The initial dissolution rates of simulated UK Magnox–ThORP blend nuclear waste glass as a function of pH, temperature and waste loading

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ABSTRACT

The first comprehensive assessment of the dissolution kinetics of simulant Magnox–ThORP blended UK high-level waste glass, obtained by performing a range of single-pass flow-through experiments, is reported here. Inherent forward rates of glass dissolution were determined over a temperature range of 23 to 70°C and an alkaline pH range of 8.0 to 12.0. Linear regression techniques were applied to the TST kinetic rate law to obtain fundamental parameters necessary to model the dissolution kinetics of UK high-level waste glass (the activation energy (E_a), pH power law coefficient (n) and the intrinsic rate constant (k_0)), which is of importance to the post-closure safety case for the geological disposal of vitreous products. The activation energies based on B release ranged from 55 ± 3 to 83 ± 9 kJ mol⁻¹, indicating that Magnox–THORP blend glass dissolution has a surface-controlled mechanism, similar to that of other high-level waste simulant glass compositions such as the French SON68 and LAW in the US. Forward dissolution rates, based on Si, B and Na release, suggested that the dissolution mechanism under dilute conditions, and pH and temperature ranges of this study, was not sensitive to composition as defined by HLW-incorporation rate.

KEYWORDS: glass, dissolution mechanism, geological disposal.

Introduction

To predict the performance of nuclear waste glasses in a geological disposal facility (GDF), an understanding of the glass dissolution rate, in the context of the geochemical settings, is required. In recent years, several studies have focused on understanding the mechanism of glass alteration (for a recent overview, see Gin et al., 2013a, and references therein) as a function of composition, temperature, pH and solution chemistry; e.g. French SON68 glass (Curti et al., 2006; Gin et al., 2013b) and USA LAW glasses (e.g. McGrail et al., 1997; Pierce et al., 2008). The kinetics of glass dissolution are typically modelled using Transition State Theory (TST), which, in its simplified form, is given by:

\[ R_i = k_0 v_i e^{-E_a/RT} a_H^n \left[ 1 - \left( \frac{Q}{K} \right)^\frac{a}{a_H} \right] \]  

where \( R_i \) is the release rate of glass component \( i \), \( k_0 \) is the intrinsic rate constant, \( v_i \) is the stoichiometric coefficient for element \( i \), \( E_a \) is the activation energy, and \( a \) and \( a_H \) are the activity of the glass and solution, respectively, and \( Q \) and \( K \) are the partition coefficients of the solute and solvent in the glass, respectively.
RT is the product of the gas constant and the absolute temperature, \( a_{H^+} \) is the hydronium ion activity, \( \eta H^+ \) is the reaction order with respect to \( a_{H^+} \), \( Q \) is the activity product of the rate-limiting reaction, \( K \) is the equilibrium constant for the reaction, and \( \sigma \) is the overall reaction order (McGrail et al., 1997). Several different experimental methods have been applied to determine glass-dissolution behaviour: conventional static PCT and MCC-1 methods are most widely applied (ASTM, 1994; MCC, 1981). Flow-through approaches, including single-pass flow-through (SPFT) and micro-channel flow-through (MCFT) methodologies, however, are considered most appropriate to determine the reaction kinetics of glass dissolution (McGrail and Peeler, 1995). The continual introduction of fresh reaction media in the ‘flow-through’ methodology ensures that conditions are dilute, which is necessary to prevent the accumulation of reaction products. This maintains the chemical affinity term, \( Q/K \), at near zero so that the inherent ‘forward rate’ of dissolution is sustained and experimental parameters such as temperature and pH can be varied to yield an accurate quantitative description of their impact on dissolution kinetics.

In the UK, the high-level waste (HLW) calcine resulting from Magnox and ThORP (Thermal Oxide Reprocessing Plant) reprocessing operations is combined in a \( \sim 1:3 \) ratio (Magnox:ThORP calcine) and vitrified in a borosilicate glass. Waste loadings of this vitrified product have typically been in the range of 25–28 wt.% (on the basis of metal oxides), although increased waste loadings have been demonstrated and produced successfully (Harrison et al., 2012). In comparison, the waste loading of a similar French product is typically 15–18 wt.% (Curti et al., 2006). To date, studies of the mechanism and kinetics of the dissolution of non-radioactive analogues of this complex glass blend have been limited to static batch experiments. For example, Corkhill et al. (2013) determined the leaching mechanisms of monolith samples for 168 days in water; Hyatt et al. (2004) performed an evaluation of the dissolution behaviour under the likely conditions of very deep borehole geological disposal and Utton et al. (2012) and Corkhill et al. (2013) investigated the static dissolution behaviour in simulated cement pore waters. The dissolution kinetics of inactive simulant Magnox glass have also received limited attention; a small matrix of static experiments and flow-through experiments at 40°C and pH 10 were performed by Abraitis et al. (2000a,b,c), while Curti et al. (2006) performed long-term (548 days) leaching experiments on Magnox glass powder at 90°C in distilled water and showed that SON68 is approximately seven times more durable than Magnox glass. Note, however, that HLW glasses produced from a pure Magnox waste composition will ultimately form a small fraction of the total 2900 tonnes of vitrified product destined for geological disposal (NDA, 2014); the majority of the inventory will be of a blend composition. Consequently, it is imperative to understand the mechanism and to quantify the kinetics of Magnox–ThORP blend glass.

