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Corrosion of alkali–borosilicate waste glass K-26 in non-saturated conditions

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Abstract

Experimental data obtained during long term environmental tests of a nuclear waste alkali–borosilicate glass K-26 in an experimental near-surface repository are examined. Average leaching rates of the radionuclides were calculated: the leach rates gradually diminished from $9.4 \times 10^{-7}\,\mathrm{g\,cm^{-2}\,day^{-1}}$ over the first year to $2.2 \times 10^{-7}\,\mathrm{g\,cm^{-2}\,day^{-1}}$ over 16 years of tests. Radionuclide losses obey a square root time dependence indicating a diffusion-controlled release mechanism. The main parameters, which control the corrosion of waste glass K-26 in the near-surface repository, are the effective diffusion coefficient of radiocaesium D_{Cs} and the rate of glass hydrolysis r_h. Analysis of 16 years experimental data gave $D_{\mathrm{Cs}} = 4.5 \times 10^{-12}\,\mathrm{cm^2\,day^{-1}}$ and $r_h = 0.1\,\mu\mathrm{m\,years^{-1}}$. Diffusion is predicted to be dominant for 16.4 years after which diffusion and hydrolytic dissolution are expected to be similarly important. This mixed stage is predicted continue for 262 years after which hydrolytic dissolution will be the dominant mechanism.
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1. Introduction

Vitrification is one of the most advanced immobilisation options for radioactive and toxic wastes which provides long-term, safe isolation of radionuclides and toxic species from the environment [1]. It has been used for more than 40 years to immobilise high-level waste (HLW) arising from nuclear fuel reprocessing and currently is attracting great interest for other types of wastes, such as operational radioactive wastes from nuclear power plants as well as radioactive and toxic legacy wastes [2–4]. Large scale vitrification programmes are underway in a number of countries and new applications can be expected in the future [1–5]. Utilisation of glass as a waste form requires appropriate performance assessment support for waste disposal facilities, which presumes an understanding of the main glass corrosion mechanisms. One of possible disposal options for vitrified radioactive waste is emplacement in a non-saturated wet environment such as near-surface repositories. These are only intended for vitrified low and intermediate level waste [6,7] and can be characterised by non-saturated and near-neutral water solutions in potential

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contact with waste glasses. Temperatures of the disposal environment in near-surface repositories are relatively low which result in slower-occurring thermally-activated processes including those causing corrosion of waste glass. Corrosion of nuclear waste glasses in such conditions has not been as intensively studied as that of high-level vitrified waste at temperatures far exceeding normal ambient temperatures. The reactions of silicate glasses in aqueous media have frequently been discussed [8–11]. A series of complex processes occurs, involving first of all ion exchange and glass network dissolution. However activation energies of the rate-limiting reactions are different for the different processes and thus for the same glass a change in temperature may result in a change of the governing corrosion mechanism. Borosilicate glasses in near-neutral water solutions have minimal corrosion rates making analysis of their behaviour based on relative short duration laboratory tests difficult. This paper examines 16 years of corrosion data obtained on a radioactive borosilicate glass K-26 in a wet disposal environment. This glass is currently being extensively studied with the aim of identifying the most important parameters determining its long-term performance as a host for nuclear waste [12–14].

2. Experimental

K-26 glass is a borosilicate glass which is designed to immobilise intermediate level operational nuclear power plant (NPP) radioactive waste. It has a density of 2.46 g cm^{-3}. Its composition in wt% is 48.2SiO_2–7.5B_2O_3–2.5Al_2O_3–15.5CaO –16.1Na_2O–1.7Fe_2O_3–1.2NaCl–1.1Na_2SO_4–6.2 others [15]. Several tonnes of this glass were produced in the 1980s using radioactive waste from the Kursk NPP in Russia (a channel type RBMK reactor) and a number of glass blocks have been placed in an experimental shallow land facility for long-term corrosion tests [6]. The main radioactive contaminant of K-26 glass is ^{137}Cs which is present in the waste glass at a level of up to 3.73×10^6 Bq kg^{-1}. Fig. 1 shows a γ-spectrogram (spectrometer DGDK with Ge-semiconducting detector) of K-26 glass after 12 years in the near surface experimental repository. It can be seen that K-26 glass contains ^{137}Cs as the only γ-emitter.

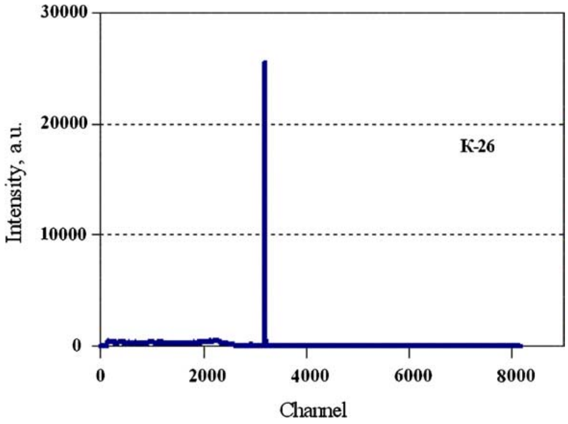

Fig. 1. γ-Spectrum of glass K-26.

Field tests of K-26 glass have been run since 1987 to evaluate the behaviour of the glass near surface disposal conditions [6,11–14]. Six blocks of waste glass K-26 (each weighing about 30 kg and 30 cm in height) were placed in a single 40 cm high stainless steel tray supplied with a water trap and a tube for water extraction by pumping. The experimental repository is 1.7 m deep which is below the freezing depth of soil (0.7 m). Pure coarse sand was used to backfill the glass blocks in the tray to facilitate infiltration of water to the blocks and to isolate them from direct contact with the host rock. The space outside the containers was filled with host loamy soil to the land surface. Testing conditions have been described in detail by Ojovan et al. [6]. The conditions may be considered as water saturated with an average pH of 7.6 and mineralisation of 600 mg L^{-1}. The amount of radionuclides leached from the glass was quantified by measuring the volume and radioactivity of the collected water. Water sampling was performed periodically, usually twice a month (except in winter). The volume of water v_j (L) was recorded at each sampling time. Water aliquots were retained for analysis. Standard radiometrical, radiochemical, and chemical analytical techniques were applied including measurement of specific radioactivity of water samples a_{ij} (Bq L^{-1}) [6]. Overall measurement errors were not higher than 10%. The volume of groundwater, $V(t)$, collected over time t, was calculated as a sum of the volume of the individual batches (v_j) collected i.e.

$$V(t) = \sum_j v_j. \tag{1}$$

Fig. 2 shows time dependence of the volume (left) and specific radioactivity (right) of the groundwater that had contacted the waste glass. The total amount of groundwater collected that had been in contact K-26 glass during the first 16 years of testing was V(16 years) = 1097.7 L.

