

SIGNIFICANCE OF THE ION EXCHANGE PERIOD IN CORROSION OF BRITISH MAGNOX-WASTE IMMOBILISING GLASSES

M. I. Ojovan, A. S. Pankov, W. E. Lee, R. J. Hand
Immobilisation Science Laboratory, Department of Engineering Materials
University of Sheffield
S1 3JD, United Kingdom

C. R. Scales
BNFL
plc Sellafield, Cumbria, CA20 1PG, United Kingdom

ABSTRACT

The diffusion-controlled ion exchange period in the corrosion of British Magnox-waste glasses has been analysed and time-temperature limiting conditions determined from available data. Experiments were carried out using the MCC-1 standard as a basic leaching procedure to quantify ion exchange rates and cation releases were investigated at several temperatures. The ion exchange period is likely to persist for over ten years at ambient temperatures ~10-15°C.

INTRODUCTION

In the UK high-level radioactive waste (HLW) from spent nuclear fuel reprocessing is vitrified at the Sellafield Waste Vitrification Plant [1]. Vitrified wastes are stored for long periods of time before eventual disposal. Key aspects are possible corrosion mechanisms and potential radionuclide release from vitrified HLW in an envisaged repository environment arising from corrosion of the glass in contact with groundwater. Corrosion of nuclear waste glasses is a complex process which depends on many parameters such as time, temperature, groundwater chemical composition and pH. The best approach to quantify its functional dependence is to determine the basic parameters governing the corrosion so that various scenarios can be modelled in the performance assessment of a future repository. Corrosion of silicate glasses including nuclear waste borosilicate glasses involves two major processes – diffusion-controlled ion exchange and glass network hydrolysis [2-5]. However, activation energies of the rate-limiting reactions vary for different processes and thus for the same glass a change in temperature may result in a change of the governing corrosion mechanism [6, 7]. This paper studies the ion exchange phase in the corrosion process of simulated British Magnox-waste vitrified product in deionised water and diluted near-neutral solutions.

Ion Exchange Phase of Corrosion

The potential contact of water with vitrified HLW is deferred in actual disposal systems to times after the waste container has been breached. These times can be of the order of many hundred or even thousands years. High temperatures and radiation dose rates are likely only for the first few hundred years after waste vitrification. Container temperatures are likely to be close to those of ambient rock by the time of expected contact of ground waters with vitrified waste. Moreover the role of $\beta\gamma$ -radiolysis will also be negligible because of low radiation dose rates. However, the

alteration of glass caused by irradiation may become important at these times due to high absorbed doses of radiation and may affect the rates of ion exchange [8]. Hence experiments on water durability of non-radioactive pre-irradiated simulant glasses are relevant for the most likely scenario of waste glass contact with water. In the following the case of waste glasses in contact with deionised water or diluted near-neutral solutions is considered.

It is known that the release of cations from silicate glasses into water occurs via two basic mechanisms: diffusion-controlled ion-exchange (also termed leaching) and hydrolysis [1]. In dilute near-neutral solutions ion-exchange controls the initial stages of glass corrosion and incongruent dissolution of cations is observed. However, over time the rate of ion-exchange diminishes, whereas the rate of hydrolysis, although small in near-neutral conditions, remains constant. Hence hydrolysis will eventually dominate, once the near-surface glass layers have become depleted in cations [2-7] except under saturated conditions when the rate of hydrolysis is negligible. The time required for silicate glasses to reach the hydrolysis stage in near-neutral solutions depends mainly on glass composition and temperature. More highly polymerised glasses require longer times for hydrolysis to start. Thus glasses with higher silica contents require longer times before hydrolysis becomes dominant compared to high sodium content glasses. Previous work by the authors has suggested that the corrosion regimes of silicate glasses should be characterised in terms of time-temperature parameters [6, 7, 9] as the higher the temperature the sooner hydrolysis becomes dominant [1, 6, 7, 9]. This occurs because the activation energy for hydrolysis, E_a , is significantly higher than the activation energies of diffusive processes E_{di} . It has been shown that the diffusion-controlled ion exchange stage is dominant up to a time, $\tau(T)$, given by

$$\tau(T) = \tau_0 \exp\left(\frac{2E_a - E_{di}}{RT}\right), \quad (\text{Eq.1})$$

where τ_0 is a pre-exponential term (days), T is temperature (K) and R is the molar gas constant [6, 7, 9]. The hydrolytic stage of glass corrosion is dominant when time $t \geq 16\tau$, whereas within $\tau \leq t \leq 16\tau$ the glass corrodes with equivalent contributions from both ion exchange and hydrolysis.

