

Fission Product Immobilisation in Secondary Phases Formed During Magnox Waste Glass Dissolution at 60 °C: Experimental Results and Modelling.

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ABSTRACT

Dissolution of a complex, simulated Magnox Waste (MW) glass in batch dissolution experiments at 60 °C over a period of 56 days is accompanied by extensive development of secondary gels. Gel development has been followed using a range of chemical, spectroscopic and physical means. Initially, a surface layer comprising (hydr)oxides of Fe, Zr and the lanthanides develops at the glass surface. Aluminosilicate gels containing Si, Al, Mg, Sr, Cs and Rb develop in systems where sufficient quantities of glass derived solutes accumulate in the leachate. These gels are hydrous and readily soluble in acidic oxalate solutions. Solution chemistry data is consistent with the development of Cs,Sr-bearing aluminosilicates, silica gel and (hydr)oxides of hydrolysis prone waste components. The experimental results are compared with the predictions of a model that considers kinetically constrained glass dissolution and the precipitation of secondary phases, including a Cs,Sr-bearing aluminosilicate gel.

INTRODUCTION

Silicate glasses are thermodynamically unstable materials that react sluggishly with water and water vapour. A considerable body of research has investigated the likely behaviour of nuclear waste glasses on contact with repository groundwaters. Much of this research has concentrated on the rates and mechanisms of glass dissolution and approaches to modelling the processes that may result in radionuclide release in the groundwater pathway [1]. However, far less research effort has been directed towards identifying the secondary products of glass-water reaction. These include secondary solid phases that may act as radionuclide hosts under repository conditions, therefore further retarding radionuclide migration. Experiments conducted at high temperature (>150 °C) often yield crystalline secondary phases, including clays and zeolites [2]. However, over experimental timescales and at temperatures more representative of likely long-term repository environments (< 100 °C), amorphous gels predominate, together with small quantities of poorly ordered clay minerals and oxy(hydr)oxides [3].

EXPERIMENTAL DETAILS

The nonradioactive glass investigated here contained a complex mixture of fission product oxides representative of HLW glasses resulting from Magnox fuel reprocessing operations at Sellafield. Excluding RuO₂, which was present as a discrete crystalline phase identified by powder X-ray diffraction, the glass chemistry can be expressed by the formula:

MWGLASS =

Al_{0.064}B_{0.319}Ba_{0.002}Ce_{0.003}Cr_{0.003}Cs_{0.005}Fe_{0.018}La_{0.002}Li_{0.156}Mg_{0.082}Mo_{0.008}Na_{0.166}Nd_{0.006}Ni_{0.002}P_{0.001}Rb_{0.001}Pr_{0.002}Si_{0.519}Sm_{0.001}S_{0.001}Sr_{0.002}Te_{0.001}Y_{0.001}Zr_{0.009}O_{1.9705}.

Static batch dissolution experiments were performed in high purity water (electrical resistivity $>18 \text{ M } \Omega$) at $60 \text{ }^\circ\text{C}$ for 3, 7, 21, 35 and 56 days, using 2.5g glass powder (N_2 BET surface area $0.13 \text{ m}^2 \text{ g}^{-1}$) per litre of leachant. Following reaction at $60 \text{ }^\circ\text{C}$ for the allotted time period, the reaction vessel was removed from the oven and a 20 ml aliquot of the solution was rapidly filtered through a $0.22 \text{ } \mu\text{m}$ cellulose nitrate membrane filter. A sample of this filtrate was diluted by a factor of 5 and acidified to 2% nitric acid for ICP-AES analysis. For ICP-MS analysis, samples of the filtered leachate were diluted by a factor of 100 and acidified to 2% nitric acid. Glass powders were retained by filtration of the slurry at the base of the reaction vessel. Passing 50 ml of deionised water through the glass powder (under vacuum) gently washed powders retained on the filter paper. After rinsing in deionised water, glass samples were dried at $50 \text{ }^\circ\text{C}$ and stored in a vacuum dessicator. Samples of the unreacted glass and the leached glass powders were treated with an ammonium oxalate/oxalic acid reagent at pH 3, using a selective extraction procedure [4]. Extracts were filtered through a $0.22 \text{ } \mu\text{m}$ cellulose nitrate membrane filter and prepared for analysis by ICP-AES and ICP-MS. Diffuse reflectance Fourier transform infrared (DR-FTIR) spectra were acquired for glass powders using an ATI Genesis spectrometer fitted with a Graesby 'Mini-Diff' diffuse reflectance accessory. Samples were prepared by milling and grinding in a KBr matrix (at a mass ratio of 0.075g sample to 5g KBr). All samples were stored in a vacuum desiccator at room temperature prior to analysis. Diffuse reflectance spectra were obtained in the region $4000 - 500 \text{ cm}^{-1}$, using KBr as a reference.