The amount of radionuclide i leached out from the waste glass $A_i(t)$ (Bq) was calculated using

$$A_i(t) = \sum_j a_{ij} v_j. \tag{2}$$

The normalised mass loss of radionuclide, i, NM_i (g/cm^2) was obtained using

$$\mathrm{NM}_i = \frac{A_i(t)}{q_i S}, \tag{3}$$

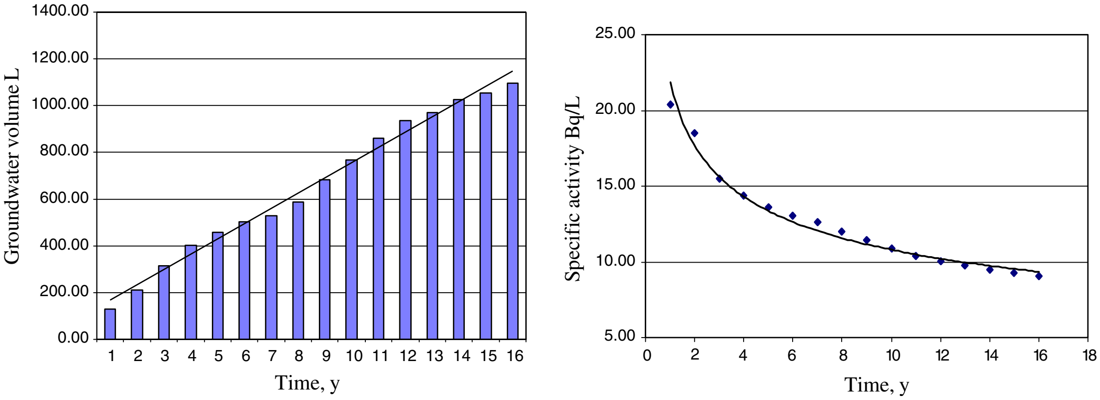

Fig. 2. Volume of groundwater contacted radioactive glass K-26 (left) and its specific radioactivity (right) as functions of time.

where $S = 2052\,\mathrm{cm}^2$ is the surface area of the glass in contact with groundwater and $q_i = 3.73 \times 10^3\,\mathrm{Bq\,g}^{-1}$ is the specific ^{137}Cs content in K-26 glass. The leached fraction of the radionuclide i, ϕ_i, from K-26 glass was calculated using

$$\phi_i = \frac{A_i(t)}{A_i(0)}, \tag{4}$$

where $A_i(0) = 7.09 \times 10^8\,\mathrm{Bq}$ was the initial level of radioactivity due to radionuclide i in K-26 glass. Fig. 3 shows the normalised mass loss and leached fraction of ^{137}Cs with time.

The average normalised leaching rate of radionuclide i, NR_i, was calculated using

$$\mathrm{NR}_i = \frac{\mathrm{NM}_i}{t}, \tag{5}$$

where t is the duration of test in days. Fig. 4 (left) shows the normalised leaching rate as a function of time. It can be seen from Fig. 4 (left) that, although the rates fluctuate, overall the leaching rate of ^{137}Cs progressively diminishes with time resulting in a rate almost an order of magnitude smaller for the 16th year of testing as compared to the leaching rate during the first year of testing. This is an intrinsic characteristic of a diffusion-controlled process rather than glass-matrix dissolution via hydrolysis, which would show a constant leaching rate. Generally, a square root or a linear time dependence of the leached mass separates ion exchange and hydrolysis mechanisms of glass corrosion [8,9,16–19]. Fig. 4 (right) shows the time dependence of the normalised mass losses of ^{137}Cs divided by square root of time ($\mathrm{NM}_i/\sqrt{t}$). As seen this ratio remains almost constant during tests, which demonstrates that the radionuclides are released from K-26 glass via a diffusion-controlled process. This is consistent with indications of [20] on the major role of ion-exchange in leaching of low-level vitrified wastes. The effects of waste glass leaching on groundwater chemistry are summarised in Table 1.

Over time the mineralisation of the water that has been in contact with the glass has altered from ($\mathrm{HCO_3^-}$ – $\mathrm{Ca^{2+}}$)-type to ($\mathrm{HCO_3^+}$–$\mathrm{Na^+}$–$\mathrm{K^+}$–$\mathrm{Ca^{2+}}$–$\mathrm{NO_3^-}$–$\mathrm{Cl^-}$)-type, being

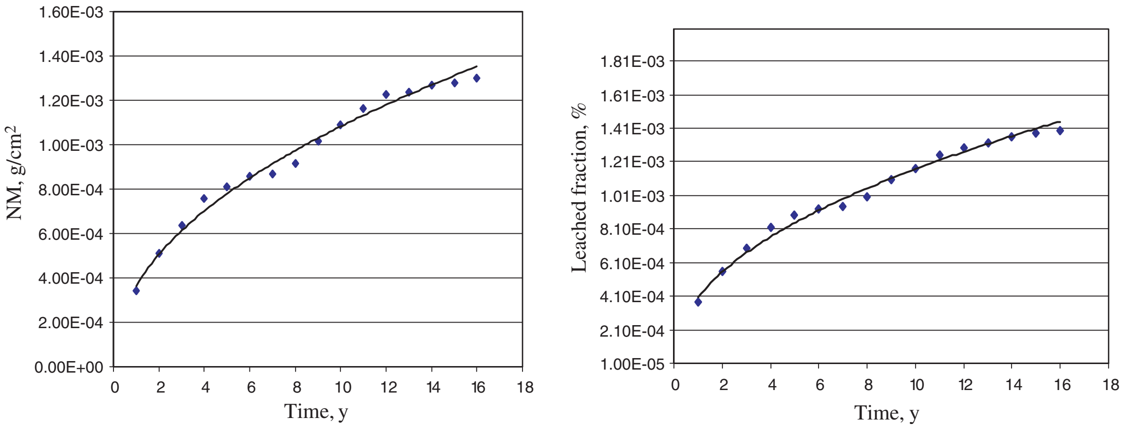

Fig. 3. Normalised mass losses (left) and leached fraction of ^{137}Cs (right) from K-26 glass.