A previous study [10] has demonstrated that in near-neutral water solutions the UK Magnox-waste glass undergoes incongruent ion-exchange over a period of 28 days even at temperatures as high as 60-90°C. Based on this work we can estimate $\tau(60^\circ\text{C}) \approx 28\text{d}$, $E_a \approx 60\text{kJ mol}^{-1}$ and $E_{di} \approx 36\text{kJ mol}^{-1}$ to enable a tentative identification of the most likely scenarios for the corrosion of UK Magnox-waste glass as a function of temperature and time (Fig.1).

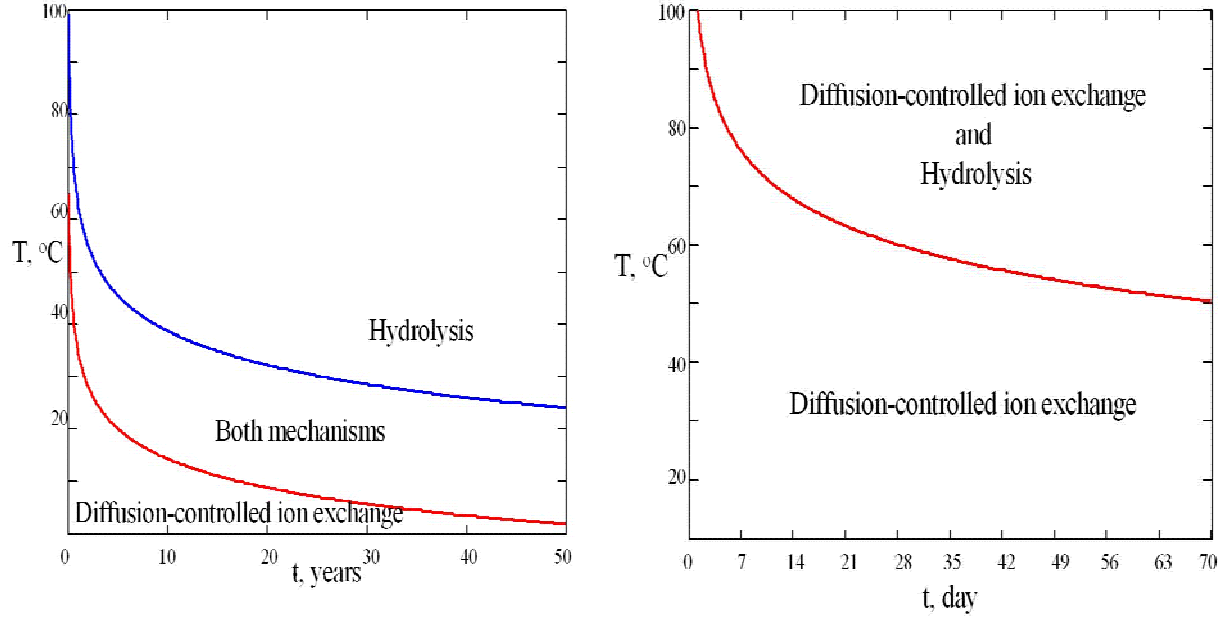


Fig. 1. Corrosion mechanisms for British Magnox-waste glass in near-neutral water solutions estimated using experimental data from [10].

Figure 1 shows that at temperatures below 10-15°C the ion exchange period of glass corrosion lasts over ten years. At higher temperatures the duration of the ion exchange period is shorter, for example this stage is limited to 28 days at 60°C (assumed in these calculations), 10 days at 70°C and 5 days at 80°C. Moreover Fig.1 can be used to identify time constraints on the leaching experiments as a function of temperature for both long-term (Fig.1 left) and short-term experiments (Fig.1 right).