This investigation utilizes the single-pass flow-through methodology in order to provide the first comprehensive study of the dissolution kinetics of simulant UK Magnox–ThORP blended HLW glass. Furthermore, because it is important from an economic and operational perspective to maximize the waste loading of the vitrified HLW product, we investigate the effect of increasing the percentage of the Magnox component of the blend glass on the forward rate of dissolution.

**Experimental procedure**

**Glass synthesis**

Simulant Magnox–ThORP blend glasses (blended at a ratio of 1:3) were prepared at two different waste loadings: 25 wt.% (referred to as MT25 throughout the investigation) and 30 wt.% (referred to as MT30 throughout the investigation). Glasses were prepared using a baseline glass frit and a blended nuclear waste simulant calcine, both kindly provided by the National Nuclear Laboratory, UK. Batched frit and calcine were mixed by hand in HDPE bottles for 2 min, added to a pre-heated mullite crucible and placed in a furnace at 1060°C for 1 h. Subsequently, the batch was stirred for a further 4 h at 1060°C, cast into a block using a pre-heated stainless steel mould, annealed at 500°C for 1 h, and then cooled at 1°C min\(^{-1}\) to room temperature. Final glass compositions, as measured using X-ray fluorescence (Assay Office, Sheffield, UK) are given in Table 1. X-ray diffraction and SEM/EDX analysis confirmed the homogeneous nature of the glass compositions formed.

Glasses were crushed and powdered using a Tema ring and puck mill and sieved to the 75–150 \( \mu \)m size fraction, giving an average glass-particle radius of 56.3 ± 0.65 \( \mu \)m. Density measurements of both glasses were performed using the Archimedes method yielding a density of 2.77 ± 0.01 g cm\(^{-3}\). The surface area of the glass powders was calculated.
geometrically, according to Icenhower and Steefel (2013). Glass powders were cleaned prior to dissolution according to the Product Consistency Test (PCT) ASTM standard (ASTM, 1994).

**Buffer solutions**

The buffer solutions used to control the pH during single-pass flow-through experiments are summarized in Table 2. For buffer solutions at pH 8.0 and 10.0, measured amounts of the organic tris hydroxymethyl aminomethane buffer (THAM, 99% purity, Fisher Scientific) were added to ultra-high quality (18 MΩ cm$^{-1}$) water and adjusted to the desired pH at room temperature ($23 ± 2°C$) with 15 M HNO$_3$ (99.999% trace metals basis, Fisher Scientific). Final pH values at room temperature [denoted throughout the study as pH(23°C)] were pH(23°C) 8.00 ± 0.05 and pH(23°C) 10.00 ± 0.05. For buffer solutions at pH 12.0, 0.01 M LiOH and 0.01 M LiCl (both 99.99% purity, Alpha Aesar) were prepared and adjusted to pH(23°C) 12.00 ± 0.05 with 0.01 M LiOH. To ensure the accuracy of the buffered pH value, especially under the highest pH conditions, which may be susceptible to pH drift, the solution pH was measured under the desired test conditions at regular time points for 48 h. No drift in pH values was observed (within error), indicating that atmospheric CO$_2$ did not lower the pH for the duration of the SPFT experiments. Table 2 gives a summary of the pH values calculated for each test temperature (23°C, 40°C and 70°C) using the PHREEQC geochemical modelling software with the LLNL database.

**Single-pass flow-through methodology**

All single-pass flow-through (SPFT) experiments utilized Kloehn v6 syringe pumps. Buffer solutions were transferred from 1 L HDPE input reservoirs to PTFE reactors via PTFE tubing into one of two ports on the vessel lid. The buffer solutions and reaction vessels were both kept in a constant-temperature oven ($±2°C$) in order to minimize the effects of varying temperature between the buffer solution reservoir and the reaction vessel. The solution was then transferred from the second port in the reaction vessel, via PTFE tubing, to an HDPE

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**Table 1. Chemical compositions (wt.%) of simulant Magnox – ThORP blend nuclear waste glass specimens.**