RESULTS AND DISCUSSION

Solution chemistry data and gel characterisation

In Figure 1, the normalised concentrations of selected glass derived solutes are plotted versus time. Here molar elemental concentrations in the leachate solutions have been multiplied by a factor (Sf^i), which is the ratio of the number of moles of silicon to the number of moles of the element i in the glass. Boron is a soluble element that is not incorporated into the secondary products that may develop during glass dissolution. Therefore, in the discussions that follow, it is used as a soluble marker for dissolution. Boron concentrations increased with time indicating that the glass is continually dissolving over the duration of the experiments. As a result of glass dissolution the leachate pH values reached 9.6 after 3 days. Hydrolysis prone elements, such as Fe, Zr, Ni and the rare earth elements (REE) Ce, Nd, Sm and La, were not detected at significant levels in the mildly alkaline leachates, consistent with the formation of insoluble oxy(hydr)oxides. Further evidence of the formation of such secondary phases is provided by the selective extraction data, as described below. Geochemical modelling calculations also suggest that REE phosphates (e.g. $\text{NdPO}_4 \cdot 10\text{H}_2\text{O}$), which have very low solubilities, were oversaturated in these systems. Due to the small phosphate content of the waste glass, the development of secondary phosphate-bearing solid phases may also influence REE (and actinide) release under repository conditions.

The normalised molar concentrations of Al, Mg, Sr and Si were significantly lower than those of B after 3 days of reaction and the concentrations of Al, Mg and Sr decreased significantly after 14 days. Cs and Rb concentrations were lower than those of B after 21 days and the concentrations of these elements decreased markedly between 21 and 56 days. Decreases in the solution concentrations of a number of glass derived solutes indicate that these elements were removed from solution following release via glass dissolution.

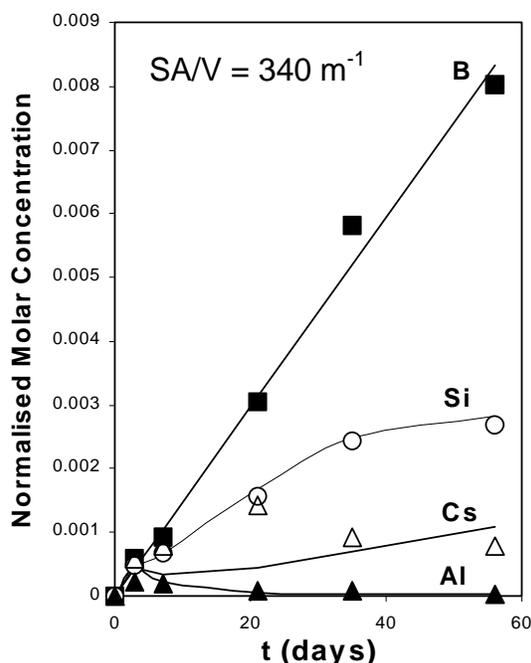


Figure 1. Normalised molar concentrations of B (■), Si (○), Cs (△) and Al (▲), compared with modelled concentrations (see text).

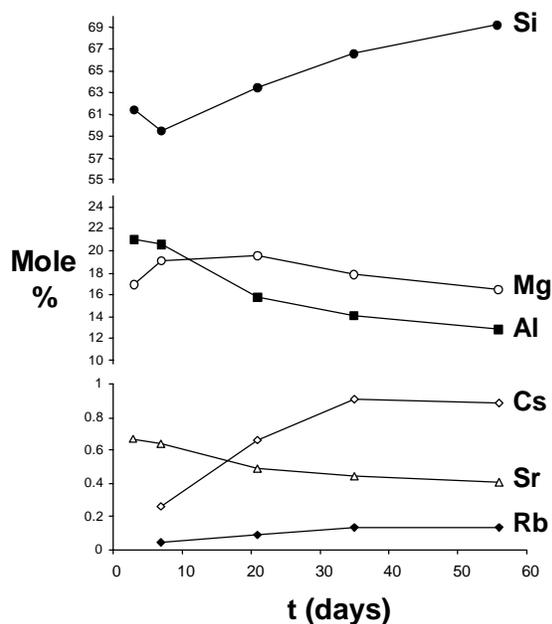


Figure 2. Gel chemistry as a function of time based on the solution chemistry data (see text).