Theoretical Treatment

The rate of release of the i -th cation into water via diffusion-controlled ion exchange rx_i ($\text{g cm}^{-2} \text{d}^{-1}$) is given by the magnitude of the flux of species through the surface of glass

i.e. $rx_i = |\vec{J}_{di}| = J_{di}$ at the glass-water interface. The diffusion flux of cations is given by Fick's first law:

$$\vec{J}_{di} = -D_i \vec{\nabla} C_i \quad (\text{Eq.2})$$

where C_i is the cation concentration in the glass (g cm^{-3}) and D_i is the effective diffusion coefficient ($\text{cm}^2 \text{d}^{-1}$). D_i can be written as $D_i = D_{0i} \exp(-E_{di}/RT)$, where E_{di} is the activation energy of effective diffusion (kJ mol^{-1}). The cation concentration gradient at the glass-water interface can be found using

$$|\vec{\nabla} C_i| = \frac{\bar{C}_i - C_{isol}}{\sqrt{\pi} L_i} \quad (\text{Eq.3})$$

where \bar{C}_i is the average cation concentration in the glass, C_{isol} is the concentration of cations in the water solution (g cm^{-3}) and L_i is the diffusion length (cm) given by the Einstein relation

$$L_i = \sqrt{D_i t}$$

As the concentration of cations in the solution is always supposed to be much smaller than in the glass *i.e.* $C_{isol} \ll \bar{C}_i$, this term can be neglected hence

$$|\bar{\nabla} C_i| \cong \frac{\bar{C}_i}{\sqrt{\pi} L_i}. \quad (\text{Eq.5})$$

Given that $\bar{C}_i = f_i \rho$, where ρ is the density of the glass (g cm^{-3}) and f_i is the mass fraction of the i -th cation in the glass, combining Eq.2, 4 and 5 gives the rate of cation release via ion exchange as

$$rx_i = \rho f_i \sqrt{\frac{D_{0i}}{\pi t}} \exp\left(-\frac{E_{di}}{2RT}\right), \quad (\text{Eq.6})$$

Ion exchange involves the interdiffusion and exchange of the cation in the glass with a proton (probably as H_3O^+) from the water $(\equiv\text{Si-O-Cation})_{\text{glass}} + \text{H}_2\text{O} \leftrightarrow (\equiv\text{Si-O-H})_{\text{glass}} + \text{Cation-OH}$ [3-5, 12]. The activation energy for interdiffusion can be written as $E_{di} = H_{mH} + H_{fNBO}$, where H_{mH} is the enthalpy of motion of protons and H_{fNBO} is the enthalpy of formation of non-bridging oxygens (NBO). Note that the activation energy of interdiffusion holds the same value for all monovalent cation because proton ingress into the glass is the limiting step. At the water-glass interface the proton concentration significantly exceeds the monovalent cations concentration [13] hence the pre-exponential coefficient of the interdiffusion coefficient can be expressed as a function of the pH of contacting water [14]:

$$D_{0i} = \frac{D_{0H}^* \kappa 10^{-pH}}{C_i(0)}, \quad (\text{Eq.7})$$

where D_{0H}^* is the pre-exponential coefficient in the diffusion coefficient of protons in glass $D_H = D_{0H}^* \exp(-E_{dH} / RT)$, E_{dH} is the activation energy of proton diffusion, $C_i(0)$ is the concentration of species at the glass surface (mol L^{-1}) and κ is a constant which relates the concentration of protons in water to the concentration at the glass surface. Eq.6 reveals that ion-exchange occurs preferentially in acidic and neutral solutions but diminishes quickly with increase of pH (proportionally to $10^{-0.5\text{pH}}$). Indeed it is normally considered that for $\text{pH} < \sim 9$ ion exchange dominates glass corrosion whereas hydrolysis reactions are significant extent when pH exceeds 9 [15]. Eq.6 indicates that the ion exchange period of corrosion is determined completely by the effective diffusion coefficient D_i which depends on the pH of the attacking solution (Eq.7) and has an Arrhenius temperature dependence on the activation energy E_{di} . We note that for irradiated glasses the temperature dependence of ion exchange is more complex [8].