| Oxide component | MT25   | MT30   |
|-----------------|--------|--------|
| SiO$_2$         | 46.28  | 44.33  |
| B$_2$O$_3$      | 18.3   | 17.74  |
| Na$_2$O         | 8.12   | 7.74   |
| Li$_2$O         | 4.81   | 4.34   |
| Gd$_2$O$_3$     | 3.86   | 4.17   |
| ZrO$_2$         | 2.40   | 2.81   |
| MoO$_3$         | 2.02   | 2.48   |
| Al$_2$O$_3$     | 1.87   | 2.35   |
| Fe$_2$O$_3$     | 1.87   | 2.06   |
| Nd$_2$O$_3$     | 1.81   | 1.86   |
| Cs$_2$O         | 1.61   | 1.99   |
| MgO             | 1.34   | 1.64   |
| Ce$_2$O         | 1.24   | 1.38   |
| BaO             | 1.22   | 1.38   |
| La$_2$O$_3$     | 0.67   | 0.73   |
| RuO$_2$         | 0.49   | 0.51   |
| Pr$_2$O$_3$     | 0.47   | 0.46   |
| Cr$_2$O$_3$     | 0.37   | 0.46   |
| SrO             | 0.32   | 0.36   |
| NiO             | 0.28   | 0.47   |
| Sm$_2$O$_3$     | 0.28   | 0.33   |
| TeO$_2$         | 0.28   | 0.30   |
| Y$_2$O$_3$      | 0.10   | 0.10   |
| Total           | 100.00 | 99.99  |

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**Table 2. Chemical compositions of buffer solutions used for single-pass flow-through experiments. Solution pH values (±0.05 pH units) above 23°C were calculated using PHREEQC (LLNL database).**

| Solution | Composition                                           | pH       |
|----------|------------------------------------------------------|----------|
|          |                                                      | 23°C | 40°C | 70°C |
| 1        | 0.05 M THAM* + 15 M HNO$_3$ pH adjustment            | 8.0    | 7.9  | 7.6  |
| 2        | 0.05 M THAM + 15 M HNO$_3$ pH adjustment             | 10.0   | 9.8  | 9.3  |
| 3        | 0.01 M LiOH + 0.01 M LiCl pH adjustment              | 12.0   | 11.5 | 10.7 |

*THAM = tris hydroxymethyl aminomethane buffer.*
collection vessel outside the oven, prior to analysis. The flow rate was determined by weighing the volume of solution collected at each sampling time; variations were typically <3%. Once constant conditions were established (e.g. buffer pH, temperature of blank solution and flow rate), crushed glass was placed within each test vessel. Experiments were run at flow rates ranging from 5 ml d⁻¹ to 125 ml d⁻¹ until steady-state effluent chemistries were observed. Blank experiments were performed in order to provide controlled blank analyses. All effluent solutions were analysed for Si, B and Na using inductively coupled plasma optical emission spectroscopy (ICP-OES) and pH was measured using a calibrated pH electrode. Due to the dilute conditions of the experiments, it was only possible to measure those elements that are present in the solution above the detection limit, therefore it was not possible to present data for the minor elements in each glass composition (the detection limits for the major elements analysed, B, Si and Na, were 10, 20 and 50 µg l⁻¹, respectively). For a detailed account of the SPFT apparatus, the reader is directed to the extensive descriptions by McGrail et al. (1997), Pierce et al. (2005, 2008), Icenhower et al. (2006) and Wellman et al. (2006).

Quantification of dissolution rates

Normalized elemental release rates were determined by equation 2:

\[ R_i = \frac{(C_i - \bar{C}_{i,b})q}{f_iS} \]  

(2)

where \( R_i \) is the normalized glass dissolution rate of element \( i \) (g m⁻² d⁻¹), \( C_i \) the concentration of element \( i \) in the effluent (g l⁻¹), \( \bar{C}_{i,b} \) the average background concentration of element \( i \) (g l⁻¹), \( q \) the flow-through rate (l d⁻¹), \( f_i \) the mass fraction of the element in the glass (unitless), and \( S \) the surface area of the sample (m²). Determination of the experimental uncertainty of the dissolution rate considered the uncertainties of each parameter described in equation 2. For uncorrelated random errors, the standard deviation of a function \( f(x_1, x_2, x_n) \) is given by:

\[ \sigma_f = \sqrt{\sum_{i=1}^{n} \left( \frac{\partial f}{\partial x_i} \right)^2 \sigma_i^2} \]  

(3)

where \( \sigma_f \) is the standard deviation of the function \( f \), \( x_i \) the parameter \( i \), and \( \sigma_i \) the standard deviation of parameter \( i \). Substituting equation 2 into equation 3 and converting to relative errors, \( \hat{\sigma}_{R_i} = \frac{\sigma_{R_i}}{R_i} \), gives:

\[ \hat{\sigma}_{R_i} = \sqrt{\frac{(\bar{C}_i C_i)^2 + (\bar{C}_{i,b} C_i)^2}{(C_i - \bar{C}_{i,b})^2} + \sigma_q^2 + \sigma_{f_i}^2 + \sigma_S^2} \]  

(4)

relative errors of \( \bar{C}_i, \sigma_{C_i}, \bar{C}_{i,b}, \sigma_{f_i}, \) and \( \sigma_S \) are 10%, 10%, 5%, 3% and 15%, respectively (Pierce et al., 2010).