The leachate chemistry data is consistent with progressive formation of a Mg, Sr, Cs, Rb-bearing secondary aluminosilicate phase (or a number of such phases), which is henceforth termed an aluminosilicate ‘gel’. The concentrations of the elements Al, Mg, Sr, Cs and Rb decrease at later times during the experiments, whilst the silica concentration tends towards a plateau (Figure 1). By comparison of the normalised molar concentrations of Si, Al, Mg, Sr, Cs and Rb relative to boron, it is possible to estimate the net chemistry of this ‘gel’ (Figure 2), which becomes progressively Si-rich with increasing reaction duration. Assuming a clay-like gel composition based on 4 Si atoms per formula unit, the gel stoichiometry may be estimated from the leachate chemistry. At 56 days the resultant formula derived on this basis is $\text{Al}_{1.052}\text{Mg}_{1.351}\text{Sr}_{0.028}\text{Cs}_{0.072}\text{Rb}_{0.014}\text{Si}_4\text{O}_{10}(\text{OH})_2$. However, the increasing Si content of the gel (Figure 2) reflects the formation of an additional discrete silica phase, and the final silica concentration is consistent with the development of silica gel in addition to the aluminosilicate gel (see below).

Samples of fresh glass powder and the reacted glass samples from the PLT experiments were subjected to the selective extraction procedure. This does not result in extensive dissolution of crystalline clays or oxide mineral phases over the timescales of the procedure, but does attack poorly-ordered gels, such as those found in soils [4]. The amount of a given glass component element (i) in extracts of the reacted glass powders may be compared with the amount in extracts of fresh (un-reacted) glass samples. The difference may be expressed in terms of the normalised moles extracted :

$$NEM_i = ([i]_{\text{Sample}} - [i]_{\text{Glass}}) \times Sf^i \quad (1).$$

NEM_i is the difference between the concentration of the element (i) in the extract of a reacted glass sample $[i]_{Sample}$ (mol l⁻¹) and the mean molar concentration of i in equivalent extracts of fresh glass samples $[i]_{Glass}$ (mol l⁻¹), multiplied by the Sf^i factor. Values of NEM_i for Al, B, Ce, Cs, Fe, Li, Mg, Mo, Na, Ni, Si, Sr and Zr are shown as a function of reaction time in Figure 2 (error bars are 95 % confidence limits based on triplicate extractions of each glass powder). Positive values of NEM_i indicate that the amount of the element (i) extracted from the reacted sample was greater than that extracted from the fresh glass. Positive NEM_i values were obtained for Al, Fe, Ce, Cs, Mg, Ni, Sr and Zr, indicating that an acid oxalate soluble fraction enriched in these elements and depleted in B, Li, Mo and Na is present at the surfaces of the reacted glass samples. Note that values of NEM_{Si} were close to zero in each case. However, NEM_{Si} values greater than zero are obtained when reacted glass samples are treated with an alkaline 0.5 M K₂CO₃ reagent [5].

The results of the acid oxalate extraction experiments are in agreement with many of the observations based on the solution chemistry data. Elements such as Ce, Fe, Ni and Zr, which were not detected in the leachates, were enriched in the acid oxalate soluble fraction of the reacted glass powders. This indicates that these elements accumulated at the glass surface in an acid oxalate soluble form during the experiment. Al, Mg and Sr were also enriched in the acid oxalate soluble fraction of the reacted glasses. Cs and Rb were enriched in extracts from the powders leached for 35 and 56 days, in agreement with the solution chemistry data. In contrast, the soluble elements B, Li, Mo and Na were depleted in the acid oxalate extracts of the reacted glasses. Extensive gel formation has also been observed in single-pass flow-through experiments with this glass [5].