The normalised cation release rate (nrx_i) via diffusion-controlled ion-exchange is given by

$$nrx_i = \frac{rx_i}{f_i} \quad (\text{Eq.8})$$

The average normalised leaching rate NRx_i is measured experimentally or it can be found theoretically by calculating the total normalised cation release (e.g. normalised mass loss NMx_i) and dividing it by the test duration

$$NMx_i = \frac{\int_0^t rx_i dt}{f_i}, \quad NRx_i = \frac{NMx_i}{t} \quad (\text{Eq.9})$$

Substituting Eq.6 into Eq.9 gives

$$NMx_i = 2\rho\sqrt{\frac{D_i t}{\pi}}, \quad NRx_i = 2\rho\sqrt{\frac{D_i}{\pi t}} \quad (\text{Eq.10})$$

These expressions are used to quantify the experimental results in the following.

Note that because of rapid dissolution of near-surface glass layers and surface contaminants the processing of experimental data when quantifying ion-exchange rates should begin after the end of these transition effects.

Experimental and Results

British Magnox-waste simulant glass batches were prepared from reagent-grade oxide and carbonate powders. The chemical composition of melted glass in this study was simplified slightly compared to published data [10, 11] in that the REE oxide content was reduced to only La and Nd and elements such as Ru and Te, which tend to form crystalline phases, were excluded as were Cr and Ni oxides (Table I).

Table I. Chemical Compositions of British Magnox-Waste Glasses, wt. %.

Oxide	Data from [10]	Data from [11]	This work
Al ₂ O ₃	4.82	6.57	4.90
B ₂ O ₃	16.90	15.87	17.17
BaO	0.61	0.50	0.62
CaO	-	0.01	-
CeO ₂	0.90	-	-
Cr ₂ O ₃	0.41	0.58	-
Cs ₂ O	1.02	1.11	1.03
Fe ₂ O ₃	2.43	3.00	3.13
Gd ₂ O ₃	-	-	-
HfO ₂	-	0.02	-
K ₂ O	-	0.01	-
La ₂ O ₃	0.47	0.48	3.61
Li ₂ O	3.76	4.06	3.82
MgO	5.29	5.73	5.37
MoO ₃	1.59	1.62	1.62
Na ₂ O	8.38	8.28	8.51
Nd ₂ O ₃	1.45	1.44	-
NiO	0.24	0.37	-
P ₂ O ₅	0.18	0.26	0.20
Pr ₆ O ₁₁	0.44	0.44	-
Rb ₂ O	0.12	-	-
RuO ₂	0.85	0.70	-
SiO ₂	47.20	46.03	47.94
Sm ₂ O ₃	0.29	0.22	-
SrO	0.32	0.30	0.32
TeO ₂	0.17	-	-
TiO ₂	-	0.01	-
Y ₂ O ₃	0.19	0.1	0.19
ZrO ₂	1.55	1.45	1.57
LOI (at 500°C)	-	-	-
Total	99.58	99.16	100.00

Glasses (~400g) were melted at 1100°C in a Pt crucible in air for two hours applying stirring during last 40 min. Then several glass fibres of about 1 m length and 1 mm in diameter were drawn from the melt; the rest of melt was cast into bars and annealed for 1 h at 560°C. After 1h the samples were gradually cooled down at a cooling rate 1K/min. The fibres were characterised by scanning electron microscopy (SEM) and powder X-ray diffraction (XRD) and then used for leaching tests. The annealed bars were also studied using SEM techniques and were used for analysis of thermal properties.

Thermal expansion was measured in the temperature interval 30-580°C, and indicated that the glass transition temperature $T_g = 494^\circ\text{C}$, softening point $T_s = 538^\circ\text{C}$ and thermal expansion coefficient $\kappa = 8.9 \cdot 10^{-6} \text{ K}^{-1}$.

SEM characterization, performed using a JEOL 6400 scanning electron microscope operating at 20kV, reveals heterogeneities, in line with to previous studies [11]. Moreover some phase

separation was observed (Fig. 2), characterised by small droplets of 10 to 20 μm sizes, in which further fine segregation on a scale of about 100nm was observed.