Results and Discussion

Effect of flow rate (q) to sample surface area (S) ratio on dissolution rate

Prior to performing experiments to determine the dependence of dissolution rate on temperature and pH, the effect of varying the ratio of flow rate, \( q \), to sample surface area, \( S \), was determined experimentally by altering the flow rate or the mass of the glass sample used in an SPFT experiment. Varying the \( q/S \) ratio can influence the chemical potential between the glass and a solution; at low \( q/S \) values the concentration of elements dissolved in solution from the glass is high; conversely at high \( q/S \) values, the concentration of elements dissolved in solution is low, thereby minimizing the effect of chemical potential on dissolution. The desired \( q/S \) value is relatively high, ensuring that the dissolution is independent of \( q/S \), such that the forward rate of dissolution is acquired.

The variation of \( q/S \) was investigated at 40°C and pH(23°C) = 8.0. The normalized dissolution rates based on the concentrations of Si, B and Na as a function of \( q/S \) are shown for the MT25 (Fig. 1a) and MT30 (Fig. 1b) glass blends. For MT25, the normalized dissolution rates of the elemental components were found to reach a constant value of \( R_B = 0.049 \pm 0.006 \) g m⁻² d⁻¹ at \( \log_{10} (q/S) \approx -7.5 \) m s⁻¹ (Fig. 1a). For the MT30 glass, shown in Fig. 1b, a constant value of \( R_B = 0.020 \pm 0.001 \) g m⁻² d⁻¹ was achieved at \( \log_{10} (q/S) \approx -7.5 \) m s⁻¹. For both glass compositions, \( \log_{10} (q/S) \) values of -6.8 to -9.2 m s⁻¹ were attempted; variations from set flow rates were observed at low \( q/S \) values, however, between \( \log_{10} (q/S) \) values of -9.2 and -8.0 m s⁻¹ for MT25, and \( \log_{10} (q/S) \) values of -9.2 and -8.3 m s⁻¹ for MT30. This deviation was due to air becoming trapped within the tubing that transfers effluent from the reaction vessel to the collection vessel. Previous SPFT investigation of Magnox glass found that the normalized
dissolution rate of B and Si became constant, i.e. independent of \( q/S \), at a \( \log_{10}(q/S) \) value of \(-6.3\) \( \text{m s}^{-1} \) at 40°C and \( \text{pH}(23^\circ\text{C}) = 10.0 \) (Abraitis et al., 2000b). Similarly, in their study of simulated vitrified Hanford Low Activity Waste (LAW), McGrail et al. (1997) reported that Na and Si dissolution rates became independent of \( q/S \) at a \( \log_{10}(q/S) \) value of \(-7.3\) \( \text{m s}^{-1} \) at 40°C and \( \text{pH}(23^\circ\text{C}) = 9.0 \). As such, although it was not possible to report the full range of \( \log_{10}(q/S) \) values due to experimental issues, we are confident that the selection of a \( \log_{10}(q/S) \) value of > \(-7.5\) \( \text{m s}^{-1} \) is suitable for analysis of a \( q/S \) independent dissolution rate. Furthermore, as it is understood that using the highest possible \( q/S \) value eliminates the potential effects of temperature increase on the dissolution rate (McGrail et al., 1997), a \( \log_{10}(q/S) \) value of \(-6.5 \pm 10\% \text{ m s}^{-1} \) was...
selected to determine the forward rate of dissolution for both MT25 and MT30 blend glasses. Figure 1 also illustrates that over the range of \( q/S \) values investigated, the constituent elements Si, B and Na were released congruently from both glass compositions, within experimental error. This further confirms the appropriate choice of a higher \( \log_{10}(q/S) \) value.

**Effect of temperature on dissolution rate**

Experiments were performed at a range of temperatures (23°C, 40°C and 70°C) to evaluate the effect of temperature on the rate of MT25 and MT30 blend glass dissolution. The normalized dissolution rates for Si, B and Na as a function of temperature at three different pH(23°C) values are given in Table 3 and Fig. 2.

The normalized dissolution rates of MT25 and MT30 blend glass compositions are comparable with those for Magnox glass studied under SPFT conditions. For example, Abraitis et al. (2000b), who reported rates based on B release only, observed a dissolution rate, \( R_B \), of 0.139 ± 0.034 g m^{-2} d^{-1} at 40°C and pH 10, compared with an \( R_B \) of 0.106 ± 0.032 g m^{-2} d^{-1} for MT25 under the same conditions in the current study (Table 3). The similarity of the B release rates reported here to those of Abraitis et al. (2000b)

### Table 3. Normalized dissolution rate (g m^{-2} d^{-1}) of Si (R_Si), B (R_B) and Na (R_Na) and for MT25 and MT30 blend simulated waste glass as a function of pH and temperature, including the difference in normalized dissolution rate (\( \Delta R \)) between the two compositions.

