The effect of magnesium on the local structure and initial dissolution rate of simplified UK Magnox waste glasses

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ABSTRACT

A series of simplified glasses were prepared to mimic the United Kingdom's Magnox radioactive waste glasses and determine the separate effect of the presence of Mg on the glass structure and the initial dissolution rate. These glasses had an alkaline earth (Ca/Mg) content of 6.5 mol% and relative ratios of Si, B and Na similar to 25 wt% waste loaded Magnox waste glass simulant. Each simplified glass had similar macroscopic properties, differing only in Ca/Mg ratio. ^{25}Mg magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of the simplified Mg endmember (MgEM) glass (with no Ca) and the full-component simulant glass were similar, consistent with the similar Mg local environments in both glasses. ^{11}B MAS NMR spectra of the series of simplified glasses showed a systematic increase in the amount of three-coordinated boron ($^{[3]}B$) with increasing amounts of Mg. A clear change in the charge balancing of four-coordinated boron ($^{[4]}B$) by Mg compared with Ca is observed. However, ^{11}B NMR measurements of the leached material showed that the additional $^{[3]}B$ was not preferentially leached from the Mg containing samples. Despite the structural changes in the glass induced by Ca/Mg substitution, initial dissolution rates (r_0) remained invariant, within error, with Ca/Mg ratio. This indicates that the poorer aqueous durability of Mg-containing Magnox waste glass measured experimentally in long-term leaching experiments, compared with SON68 glass containing Ca, is not caused by a primary structural effect in the glass.

1. Introduction

The majority of radioactive waste glass produced in the UK contains magnesium (Mg). This arises for historical reasons from the Mg-containing alloy cladding used on the natural uranium fuel of the first generation UK Magnox reactors. This Mg is entrained in the fission product fraction following fuel re-processing operations and becomes incorporated into the glass wasteform on vitrification. At least two studies [1,2] have shown that in long-term (up to 12.2 years), simulant UK Magnox waste glass containing Mg (and nominally no calcium (Ca)) have significantly poorer aqueous durability compared with Ca-based glasses such as the French benchmark SON68 inactive glass simulant. This paper describes a separate effect study of the influence of substitution of Mg on the pristine structures and initial dissolution rate of simplified UK Magnox waste glasses.

The simulant Magnox waste glass with a 25 wt% waste loading (herein referred to as MW25) contains 23 oxide components (see Supplementary materials), the aim of this work is to produce a simplified glass with 6–7

components that represents the main compositional features of the complex glass and allows the separate effect of Ca and Mg on glass structure to be established with all other parameters being equal. As the major structural probe will be NMR (nuclear magnetic resonance), paramagnetic lanthanides have been substituted by lanthanum (La) and iron (Fe) has been left out of the compositional mapping.

The similarity between MW25 and the simplified analogue needs to be verified for the use of simplified glass to study its full-component counterpart to be valid, especially from a Mg point of view. ^{25}Mg MAS (magic angle spinning) NMR provides a powerful tool to investigate the local Mg environments in glasses. The major cations present in the glass are boron (B) and silicon (Si), these act as the network formers which are linked via bridging oxygens to form the network of the glass structure. Si is primarily in four-fold coordination, this is the origin of the Q^n (quaternary) Si speciation. The number n, ranging from 1 to 4, denotes the number of bridging oxygens attached to a silicate tetrahedron. B is distributed in either three- or four-fold coordination depending on the nature and the availability of charge balancing cations.

This was explored in the series of simplified glasses by ^{11}B MAS NMR. Other structural changes due to Mg substitution, similarly, were examined by using ^{23}Na and ^{27}Al nuclei as NMR probes to elucidate the local coordination changes and overall charge balancing scheme.

In long-term experiments, B release is considered as the proxy for measuring overall glass dissolution in water owing to its almost complete leachability and absence from any secondary phases [1–3] although its slight retention in the alteration layer has been directly probed [4,5]. ^{11}B MAS NMR can also be used to compare the [3]B/[4]B ratio before and after leaching experiments to investigate whether there is preferential dissolution occurring from these glasses. This in turn would indicate whether the poorer aqueous durability of Mg-containing glasses is due to a change in B speciation. On the other hand, whether B speciation and other structural changes would fundamentally affect the aqueous durability of these glasses could be readily addressed by measuring the initial dissolution rate (r_0) before secondary effects, such as solution saturation and altered layer formation, start to influence the dissolution process. Comparison of r_0 with Ca/Mg ratio will help to discriminate the relative importance of structural and secondary effects on glass dissolution.