Fig. 2. British Magnox-waste glass secondary electron image.

XRD was conducted using a Philips PW 1050 goniometer with PW 1710 control device fitted with a Co tube and indicates (Fig.3) that the glass is amorphous as the only peaks observed were due to the Al sample-holder.

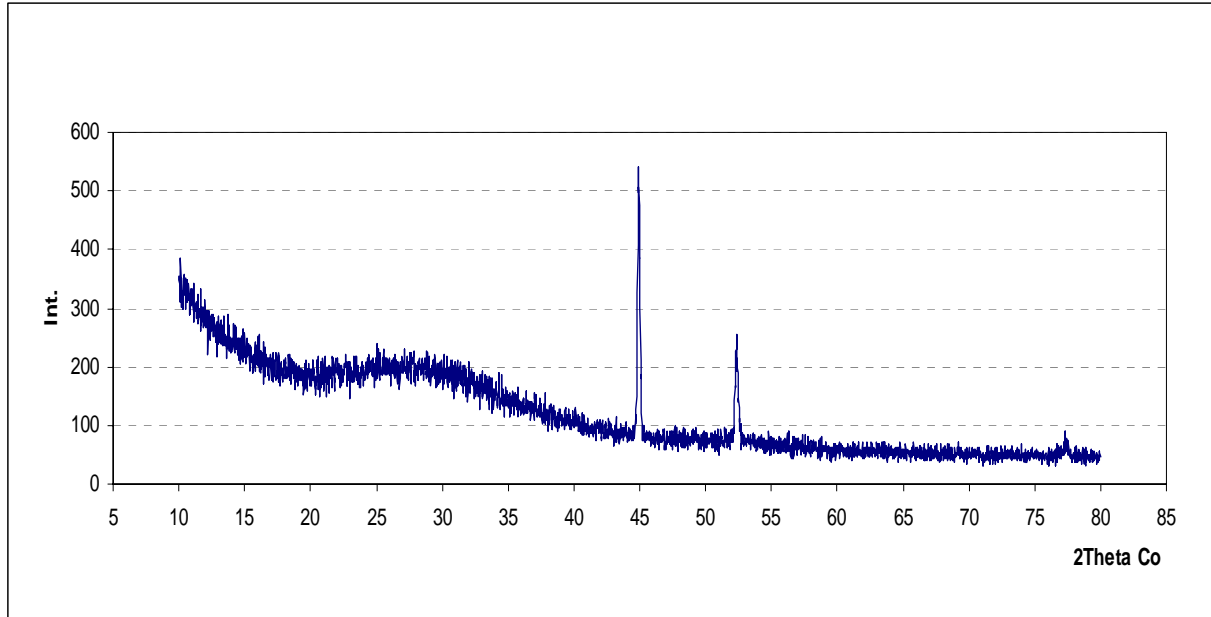


Fig. 3. XRD pattern of the British magnox-waste glass.

Leaching tests were carried out using the MCC-1 standard as a basic leaching procedure. Cation releases were investigated at 40 and 50°C in pseudo-dynamic conditions. The duration of leaching tests was limited to one month ensuring a pure ion exchange phase of glass corrosion (Fig. 1). PTFE containers of 100ml capacity filled with 90ml of deionised water were used. The surface area of glass in each experiment was in the range $S=(2.8-4.5) \text{ cm}^2$ giving a surface area to contacting water volume ratio $S/V=3-5\text{m}^{-1}$. Aliquots for chemical analysis were taken from the containers after 3, 15 and 27 days. The solution pH was measured during sampling and found to be in the range 6.7-7.0. After sampling half (45ml) of leachates were replacing by fresh deionised water. Solutions taken were filtered through a 45 μm 3M-filter then analysed using an inductively coupled plasma mass spectrometer, ICP-MS 4500.

Experimental normalised leaching rates of cations NR_i ($\text{g cm}^{-2}\cdot\text{d}^{-1}$) were calculated using

$$NR_i = \frac{m_i}{f_i S t}, \quad (\text{Eq.11})$$

where m_i is the total leached mass of the i -th component (g), S is the geometric surface area of the specimen in contact with water (cm^2) and t is the duration of the leaching period (d). Measured normalised leaching rates at 40°C, given in Fig.4, decrease with time in line with the above theoretical description (Eq.10).