| pH  | Temperature (°C) | MT25 R_i (g m^{-2} d^{-1}) | MT30 R_i (g m^{-2} d^{-1}) | \( \Delta R_i \) (g m^{-2} d^{-1}) |
|-----|-----------------|-----------------------------|-----------------------------|-----------------------------------|
| 8   | 23              | 0.011 ± 0.004               | 0.020 ± 0.001               | 0.009                             |
| 8   | 40              | 0.119 ± 0.036               | 0.105 ± 0.032               | 0.014                             |
| 8   | 70              | 0.945 ± 0.284               | 0.369 ± 0.091               | 0.576                             |
| 10  | 23              | 0.027 ± 0.010               | 0.024 ± 0.009               | 0.003                             |
| 10  | 40              | 0.321 ± 0.096               | 0.436 ± 0.143               | 0.115                             |
| 10  | 70              | 4.148 ± 1.245               | 6.038 ± 3.156               | 2.890                             |
| 12  | 23              | 0.642 ± 0.249               | 0.778 ± 0.217               | 0.136                             |
| 12  | 40              | 4.403 ± 1.323               | 7.638 ± 3.156               | 3.235                             |
| 12  | 70              | 45.786 ± 6.767              | 61.292 ± 9.016              | 15.506                            |
| 8   | 23              | 0.005 ± 0.001               | 0.005 ± 0.002               | 0.000                             |
| 8   | 40              | 0.051 ± 0.015               | 0.022 ± 0.003               | 0.029                             |
| 8   | 70              | 0.395 ± 0.119               | 0.369 ± 0.091               | 0.026                             |
| 10  | 23              | 0.027 ± 0.010               | 0.024 ± 0.003               | 0.003                             |
| 10  | 40              | 0.106 ± 0.032               | 0.189 ± 0.080               | 0.083                             |
| 10  | 70              | 2.548 ± 0.772               | 1.570 ± 0.471               | 0.978                             |
| 12  | 23              | 0.489 ± 0.189               | 0.536 ± 0.208               | 0.047                             |
| 12  | 40              | 2.160 ± 0.651               | 2.643 ± 0.401               | 0.483                             |
| 12  | 70              | 12.059 ± 5.220              | 4.915 ± 1.480               | 7.144                             |
| 8   | 23              | 0.011 ± 0.001               | 0.015 ± 0.004               | 0.004                             |
| 8   | 40              | 0.057 ± 0.022               | 0.050 ± 0.019               | 0.006                             |
| 8   | 70              | 1.006 ± 0.305               | 0.497 ± 0.497               | 0.509                             |
| 10  | 23              | 0.010 ± 0.030               | 0.067 ± 0.022               | 0.034                             |
| 10  | 40              | 0.225 ± 0.068               | 0.394 ± 0.167               | 0.169                             |
| 10  | 70              | 4.827 ± 2.064               | 5.684 ± 0.859               | 0.857                             |
| 12  | 23              | 1.963 ± 0.760               | 0.899 ± 0.221               | 0.164                             |
| 12  | 40              | 6.827 ± 2.064               | 3.146 ± 1.335               | 3.681                             |
| 12  | 70              | 33.049 ± 5.749              | 18.763 ± 5.647              | 14.286                            |
Fig. 2. Ln normalized dissolution rate ($R_i$, g m$^{-2}$ d$^{-1}$) as a function of the inverse of temperature (from 23 to 70°C) and pH (23°C) of 8.0, 10.0 and 12.0 of: (a) Si; (b) B; and (c) Na, for MT25 and MT30 blend simulated waste glass.
suggest that the dependence of dissolution on glass composition is weak in the case of Magnox and Magnox–ThORP blend glass; it is not possible, however, to confirm this observation without additional comparison of Si and Na release rates under the full range of conditions investigated.

Dissolution rates for Magnox glass and Magnox–ThORP blend glass obtained through conventional static leaching methods at pH(23°C) = ~10 show a high degree of variability in the dissolution rate. For example, Utton et al. (2012) reported an $R_b$ of 0.024 ± 0.004 g m$^{-2}$ d$^{-1}$ for MT25 blend glass powders at pH(23°C) = ~10.0 for 89 days (a factor of two greater than reported in the current study) while Curti et al. (2006) reported a significantly lower value of $R_b$ ($9.6 ± 5.3 \times 10^{-4}$ g m$^{-2}$ d$^{-1}$) for Magnox simulant glass powders leached at pH 9.6 for 548 days; the lower value may reflect the potentially passivating nature of the alteration products formed on the glass surface. Interestingly, although alteration layers were also formed on the surface of monolith MT25 blend glass samples leached in water for 168 days at pH(23°C) = ~10.0, Corkhill et al. (2013) reported an $R_b$ of 0.030 ± 0.003 g m$^{-2}$ d$^{-1}$, similar to that reported for the forward rate under the same conditions in the current study. This variability is probably due to the methodology employed; as discussed previously, static experiments are subject to solution feedback effects, i.e. the accumulation of reaction products, which influence the dissolution rate. These results highlight the importance of using flow-through methodologies to accurately, and reproducibly, determine the dissolution kinetics of high-level waste glasses under conditions relevant to geological disposal.

