusion value a little higher compared to the longer leaching time. As the glass is leached at longer times there is a possibility of increase in thickness of the alteration layer. This would make diffusivity of water into the pristine glass or mobile ions to the water become lower because of the formation of the microporous hydrated layer or precipitation/sorbed metal silicates (Gin et al., 2013; Lucksheiter and Nesovic, 2004). Assuming the thickness of the ‘alteration layer’ of this glass will increase with time, this layer will act as a barrier which slows down the diffusion process. This assumption will be true if the value of diffusion coefficient calculated is lower than as calculated which will then may be a proper clarification to an assumption of these layers behaving as a passivating layer that protects the glass from further ions leaching. Further work will be done to prove this statement.

4. Conclusion

By examining a wedge milled into a corroded glass sample, SIMS can show the details of ion distributions from the sample surface through the bulk by ion mapping. The wedge angle ramp plays an important role in determining depth through the sample. The advantage of wedge milling is that extended profiles can be done to a greater depth. Hence more complex layers can be observed through a leached sample and it is more accurate as sample charging can be overcome. The depleted regions near the surface layer explain the ion exchange process that arising due to

glass-water interactions. It is suspected precipitation occurs forming a crystalline ‘alteration layer’ on top of the glass surface.

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