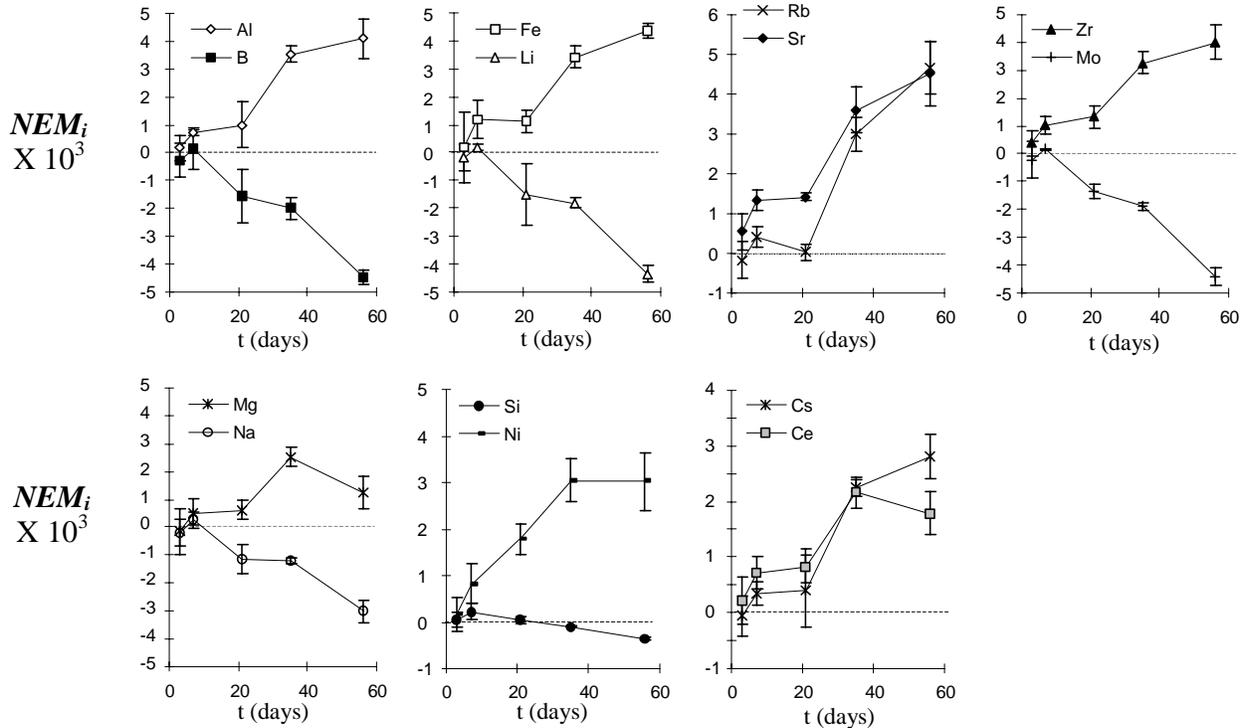


Figure 3. Selective extraction data. NEM_i values versus time for leached glass powders.

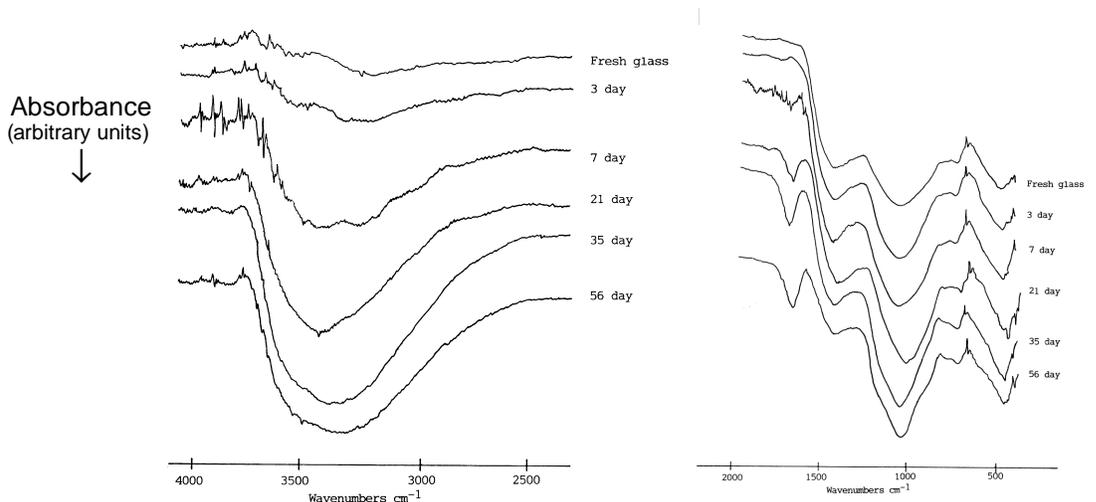


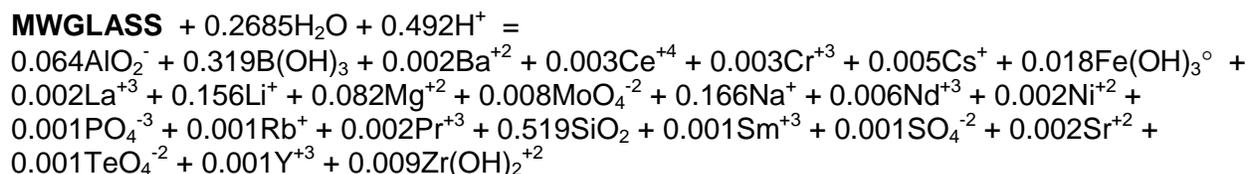
Figure 4. DR-FTIR data for fresh and leached glasses.