The results in Table 3 show that increasing the temperature resulted in an increase in the normalized dissolution rate of each element. The observed dependence of temperature on the dissolution rate can be described by the Arrhenius equation:

$$ r = A \frac{E_a}{R T} $$

(5)

where $r$ is the dissolution rate (g m$^{-2}$ d$^{-1}$), $A$ is the Arrhenius parameter (g m$^{-2}$ d$^{-1}$), $E_a$ is the activation energy (kJ mol$^{-1}$), $R$ is the ideal gas constant in J (mol K)$^{-1}$ and $T$ is the temperature (K). Using the Arrhenius dependence of dissolution rate on temperature, linear regression of the data plotted in Fig. 2 was used to calculate the activation energy for Si, B and Na at each pH value, in both MT25 and MT30 blend glass compositions. The resulting values and 2σ errors are shown in Table 4. The $E_a$ values for both glass blends were found to range between 67.5 ± 0.9 and 96.4 ± 28.8 kJ mol$^{-1}$ for Si, 55.1 ± 3.2 and 83.1 ± 9.1 kJ mol$^{-1}$ for B and between 52.2 ± 2.8 and 84.2 ± 9.2 kJ mol$^{-1}$ for Na. These values are comparable to activation energy values for Magnox glass ($E_a = 56$ to 74 kJ mol$^{-1}$, Abraitis et al., 2000a); pure silica ($E_a = 74.5$ kJ mol$^{-1}$, Dove, 1994; Icenhower and Dove, 2000), Hanford HAW glass ($E_a = 74.8$ kJ mol$^{-1}$, McGrail et al., 1997) and a number of other glass compositions in the aluminoborosilicate glass family (e.g. Wolf–Boesnich et al., 2004; Pierce et al., 2008, 2010; Jollivet et al., 2012).

Within the limits of precision, the activation energy values for the MT25 and MT30 blend glasses are in the range proposed by Lasaga (1981) to be consistent with a surface–controlled dissolution mechanism (typically from 41 and 84 kJ mol$^{-1}$). This mechanism is widely agreed to occur by the inter-diffusion between H (as H$^+$ or H$_3$O$^+$) in solution and network modifying cations in the glass, whilst ionic–covalent bonds of the network forming elements (Si–O–Si, Si–O–B, Si–O–Na, etc.) undergo hydrolysis, resulting in nucleophilic attack by OH$^-$ (Gin et al., 2013a). The rate-limiting

| pH | $E_{a(Si)}$ (kJ mol$^{-1}$) | $E_{a(B)}$ (kJ mol$^{-1}$) | $E_{a(Na)}$ (kJ mol$^{-1}$) |
|----|--------------------------|--------------------------|--------------------------|
|    | MT25 | MT30 | $\Delta E_{a(Si)}$ | MT25 | MT30 | $\Delta E_{a(B)}$ | MT25 | MT30 | $\Delta E_{a(Na)}$ |
| 8  | 78.1 ± 5.9 | 67.5 ± 0.9 | 10.6 | 55.1 ± 3.2 | 57.9 ± 2.4 | 2.8 | 58.4 ± 4.8 | 52.2 ± 2.8 | 6.2 |
| 10 | 90.5 ± 5.7 | 85.4 ± 0.3 | 5.1 | 79.7 ± 9.6 | 66.1 ± 3.2 | 13.6 | 80.4 ± 7.5 | 77.3 ± 10.9 | 3.1 |
| 12 | 96.4 ± 28.8 | 86.2 ± 20.2 | 8.4 | 83.1 ± 9.1 | 70.8 ± 2.0 | 12.3 | 84.2 ± 9.2 | 76.6 ± 8.1 | 7.6 |

Table 4. Calculated activation energies ($E_{a(i)}$ kJ mol$^{-1}$) for MT25 and MT30 blend simulated waste glass, derived from regression analysis based on the steady-state release of Si, B and Na, including the difference in $E_{a(i)}$ between the two glass blend compositions.
Effect of solution pH on dissolution rate

Experiments were performed at a range of alkaline pH(23°C) values, from 8.0 to 12.0. These alkaline values were chosen for investigation for several reasons: firstly, under slow groundwater-flow conditions the repository environment is expected to buffer to slightly alkaline pH, for example, bentonite is predicted to buffer groundwater to a pH between 7.0 and 10.5 (Marsal, 2007); secondly, although UK HLW vaults will probably be backfilled with clay, the potential interaction of concrete vault structures with vitrified HLW cannot be precluded on the timescales of GDF operation (105–106 y); and finally, the potential co-location of vitrified UK HLW with cementitious UK intermediate level waste may lead to the interaction of vitrified products with a high-pH groundwater derived from interaction with cementitious waste and backfill in the long term.