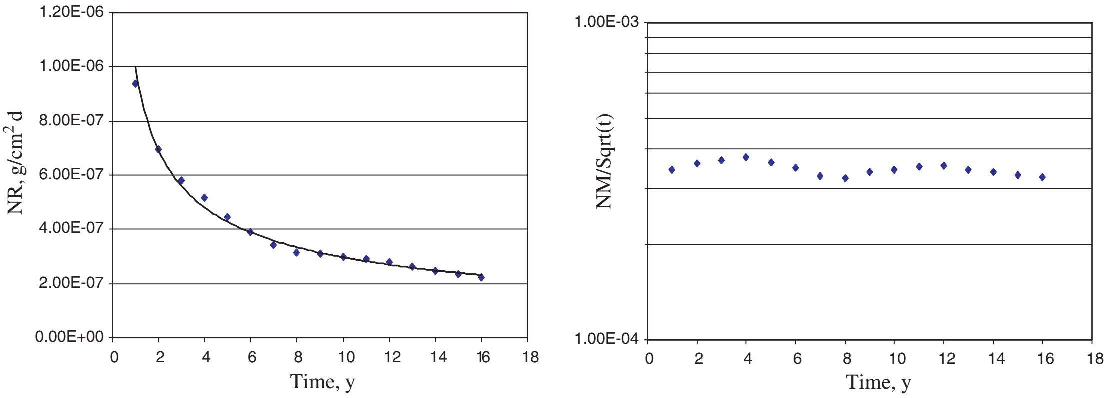

Fig. 4. Average normalised leaching rates (left) and normalised mass loses divided by square root of time (right) for K-26 glass.

Table 1
Composition of groundwater in contact with the waste glass (concentrations in $\mathrm{mg\,L^{-1}}$)

Ions	1st year	8th year	12th year	Background
pH	7.5	7.8	7.9	7.6–7.7
Na^+	34.64	54.55	63.40	13.11
K^+	3.70	3.82	3.72	1.26
Ca^{2+}	78.93	54.26	46.30	48.74
Mg^{2+}	32.30	30.26	27.75	20.91
Fe	9.33	2.64	2.02	1.16
Cl^-	33.11	26.49	24.08	13.17
NO_3^-	2.22	4.18	4.23	2.30
HCO_3^-	435	390	373	258.03
SO_4^{2-}	13.93	12.45	10.62	4.73
B	Not measured	24.75	27.72	Not measured
Mineralisation	710	830	810	600

numerically higher than background by a factor of about 1.35. Progressive decreases in concentration with time were observed for Ca^{2+}, Mg^{2+}, Fe, Cl^-, HCO_3^-, SO_4^{2-} and mineralisation. For boron, Na^+ and NO_3^-, the opposite concentration trends were observed throughout the experiment as well as a small but progressive pH change from 7.5 to 7.9.

3. Mechanisms of cation release

Corrosion of alkali–silicate glasses in aqueous solutions has been described by many authors [6–14,16–32]. The corrosion of glasses in aqueous solutions is governed by two mechanisms: diffusion-controlled ion exchange and dissolution of the glass network. The release of cations into the water via ion exchange mechanism from glasses was quantified by Doremus [18,31] whereas the release of alkali via hydrolysis was described by the model of Agaard and Helgeson [32]. Ion exchange is characteristic of the initial phase of corrosion and involves replacement of alkali ions in the glass by a hydronium (H_3O^+) ion from the solution. It causes an ion-selective depletion of near surface layers of glasses and gives an inverse square root dependence of corrosion rate with exposure time. Glass network dissolution is characteristic of the later phases of corrosion and causes a congruent release of ions into the water solution at a time-independent rate. In closed systems the consumption of protons from the aqueous phase increases the pH and causes a fast transition to hydrolysis. However further silica saturation of solution impedes hydrolysis and causes the glass to return to an ion-exchange, e.g. diffusion-controlled regime of corrosion. Saturation-related effects however are not considered in this paper.

A mathematical description of alkali release into water is inevitably based on a number of simplifying assumptions [8,9]. Consider an alkali–silicate glass under aqueous attack (Fig. 5). The glass is characterised by the interface surface area S ($\mathrm{cm^2}$) and the concentration of species C_i ($\mathrm{g/cm^3}$), which is initially constant within the glass. The concentration of a species can be expressed using its weight fraction content in glass f_i as $C_i = \rho f_i$, where ρ is the density of glass. The water solution is

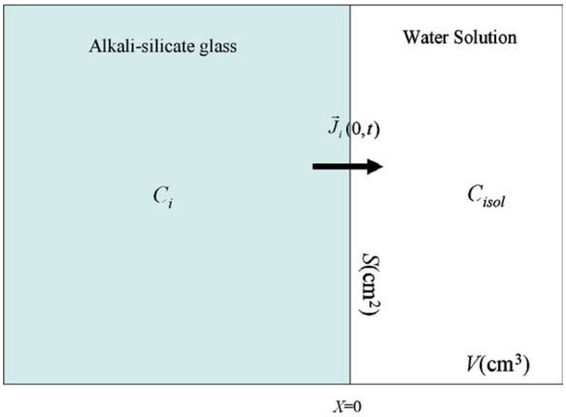

Fig. 5. Schematic of a glass in contact with water.

characterised by the volume V (cm^3) and concentration of species $C_{i_\mathrm{sol}} \ll C_i$. Moreover for dilute solutions such as those found in near-surface disposal facilities C_{i_sol} may be assumed to be close to zero.