2. Materials and methods

2.1. Glass preparation

The simplified glass was made according to the composition of the full-component MW25 glass (listed in Table S1). In order for the composition to represent the full-component glass as closely as possible, the molar ratios of Si, B, Na, Al and Mg were fixed at the same ratios as in the full-component glass. Meanwhile, the REE (rare-earth element) load was represented by La on a charge for charge basis except cerium which was attributed its fully oxidised charge of (4^+). Paramagnetic transition metals such as Fe and Ni were omitted to facilitate examination of the glass structure with NMR spectroscopy. The nominal composition is listed in Table 1. Mg was then successively substituted by Ca, on an atom-for-atom basis, to produce 0, 25, 50, 75 and 100 mol% Ca-substituted simplified glasses. The glasses are denoted as MgEM, Mg75Ca25, Mg50Ca50, Mg25Ca75 and CaEM respectively. The final glass-making process consisted of a controlled heating (10 °C/min) of weighed amounts of the precursors (SiO_2, $Na_2B_4O_7$, Al_2O_3, Na_2CO_3, MgO/$CaCO_3$, La_2O_3) in a platinum90/rhodium10 crucible to 1500 °C. The melt was poured onto a steel block and allowed to cool to room temperature (RT). The glass was then broken up and re-melted using the same ramp rate to reach 1500 °C. The second melt was poured onto a heated steel block at 250 °C then left cooled to RT. Finally, the glass was annealed at 550 °C for 2 h and subsequently cooled slowly in the furnace over a period of 16 h. The compositions of these simplified glasses were analysed (Table 1) by a combination of acid digestion/ solution ICP-MS and solid source LA-ICP-MS ((Laser Ablation) Inductively Coupled Plasma Mass Spectrometry) and EPMA (Electron probe microanalysis) techniques (Table S2 shows the original data presented in oxide wt%).

2.2. Leaching experiments

The glasses made as outlined in Section 2.1 were crushed and ground and then sieved to a size range between 75 μm and 150 μm. After the sieving procedure, the glass particles were washed in a controlled manner with Type I water and absolute ethanol according to the PCT-B (Product Consistency Test Type B) protocol [6] in order to remove any adhering fines and contaminants. The theoretical median diameter of 112.5 μm was then used for determining the specific surface area (SA) of each glass sample.

For the initial dissolution rate experiments, a sample of each glass composition ranging from 0.05 to 0.1 g was leached in a sealed PFA (Perfluoroalkoxy alkane) vessel in 100 mL 18.2 MΩ deionised water (DI) at 90 ± 1 °C and the whole system was agitated with a magnetic stirrer. This setup results in the SA/V (surface area to volume) ratios being no > 22 m^{-1} to ensure that the initial dissolution rate (r_0) was measured in very dilute conditions i.e., the forward hydrolysis reactions are not hindered and the formation of effective barrier layers is precluded [7]. This should be the maximum dissolution rate of the glass for these (temperature, DI) conditions.

The values of r_0 can be determined from the change in normalised release of Si (NL_{Si}) within the first 7.2 h of leaching, with the application of the shrinking core model [3] to correct for the change in SA/V ratio over time as dissolution proceeds, as follows:

$$AG(t) = AG(t-1) + 10^{-6} \times \left[\frac{Ci(t) - Ci(t-1)*V}{m_0 * Xi} \right] \tag{1}$$

$$ET(t) = \frac{3}{\rho * SA} \times \left[1 - (1 - AG(t))^{\frac{1}{3}} \right] \times 10^3 \tag{2}$$

$$r_0 = \frac{NLi}{t} = \frac{\rho \times ET(t)}{t} \tag{3}$$

(AG – altered glass fraction; C_i – concentration of element i in leachate (mg/L); V – solution volume (mL); m_0 – initial mass of glass sample (g); X_i – mass fraction of element i in glass; ET – equivalent thickness of dissolved glass (nm); SA – initial specific surface area (geometric in m^2/ g); ρ – glass density (g/cm^3); r_0 – initial dissolution rate (g/m^2/d); NL_i – normalised release of element i (g/m^2); t – time interval (d)). The rationale of using Si concentration rather than that of Na is to bypass the initial ion-exchange stage and reflect the direct dissolution of the glass network.

For long-term 112-day leaching experiments, a glass sample of each composition (only ^{11}B NMR data of 112-day leached MgEM and MW25 is presented in this paper) of 0.22–0.23 g was leached in a PTFE linear, which was sealed inside a stainless steel vessel, in 4.0 mL 18.2 MΩ DI at 90 ± 1 °C. The resulting SA/V ratio for the experiments from this setup was accordingly 1200 m^{-1} across all compositions.

2.3. Solid-state NMR characterisation

[11]B, [27]Al and [23]Na are all non-zero spin nuclei and therefore their local environments can be detected by solid-state NMR techniques even without long-range atomic order. As presented in this paper, apart from [25]Mg, their spectra were all obtained by single-pulse excitation. [11]B

Table 1

Nominal composition of the simplified MW25 glass (MgEM) and analysed compositions of the simplified glass series (cation mol%).

Cation (mol%)	Al	B	La	Mg	Ca	Na	Si
MgEM (Nominal)	4.87	27.58	1.72	6.54	-	15.38	43.91
MgEM	4.81 ± 0.20	28.26 ± 3.56	1.68 ± 0.16	6.54 ± 0.30	-	15.08 ± 0.81	43.63 ± 3.02
Mg75Ca25	4.82 ± 0.35	28.32 ± 6.64	1.66 ± 0.17	4.24 ± 0.32	1.57 ± 0.11	14.80 ± 1.20	44.61 ± 5.59
Mg50Ca50	4.89 ± 0.21	26.46 ± 2.06	1.73 ± 0.15	3.08 ± 0.12	3.15 ± 0.14	14.72 ± 0.71	45.98 ± 3.61
Mg25Ca75	4.93 ± 0.24	26.24 ± 2.40	2.01 ± 0.42	1.57 ± 0.07	4.78 ± 0.23	15.28 ± 0.82	45.18 ± 4.33
CaEM	4.71 ± 0.19	26.44 ± 2.97	1.69 ± 0.10	-	6.11 ± 0.22	14.92 ± 0.58	46.13 ± 2.75