Figure 3 shows the log10 dissolution rates for Si, B and Na (Figs 3a–c, respectively) as a function of pH(23°C) at 23°C, 40°C and 70°C. The normalized dissolution-rate data are also given in Table 3. The dissolution rates were shown to increase with increasing pH for all of the components within each blend glass composition, e.g. for MT25 at 23°C, the $R_B$ increased from 0.020 ± 0.005 at pH(23°C) = 8.0, to 0.027 ± 0.010 at pH(23°C) = 10.0, and to 12.059 ± 5.220 at pH(23°C) = 12.0. Interestingly, the dissolution rates derived from boron release were consistently lower than those derived from Na or Si, especially at higher pH values (Table 3). In their molecular-dynamics investigation of the hydrolysis of Na-borosilicate glass surfaces, Zapol et al. (2013) found B–O–B and B–O–Si bridges were likely to be more stable at high pH compared with Si–O–Si bridges, which may explain the incongruent dissolution observed here for Si and B. A similar effect was observed experimentally by Pierce et al. (2008), who concluded that this reflected an increased rate of alkali ion exchange at high pH, associated with the breakdown of silanol bonds at the surface, which in effect ‘masked’ the matrix dissolution and resulted in a reduced B release rate. The solubility of silica above pH 9 is known to dramatically increase due to the dissociation of $\text{H}_2\text{SiO}_4^-$ into $\text{H}_2\text{SiO}_3^-$ and $\text{H}_2\text{SiO}_3^-$. As a consequence, it may be expected that the rate of Si release, and hence alkali ion release through ion exchange processes, above pH 9 is increased and the glass network, particularly at the surface, begins to break down. The behaviour of the two UK blend glasses investigated in this study appears consistent with this general mechanism.

A linear regression of the log10 normalized dissolution rates of Si, B and Na shown in Fig. 3 was performed using equation 6 to calculate the pH power-law coefficient (e.g. order of reaction), $\eta$ (dimensionless), and intrinsic rate constant, $k_0$ (g m$^{-2}$ d$^{-1}$), for the MT25 and MT30 blend glasses at each of the temperatures investigated. The results are shown in Tables 5 and 6, respectively.

$$R = k_0 10^{\eta \cdot \text{pH}}$$ (6)

The $\eta$ values reported for MT25 and MT30 are similar, and are in the range of $\eta_{\text{Si}} = 0.39 \pm 0.02$ to $0.49 \pm 0.02$, $\eta_{\text{B}} = 0.33 \pm 0.02$ to $0.53 \pm 0.03$, and $\eta_{\text{Na}} = 0.42 \pm 0.02$ to $0.58 \pm 0.03$ (Table 5). These values are similar to those reported for other glass materials, e.g. Magnox glass ($\eta_{\text{B}} = 0.43 \pm 0.07$, Abraitis et al., 2000a); R7T7 ($\eta_{\text{B}} = 0.39$, Vernaz and Dussossoy, 1992); basaltic and pure silica glass ($\eta_{\text{B}} = 0.40$, Brady and House, 1996) and other glasses in the aluminoborosilicate family, e.g. $\eta_{\text{Si}} = 0.40 \pm 0.03$ (McGrail et al., 1997), $\eta_{\text{B}} = 0.40 \pm 0.04$ (Pierce et al., 2008) and $\eta_{\text{Na}} = 0.45 \pm 0.14$ (Pierce et al., 2010).

The intrinsic rate constants for each element, calculated using a linear regression of data in Fig. 3 according to equation 6, were found to increase with increasing temperature (Table 6). For MT25, $k_{\text{Si}}$ was found to be $(2.84 \pm 0.31) \times 10^{-6}$ g m$^{-2}$ d$^{-1}$ at 23°C and $(4.68 \pm 0.52) \times 10^{-4}$ g m$^{-2}$ d$^{-1}$ at 70°C. This is in agreement with observations of LAW simulant glass dissolution, e.g. Pierce et al. (2008) reported values for $k_{\text{Si}}$ of $(8.30 \pm 7.00) \times 10^{-7}$ g m$^{-2}$ d$^{-1}$ at pH(23°C) and $(4.74 \pm 2.09) \times 10^{-5}$ g m$^{-2}$ d$^{-1}$ at pH(70°C). Values of $k_{\text{B}}$ and $k_{\text{Na}}$ also increased with increasing temperature, although to a lesser extent than observed for $k_{\text{Si}}$, consistent with the greater activation energies derived for Si than B and Na (Table 4), and due to the participation of Si in the rate limiting step of the surface-controlled dissolution mechanism. It
Fig. 3. Log10 normalized dissolution rate ($R_i$, g m$^{-2}$ d$^{-1}$) as a function of temperature- (23, 40 and 70°C) corrected pH for: (a) Si; (b) B; and (c) Na, released from MT25 and MT30 blend simulated waste glasses.
was not possible to make a comparison of the $k_0$ values reported here with those resulting from the SPFT investigation of Magnox glass by Abraitis et al. (2000b, c) or with French simulant glasses as the values were not reported.