The concentration and flux of species, i, are denoted as $C_i(\vec{r},t)$ and $\vec{J}_i(\vec{r},t)$ respectively, where $\vec{r}$ is the position vector and t is time. Continuity requires that

$$\frac{\partial C_i}{\partial t} + \vec{\nabla} \cdot \vec{J}_i = 0. \tag{6}$$

The total amount of released species into the water at any time t is determined by the flux of species through the surface of glass $\vec{J}_i(\vec{r},t)$ at the glass–water interface $x = 0$ and is given by the integral:

$$M_i(t) = S \int_0^t \vec{J}_i|_\mathrm{surface} \vec{n}\,\mathrm{d}t, \tag{7}$$

where $\vec{J}_i|_\mathrm{surface}$ is the value of $\vec{J}_i$ at the glass surface at a given moment in time, $\vec{n}$ is the normal vector to the glass surface, t is the time of leaching. As a rule the release of elements from glasses are expressed in term of normalised leached masses NM_i (g cm^{-2}):

$$\mathrm{NM}_i = \frac{M_i(t)}{S f_i}, \tag{8}$$

Eqs. (6)–(8) are exact and together with relevant initial and boundary conditions determine the evolution of species in the glass and in the water at any time. In practice use of these equations requires many simplifications such as assumptions about initial distribution of species and specification of the flux of species. In other words assumptions have to be made about the mechanisms involved in the release of species from glasses under water attack and about the evolution of species in water such as saturation effects and precipitation reactions.

Two processes control the release of species from silicate glasses–ion exchange and hydrolysis [8,9,16–19]. The ion exchange reaction of glass with water can be written as:

$$(\equiv \mathrm{Si{-}O{-}Cation})_\mathrm{glass} + \mathrm{H_2O} \leftrightarrow (\equiv \mathrm{Si{-}O{-}H})_\mathrm{glass} + \mathrm{Cation{-}OH} \tag{9}$$

It results in an interdiffusion flux of cations replaced by the H$^+$ (or hydronium) ion [9]:

$$\vec{J}_{d_i}(\vec{r},t) = -D_{i_\mathrm{H}} \vec{\nabla} C_i, \tag{10}$$

where the interdiffusion coefficient D_{i_H} in an ideal case is given by the Nernst–Planck equation [33]:

$$D_{i_\mathrm{H}} = \frac{D_i D_\mathrm{H}}{D_i N_i + D_\mathrm{H} N_\mathrm{H}}, \tag{11}$$

D_i and D_H are the diffusion coefficients of the cations in the glass and replacement hydrogen containing ion (whether H$^+$ or H$_3$O$^+$), N_i and N_H are molar fractions of the cations and hydrogen containing ion respectively, i.e. $N_i + N_\mathrm{H} = 1$. The interdiffusion coefficient depends on concentrations of both diffusing ions and hence on position. The interdiffusion coefficient is related to the glass composition. It is not a priori clear which of D_i or D_H should be the larger diffusion coefficient in Eq. (11), i.e. what is the limiting rate ion in the interdiffusion, however many experiments indicate that $D_\mathrm{H} \ll D_i$. For example, the analysis of concentration profiles of alkali in the glass NaCa-1825 after initial leaching 90 °C resulted in $D_\mathrm{H} = 1.92 \times 10^{-15}\,\mathrm{cm^2\,s^{-1}}$ and $D_\mathrm{Na} = 1.92 \times 10^{-12}\,\mathrm{cm^2\,s^{-1}}$, and for the glass Na-25 $D_\mathrm{H} = 1.48 \times 10^{-12}\,\mathrm{cm^2\,s^{-1}}$ and $D_\mathrm{Na} = 1.48 \times 10^{-10}\,\mathrm{cm^2\,s^{-1}}$ [8,9,34,35]. If $N_H D_\mathrm{H} \ll N_i D_i$ the interdiffusion coefficient is approximately given by

$$D_{i_\mathrm{H}} \approx \frac{D_\mathrm{H}}{N_i}. \tag{12}$$

Diffusion transport in glasses is mediated by intrinsic defects [36,37]. It has been shown that migration of protons in silicate glass is possible only in the presence of non-bridging oxygen atoms (NBO) [38]. Similar results for alkali ions (Na) were obtained by molecular dynamic simulations which demonstrated that the association with NBO confines the Na ions to local motions whereas the absence of a coordinating NBO enables the Na ion to more readily explore its environment and to undergo long range migration in search for an NBO [39]. The generic expression for the cation diffusion coefficient consistent with these observations is given by [37]

$$D_i^* = D_{i_0}^* \exp\left(-\frac{E_{d_i}^*}{RT}\right), \tag{13}$$

where $D_{i_0}^* = (f\lambda^2 z \nu_i p_0/6\pi)\exp[(S_{m_i} + S_{f_\mathrm{NBO}})/RT]$, ν_i is the jump attempt frequency of cation, f is the correlation factor, λ is the nearest neighbour jump distance, z is the number of nearest neighbours, p_0 is a configuration factor proportional to total number of sites available to form a defect, e.g. NBO, S_{m_i} and S_{f_NBO} are the entropy of motion of cation *i* and the entropy of formation of an NBO respectively and$R$ is the universal gas constant. The activation energy for diffusion of cation *i* is [37]

$$E^*_{d_i} = H_{m_i} + H_{f_{\mathrm{NBO}}}, \tag{14}$$

where H_{m_i} is the enthalpy of motion of cation *i*, $H_{f_{\mathrm{NBO}}}$ is the enthalpy of formation of an NBO. The activation energy $E^*_{d_i}$ can be calculated using the structural energy barrier model [20,36,37].