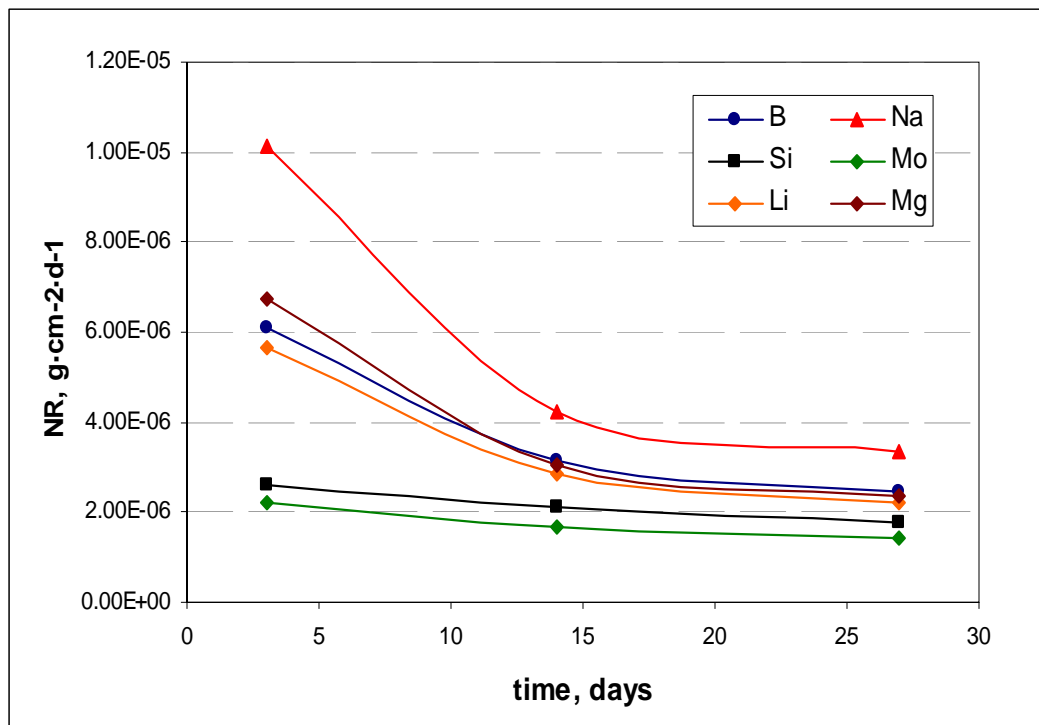


Fig. 4. Normalised cation leach rates from British Magnox-waste glass at 40°C.

Eq.6 indicated that the higher the temperature the higher the leaching rates. This is confirmed experimentally by the data in Table II, which gives cation leaching rates measured at 50°C.

Table II. Normalized Leach Rates of Cations from British Magnox-Waste Glasses Leached for 3 Days at 50°C.

Cation	NR _i , g cm ⁻² d ⁻¹
Si	7.74 10 ⁻⁶
B	1.20 10 ⁻⁵
Mo	7.32 10 ⁻⁶
Mg	3.81 10 ⁻⁶
Li	1.18 10 ⁻⁵
Na	1.31 10 ⁻⁵

Normalised leaching rates obtained to date in the present study are of the same order of magnitude as those obtained by Abratis *et al.* [10]. To fully identify the parameters governing ion-exchange of British Magnox-waste glass (such as D_i and E_{di}) the current leaching studies will be continued and extended to cover pre-irradiated glasses.

CONCLUSIONS

A research programme on the leaching behaviour of British Magnox-waste glasses is being conducted. Normalised leaching rates, measured for a number of cations, all diminished with time, which is characteristic of the ion exchange phase of glass corrosion. Based on evidence

obtained to date in dilute near-neutral solutions diffusion-controlled ion exchange in British Magnox-waste glasses is the main cation release mechanism which may persist for times exceeding ten years at ambient temperatures $\sim 10\text{-}15^\circ\text{C}$. This study is being extended to look at pre-irradiated glass.

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