Neither scanning electron microscopy nor powder X-ray diffraction analysis of the leached glass powders revealed the presence of crystalline secondary products. Further evidence of secondary gel formation is provided by DR-FTIR data obtained for the leached glass powders. Spectra obtained for fresh (non-reacted) glass powder and that reacted for 3 days are very similar. With longer reaction times the spectra show a number of differences, particularly in the regions $3000\text{--}4000\text{ cm}^{-1}$ and $400\text{--}2000\text{ cm}^{-1}$ (Figure 4). Features in the lower wavenumber region are associated with siloxane vibrations in the tetrahedral molecular glass network and spectral differences in this region are indicative of changes in the network structure at the glass surface. For glass samples reacted in excess of 7 days, and with progressive reaction duration, the spectra exhibit a sharpening of the peak centred at 1030 cm^{-1} and the development of distinct shoulders on this band. These features are consistent with the progressive development of a secondary gel layer at the leached glass surfaces. Features in the $2500\text{--}4000\text{ cm}^{-1}$ region are associated with hydroxyl stretching bands. Spectra for the fresh glass sample and that reacted for three days are largely featureless in this region. With increasing reaction duration, there is progressive development of a broad band centred at approximately 3400 cm^{-1} . The broad peak at 3400 cm^{-1} is attributable to the overlap of bands attributable to symmetric and asymmetric stretching of molecular water. The presence of molecular water in glasses reacted for periods in excess of 7 days is further expressed by the small peak at 1610 cm^{-1} in the DR-FTIR spectra of these samples. The presence of water was confirmed by thermal analysis. For samples leached for in excess of seven days and with increasing reaction duration, significant mass loss was observed on heating in the temperature range $25\text{--}220\text{ }^{\circ}\text{C}$, consistent with the progressive development of a hydrous gel layer between 21 and 56 days.

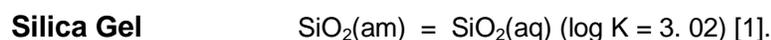
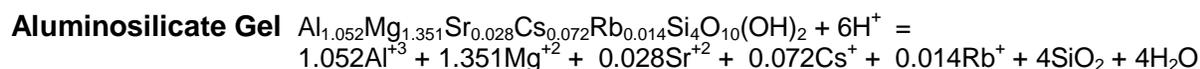
Modelling

Based on the release of boron (Figure 1), the glass dissolved at a nearly constant rate of $9.7 \times 10^{-9}\text{ moles m}^{-2}\text{ s}^{-1}$ during the experiments. A kinetic dissolution model was constructed using the PHREEQC code [6]. An aluminosilicate gel having the stoichiometry identified above was included as a phase that was allowed to precipitate to equilibrium within the model, and thus to moderate the solution concentrations of Si, Al, Mg, Sr, Cs and Rb. The glass dissolved at the experimental rate and the secondary phases (aluminosilicate gel and silica gel) precipitated to chemical equilibrium in this model. The following reactions were considered:

(i) *Kinetically moderated glass dissolution:*



(ii) *Secondary solid phases equilibrating within the model system:*



The log K for the aluminosilicate gel reaction was adjusted to obtain agreement with the experimental data and a value of log K = 12 results in the fit shown in Figure 1. In reality the composition of the aluminosilicate gel is likely to vary with reaction progress as the leachate chemistry evolves. Whilst representing only a simplified model of the possible gel chemistry, this approach is able to reproduce the major trends in solution chemistry that have been observed experimentally in this study.

SUMMARY AND CONCLUSIONS.

Batch dissolution of a simulated MW glass is accompanied by extensive secondary gel formation. A simple approach to modelling these processes has been presented. Hydrolysis moderates the solubility of Fe, Zr, Ni and the REE to very low levels. Progressive formation of a Cs, Sr-bearing aluminosilicate phase of clay-like composition has been observed experimentally. The formation of secondary gels should be considered in source-term models. This will require a greater understanding of the fundamental chemistry of such amorphous secondary phases, which may act to further retard radionuclide release under repository disposal conditions.

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