Eq. (12) demonstrates that even in case of $N_\mathrm{H}D_\mathrm{H} \ll N_iD_i$ the interdiffusion coefficient depends on coordinate requiring for calculations a further simplification such as assuming $(1/N_i) = 1/\langle N_i\rangle$, where $\langle\cdots\rangle$ designates the average molar fraction so that $\langle N_i\rangle + \langle N_\mathrm{H}\rangle = 1$. Note that because the interdiffusion coefficient depends on the local alkali concentration it will generally depend on the pH of water solution. The most common approximation is to neglect the coordinate dependence of the interdiffusion coefficient, e.g. to assume [9]: $D_{i\mathrm{H}} \approx \mathrm{const}_i$. There is much discussion as to whether water diffuses as ions of H^+, OH^-, H_3O^+ or as neutral H_2O [22,40–42]. The isotopic effect in ion exchange shows that these are ions H^+ [20], however other results show that oxygen plays an important part in the transport of protons [43,44]. In addition a good description of diffusion profiles of alumina-containing glasses is given by neutral water diffusion [41]. Our approach is to write the interdiffusion flux in 1 dimension at the glass-water boundary (taken as being at $x = 0$) in a form consistent with experimental facts

$$\vec{J}_{d_i}(x=0,t) = \rho f_i\left(\frac{D_i}{\pi t}\right)^{1/2}\vec{n}, \tag{15}$$

where D_i is an effective diffusion coefficient. D_i is an intrinsic characteristic of glass depending on its composition which can be determined via leaching experiments accordingly with IAEA test protocol ISO-6961-1982 [45]. Based on Eqs. (12) and (13) it can be written

$$D_i = D_{0_i}\exp\left(-\frac{E_{d_i}}{RT}\right), \tag{16}$$

where the pre-exponential term, D_{0_i}, and activation energy E_{d_i} are given by equations

$$D_{0_i} = \frac{D^*_{0_\mathrm{H}}}{N_i(0)} = \frac{f\lambda^2 z v_\mathrm{H} p_0}{6\pi N_i(0)}\exp\left(\frac{S_{m_\mathrm{H}} + S_{f_{\mathrm{NBO}}}}{RT}\right), \tag{17}$$

$$E_{d_i} = H_{m_\mathrm{H}} + H_{f_{\mathrm{NBO}}}, \tag{18}$$

where $N_i(0) = N_i(x = 0)$ is the molar fraction of *i*th ion in the glass at the glass surface $x = 0$ given that $N_i + N_\mathrm{H} = 1$. Note that the activation energy of *interdiffusion*, E_{d_i}, is different from the activation energy of *diffusion*, $E^*_{d_i}$ [16,17]. Moreover the activation energy of interdiffusion has the same value for all cations because proton ingress into the glass is the rate limiting step i.e. $D_\mathrm{H} \ll D_i$, which is consistent with experimental data. For example British magnox-waste glass has the same interdiffusion activation energy for Li, which is a glass modifier, and for *B*, which is a glass former, $E_{d_{\mathrm{Li}}} = E_{d_\mathrm{B}} = 36\,\mathrm{kJ\,mol^{-1}}$ [46]. Obviously cations that do not meet the condition $N_\mathrm{H}D_\mathrm{H} \ll N_iD_i$ provide an exception to this observation. Such cations will have effective diffusion coefficients given by Eq. (11) and thus will have different activation energies. The pre-exponential coefficients D_{0_i} depend on N_i, which are different for different cations. Moreover D_{0_i} values generally depend on the composition and pH of the water solution because the near surface molar fractions of species in the glass $N_i(0) = 1 - N_\mathrm{H}(0)$ can be related to those in the aqueous media [25,26]. A simple assessment of this dependence can be made accounting for secondary ion mass spectrometry depth profiles of corroded silicate glasses, which showed that at the water-glass interface ($x = 0$) the concentration of protons significantly exceeds that of cations such as Na, K [30,47], e.g. we can assume in the glass near surface $C_i(0) \ll C_\mathrm{H}(0)$. Thus the molar fraction of cation *i* in the glass at the glass surface $N_i(0) \approx C_i(0)/C_\mathrm{H}(0)$. Concentration of protons at the glass surface is proportional to concentration of protons (hydronium) in the water $C_\mathrm{H}(0) = \kappa C_{\mathrm{H_{sol}}}$, where κ is a numeric constant. From the definition of pH $C_{\mathrm{H_{sol}}} = 1\,(\mathrm{mol/L}) \times 10^{-\mathrm{pH}}$, and thus the pH dependence of the rate of ion exchange, $r_{x_i} = |\vec{J}_{d_i}(x=0,t)|$ is given by$r_{x_i} = \rho f_i 10^{-\mathrm{m\,pH}}(\kappa D^*_{0_\mathrm{H}}/C_i(0)\pi t)^{1/2}\exp(-E_{d_i}/2RT)$, where $C_i(0)$ is measured in mol/L and $m = 0.5$. This is simply the pH dependence of leaching rates of silicate glasses in acidic solutions; experimental measurements indicate that $0.48 \leqslant m \leqslant 0.69$ [48]. This demonstrates that the initial leaching of glass is correctly described by Doremus' theory of ion exchange resulting in a pH-dependent and ion-selective rate which conforms to experimental data.

Dissolution of glass network occurs in parallel to ionic interdiffusion and is caused by the hydrolysis of glass network via

$$\equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{H_2O} \leftrightarrow 2(\equiv \mathrm{SiOH}) \tag{19}$$