Effect of waste loading on dissolution rate

The two glass blend compositions investigated in this study contained 25 wt.% and 30 wt.% loadings of Magnox–ThORP blended waste, respectively, with compositions given in Table 1. The forward rates of Si, B and Na dissolution were not found to be very sensitive to the composition, defined by the waste loading. Table 3 shows that the $\Delta R_i$ for all elements were more or less within error, except for normalized rates at pH(23°C) = 12.0 at 70°C for Si, B and Na; under these particular conditions there was no clear trend observed to determine whether one glass demonstrated greater dissolution rates than the other; e.g. $R_{Si}$ of MT30 was ~1.3 times greater than that of MT25 but the $R_{Na}$ of MT25 was a factor of ~1.8 times greater than that of MT30. Furthermore, the $\Delta E_a$ for each glass was similar, within error (Table 4), and the power law coefficients ($\eta$) were of the same order (Table 5). The intrinsic rate constants ($k_0$) for each glass differed slightly, though both glasses demonstrated an increase in $k_0$ with increasing temperature. Further investigation to confirm these observations and their mechanistic origin are required.

It may be concluded that increasing the waste loading by 5 wt.% did not appear to have any measurable effect on the initial dissolution rate, within error. The compositions of the two glasses investigated in the present study represent somewhat subtle changes in glass composition (Table 1); previous studies have shown that dramatically

| Temperature (°C) | $\eta_{Si}$  | $R^2_{Si}$ | $\eta_{B}$  | $R^2_{B}$  | $\eta_{Na}$ | $R^2_{Na}$ |
|------------------|-------------|------------|-------------|------------|-------------|------------|
| MT25             |             |            |             |            |             |            |
| 23               | 0.44 ± 0.02 | 0.97       | 0.35 ± 0.02 | 0.99       | 0.56 ± 0.03 | 0.96       |
| 40               | 0.44 ± 0.02 | 0.99       | 0.45 ± 0.02 | 0.99       | 0.46 ± 0.02 | 0.98       |
| 70               | 0.49 ± 0.02 | 0.96       | 0.33 ± 0.02 | 0.94       | 0.58 ± 0.03 | 0.99       |
| MT30             |             |            |             |            |             |            |
| 23               | 0.42 ± 0.02 | 0.99       | 0.52 ± 0.03 | 0.99       | 0.51 ± 0.03 | 0.92       |
| 40               | 0.39 ± 0.02 | 0.97       | 0.58 ± 0.03 | 0.99       | 0.53 ± 0.03 | 0.98       |
| 70               | 0.40 ± 0.02 | 0.99       | 0.36 ± 0.02 | 1.00       | 0.42 ± 0.02 | 0.99       |

| Temperature (°C) | $k_{Si}$     | $k_{B}$     | $k_{Na}$     |
|------------------|--------------|-------------|--------------|
| MT25             |              |             |              |
| 23               | $(2.84 ± 0.31) \times 10^{-6}$ | $(9.77 ± 0.11) \times 10^{-7}$ | $(2.46 ± 0.27) \times 10^{-7}$ |
| 40               | $(3.93 ± 0.43) \times 10^{-5}$ | $(1.25 ± 0.14) \times 10^{-5}$ | $(1.93 ± 0.21) \times 10^{-5}$ |
| 70               | $(4.68 ± 0.52) \times 10^{-4}$ | $(1.33 ± 0.15) \times 10^{-3}$ | $(1.93 ± 0.21) \times 10^{-4}$ |
| MT30             |              |             |              |
| 23               | $(5.02 ± 0.55) \times 10^{-6}$ | $(3.38 ± 0.37) \times 10^{-7}$ | $(8.04 ± 0.88) \times 10^{-7}$ |
| 40               | $(1.21 ± 0.13) \times 10^{-5}$ | $(1.70 ± 0.19) \times 10^{-6}$ | $(3.42 ± 0.38) \times 10^{-6}$ |
| 70               | $(8.25 ± 0.91) \times 10^{-4}$ | $(6.46 ± 0.71) \times 10^{-4}$ | $(4.94 ± 0.54) \times 10^{-4}$ |
Conclusions

We report the first comprehensive study of the dissolution kinetics of simulant UK Magnox–ThORP blended HLW glasses over a range of temperatures and alkaline pH regimes, including an investigation of the effect of altering glass composition on dissolution rate. The forward rate of dissolution for MT25 and MT30 blend glasses was found to be temperature and pH dependent, and results suggested that dissolution was a surface-controlled process, limited by the rupture of Si–O bonds and detachment of Si from the glass surface. This process was influenced by the high solubility of silica at high pH, which resulted in elevated dissolution rates at the highest pH values. The addition of 5 wt.% waste to the glass composition had a negligible effect on the dissolution kinetics in the forward rate, probably because of the minimal changes in glass composition and structure through such an addition. This is consistent with the observation that the forward rate of dissolution, based on B release, was in agreement with that previously derived for pure Magnox glass under dilute conditions. In contrast, the dissolution rates found did not agree with those reported in the literature for Magnox and Magnox–ThORP blend glasses due to the experimental variability of the static methodologies employed. These data highlight the importance of using flow-through methodologies to determine the kinetic parameters (η, k0 and Ea) for UK vitrified HLW that can be applied to the derivation of the source term used in post-closure safety assessments for geological disposal of HLW glass. Extended SPFT experiments at acidic to neutral conditions will probably be beneficial to further understanding the Magnox–ThORP blend glass dissolution, as will further long-term dissolution studies of these materials under a variety of conditions relevant to geological disposal environments.

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