It results in complete dissolution of glass network and congruent release of all glass constituents into the water, the hydrolytic flux of species being given by

$$\vec{J}_{h_i}(\vec{r},t) = \rho f_i r_h \vec{n}, \tag{20}$$

where r_h is the stationary hydrolysis (dissolution) rate of the glass, e.g. the steady state rate of motion of the hydrolysis front into the glass. Note that generally r_h is not equal to the measured rate of decrease of glass thickness because of de-hydroxylation reactions and silicic acid re-precipitation as hydrated silica gel ($H_2SiO_3 n H_2O$) [9]. The rate of hydrolysis is determined by the transition state theory of silicate minerals dissolution of Agaard and Helgeson [32] and can be expressed as [7,13,32]

$$r_h = k a_{\mathrm{H}^+}^{-\eta}\left(1-\left(\frac{Q}{K}\right)^{\sigma}\right)\exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) = r_{\mathrm{oc}}\exp\left(-\frac{E_{\mathrm{a}}}{RT}\right), \tag{21}$$

where k is the intrinsic rate constant, a_{H^+} is the hydrogen ion activity, η is the pH power law coefficient, E_{a} is the activation energy, Q is the ion-activity product of the rate controlling reaction, K is the pseudo-equilibrium constant of this reaction and σ is the net reaction order. The affinity term $(1-(Q/K)^{\sigma})$ characterises the decrease in solution aggressiveness with respect to the glass as it becomes increasingly concentrated in dissolved elements and as the ion activity product Q of the reactive species approaches the material solubility product K. Grambow suggested that only silicon had to be accounted for in the affinity term of Eq. (21) thereby significantly reducing the number of elements that have to be taken into account [49]. The activation energy of network glass dissolution can be calculated using the Jantsen–Plodinec thermodynamic model [50]. For example for K-26 glass $E_{\mathrm{a}} = 68\,\mathrm{kJ\,mol^{-1}}$ [13].

A widely accepted approximation of non-equilibrium thermodynamics, which is assumed to be valid for systems which are not far from equilibrium, states that the material fluxes are linearly related to the applied forces [51]. Therefore the total flux of species i from the glass to water can be written as [9]

$$\vec{J}_i(\vec{r},t) = \vec{J}_{d_i}(\vec{r},t) + \vec{J}_{h_i}(\vec{r},t), \tag{22}$$

where $\vec{J}_{d_i}$ is the flux of cation i due to ion exchange and $\vec{J}_{h_i}$ is the flux of cation i due to hydrolysis. The rate of release of ions into the water $r_i = |\vec{J}_i(x=0,t)|$ is therefore given by

$$r_i = r_{x_i} + r_{h_i}, \tag{23}$$

where $r_{x_i} = \rho f_i (D_{0_i}/\pi t)^{1/2}\exp(-E_{d_i}/2RT)$ and $r_{h_i} = \rho f_i k a_{\mathrm{H}^+}^{-\eta}[1-(Q/K)^{\sigma}]\exp(-E_{\mathrm{a}}/RT)$. This is the well known expression used in performance assessment calculations and computer modelling of glass dissolution [7,13]. The pH dependence of r_{x_i} suggests that an increase of water-solution pH is beneficial for nuclear waste glasses as it results in a reduction of radionuclide release by ion exchange. Unfortunately the second mechanism of glass corrosion – hydrolysis – has the opposite behaviour with pH such that the higher pH the higher hydrolysis rate. The resulting behaviour of silicate glasses with pH has a U-type form with minimal overall release rates in near-neutral water solutions. Note that in saturated conditions when $Q \to K$ the affinity term vanishes resulting in $r_{h_i} \to 0$. In this case $r_i \to r_{x_i}$ i.e. the corrosion of glass becomes solely governed by ion exchange [20,23]. This shows that ion-exchange is not a tertiary process even in conditions of high pH solutions. In non-saturated conditions such as those considered herein the rate of ion exchange diminishes with time. Often conclusions are brought that the ion exchange is a transition effect which in a long term perspective has a minor impact on glass corrosion and release of radionuclides from nuclear waste glasses [52]. However this conclusion remains valid only for high pH non-saturated water solutions at relative high temperatures [52]. In aqueous solutions close to neutral and at relatively low temperatures ion exchange may persist for many tens and even hundreds years and in practice may control the release of short lived radionuclides from vitrified radioactive wastes [2,14,53].

For nuclear waste glasses Eq. (23) is incomplete because it does not contain surface-related transition effects; Eq. (23) is based on supposition that the species are initially distributed at the same concentration C_i everywhere within the glass. Generally this is an unacceptable approximation for nuclear waste glasses because they always are surface contaminated. Decontamination, which is a removal of surface-bonded radionuclides, is a routine operation in nuclear waste vitrification plants [54], it however never involves the removal of surface contamination from any piece of glass in a canister. Moreover the near surface layers of any solid including glass are different from the bulk [55] hence generally the concentration of species in the near surface layers is not equal exactly to the average concentration, C_i. The differences in the structure and composition spread for crystalline materials for several atomic layers [55]. For glasses these differences depend on the preparation method and can extend to a depth of about 100 nm [56,57], Si for example has a lower concentration in near surface layers [28,57] whereas Mo has a much higher surface concentration [58] than in the bulk. These differences lead to a short-term fast leaching of species from glasses, which precedes the diffusion-controlled ion-exchange stage with square-root time dependence [57]. This is termed instantaneous surface dissolution and is accounted by an exponential term in the dissolution rate [59–61]:

$$r_{s_i} = n_{s_i} k_i \exp(-k_i t), \tag{24}$$

where k_i is the rate of instantaneous dissolution of species i in water (day^{-1}), and n_{s_i} is the surface concentration of radionuclides ($\mathrm{g\,cm^{-2}}$). The instantaneous dissolution is incongruent, because the surface contamination has a composition different from glass. In most cases surface contamination is due to volatile radionuclides such as Cs and Ru, but in practice may involve a variety of radionuclides present in waste streams. Eq. (24) should be added to Eq. (23) to describe fully the corrosion of actual nuclear waste glasses [6]. Table 2 summarises three most important mechanisms of glass corrosion in non-saturated aqueous solutions.

Finally for nuclear waste glasses it is necessary to take into account radioactive decay, which causes an exponential decrease of radioactive cation concentrations and hence diminishes both ion exchange and hydrolytic release of the radioactive cations [61]. Normalised mass releases of radioactive species such as ^{137}Cs are given by [61,62]

$$\mathrm{NM}_i = \mathrm{NM}_{s_i} + \rho\sqrt{\frac{D_i}{\lambda_i}}\mathrm{erf}(\sqrt{\lambda_i t}) + \frac{r_h\rho}{\lambda_i}[1-\exp(-\lambda_i t)], \tag{25}$$

where NM_{s_i} is a constant accounting for instantaneous surface dissolution, λ_i is the decay constant, and $\mathrm{erf}(z)$ is the error function

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z \exp(-x^2)\,\mathrm{d}x. \tag{26}$$

For stable species $\lambda_i = 0$; hence considering short times $t < D_i/r_h^2$ and taking the limit $\lambda_i \to 0$ we can reduce Eq. (25) to the well known Rana–Douglas equation for initial glass corrosion $\mathrm{NM}_i = a + k\sqrt{t}$ [16], where $a = \mathrm{NM}_{s_i}$ (instantaneous surface dissolution) and $k = 2\rho\sqrt{D_i/\pi}$ accounts for ion exchange. In the opposite case of $t \gg D_i/r_h^2$ Eq. (25) can be reduced to $\mathrm{NM}_i = b + ct$ which is the Rana–Douglas equation of long-term glass corrosion [16], where the constant c accounts for the glass network hydrolysis $c = \rho r_h$. Hence from short time experiments the effective diffusion coefficient (D_i) can be obtained while from prolonged tests the rate of hydrolysis (r_h) can be found. Average normalised leaching rates can be found from (25) following (5) as $\mathrm{NR}_i = \mathrm{NM}_i/t$. The fraction of released radionuclides f_i from the glass can be found accordingly to (4) as:

$$\phi_i = \frac{Sf_i\mathrm{NM}_i}{f_i\rho V} = \frac{S}{\rho V}\mathrm{NM}_{s_i} + \frac{S}{V}\sqrt{\frac{D_i}{\lambda_i}}\mathrm{erf}(\sqrt{\lambda_i t}) + \frac{S}{V}\frac{r_h}{\lambda_i}[1-\exp(-\lambda_i t)]. \tag{27}$$

For radioactive samples either Eq. (25) or (27) can be fitted experimental data to identify both effective diffusion coefficient (D_i) and rate of hydrolysis (r_h). Optimal values of D_i and r_h can then be used to assess expected radionuclide releases into environment during the institutional control time which is $t = 300$ years for K-26 glass [53].

4. Parameters of K-26 glass

Fig. 6 shows the best fit to experimental data to the normalised leaching rates given by Eq. (25) and to the fraction of released radionuclides given by Eq. (27).

The best fit is achieved for an effective diffusion coefficient $D_{\mathrm{Cs}} = 4.5 \times 10^{12}\,\mathrm{cm}^2\,\mathrm{day}^{-1}$ ($5 \times 10^{-21}\,\mathrm{m}^2\,\mathrm{s}^{-1}$), and the rate of glass hydrolysis $r_h = 0.1\,\mu\mathrm{m\,years}^{-1}$. These data are consistent with the results of Aertensen et al. [63] who reported effective diffusion coefficients from 1.3×10^{-23} to $2.8 \times 10^{-21}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ for the nuclear waste glasses SM539 and SON68, as well as those of Ivanov et al. [64], who reported diffusion coefficients of boron, sodium and lithium from 10^{-22} to $10^{-20}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ for borosilicate glasses designed to immobilise incineration wastes. Dissolution rates less than $0.3\,\mu\mathrm{m\,years}^{-1}$ were reported for nuclear waste glasses in Boom clay at 16 °C ambient rock temperature [67].

Eq. (27) enables an assessment of the total possible release of radionuclides into the environment assuming preservation of current conditions. Fig. 7 (left) shows the calculated and measured fractions of released radionuclides from the glass K-26. Fig. 7 (right) shows an assessment of contributions to radionuclide releases from the two basic mechanisms of glass corrosion–ion exchange and hydrolysis.

Data obtained conform to STORM computer-code results on Na releases from this glass, which

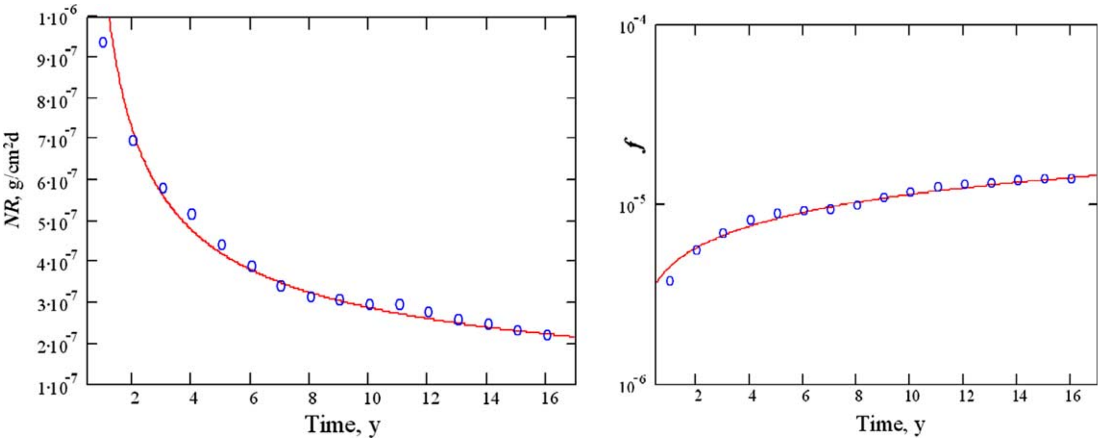

Fig. 6. Best fit to experimental data of the theoretical expressions for average normalised leaching rate (25) and fraction of released radionuclides (27) for K-26 glass.

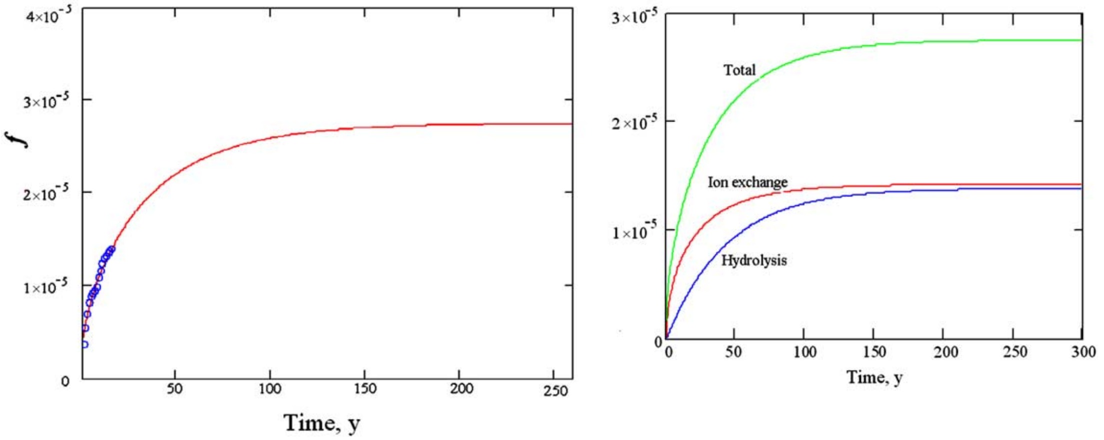

Fig. 7. Measured (circles) and calculated (line) fraction of radionuclides released from K-26 glass (left) and the relative contributions to these releases from ion exchange and hydrolysis during the institutional control time (right).

demonstrated a 60% ion exchange contribution to the total mass release [13].

5. Discussion

Since the pioneering works of Douglas and co-workers [16,17] it has been known that at sufficiently short times and at sufficiently low temperatures the extraction of alkali from silicate glasses varies as square root of time whereas at sufficiently high temperatures and at sufficiently long times the amount of both alkali and silica extracted vary linearly with time. In other words ion exchange (referred to as the first mechanism by Douglas and co-workers) [16,17] dominates in the initial stage of leaching. However with time the rate of ion exchange diminishes, whereas the rate of hydrolysis (referred to as the second mechanism by Douglas and co-workers [16,17]) remains constant with time. Hence hydrolysis will eventually dominate, except under special conditions such as saturated solutions when the rate of hydrolysis becomes close to zero. The lower the temperature the longer the time before hydrolysis becomes dominant because hydrolysis usually has a higher activation energy compared to ion exchange i.e. $E_{\mathrm{a}} > E_{d_i}$. To estimate the transition time from one mechanism to another we need to compare contributions to the total leached mass from the different mechanisms. This time can be defined as the characteristic time after which the alteration front is formed, i.e. we divide the effective diffusion coefficient D_i by the square of the rate of hydrolysis r_h [52]. Using Eqs. (16) and (21) this definition of transition time can be rewritten as [2,14,52,53]

$$\tau_i(T) = \frac{D_i}{r_h^2} = \frac{D_{0_i}}{r_{\mathrm{oc}}^2} \exp\left(\frac{2E_{\mathrm{a}} - E_{d_i}}{RT}\right), \tag{28}$$

where $r_{\mathrm{oc}} = k a_{\mathrm{H}^+}^{-\eta}(1 - (Q/K)^{\sigma})$.

The evolution of corrosion with time in non-saturated conditions can therefore be described as follows: corrosion begins with dissolution of surface contamination and other near-surface layers, which precedes steady state ion exchange stage. This is a short-term transition effect taken into account by the constant NM$_{s_i}$. Comparing the contributions to mass releases from ion exchange and hydrolysis at different exposure time of an aqueous attack in non-saturated conditions we can identify three main stages apart from instantaneous surface dissolution. The first stage is the diffusion-controlled leaching, which occurs at sufficiently short times $t \leqslant \tau$. At this stage the contribution of hydrolysis is less than 1/3 of the total released mass, hence it can be identified as ion exchange stage or Doremus' stage, as the quantification is done accordingly with Doremus' theory. This stage is characterised by an incongruent release of cations from glasses although activation energies can be the same (see Eq. (18)). Note that in saturated conditions and at very low temperatures the Doremus' stage extends to extremely long times $\tau_i \to \infty$ which reflects the negligible role of hydrolysis under such conditions. During the second, intermediate, stage the contributions to the released mass inventory from both ion-exchange and hydrolysis are of the same order of magnitude; this stage can be judged to occur in the time interval $\tau \leqslant t \leqslant 16\tau$. In the third stage, which occurs for $t \geqslant 16\tau$, glass dissolution occurs practically entirely through hydrolysis and there is an insignificant contribution of ion exchange into the mass release, i.e. less than 1/3 of the total mass. This stage is characterised by congruent release of cations from glasses. Table 3 summarises the characteristics of three main stages of glass corrosion.

The K-26 glass has in the near surface repository conditions $D_{\mathrm{Cs}} = 4.5 \times 10^{-12}\,\mathrm{cm^2\,day^{-1}}$ and $r_h = 0.1\,\mu\mathrm{m\,year^{-1}}$. Substituting these values into Eq. (28)

Table 2
Characteristics of corrosion mechanisms

Mechanism, rate behaviour	Instantaneous surface dissolution	Ion exchange	Hydrolysis
Time[a]	Short-term effect $\propto \exp(-kt)$	Diminishes $\propto t^{-1/2}$	Independent*
Temperature	Arrhenian	Arrhenian, Universal activation energy	Arrhenian, One high activation energy
pH	Dependent	Decreasing $\propto 10^{-0.5\mathrm{pH}}$	Increasing $\propto 10^{0.5\mathrm{pH}}$
Solution saturation effects[b]	Unlikely	Unlikely	Impeded $\propto(1 - C_{\mathrm{Si}}/C_{\mathrm{Si\,saturation}})$
Selectivity	Selective	Selective	Congruent

[a] Time behaviour may be affected by saturation effects.

[b] Changes in solution chemistry may affect solution pH.

Table 3
Glass corrosion stages in non-saturated conditions

Exposure time	$t < \tau$	$\tau < t < 16\tau$	$t > 16\tau$
Mechanism of corrosion	Diffusion-controlled ion exchange	Mixed	Network hydrolysis
Instantaneous normalised mass loss rates $\frac{\partial NM_i}{\partial t}$	$\rho\sqrt{\frac{D_i}{\pi t}}$	$\rho\sqrt{\frac{D_i}{\pi t}} + r\rho$	$r\rho$
Selectivity of leaching	Ion-selective, incongruent	Less ion-selective, more congruent	Congruent

gives $\tau = 16.4$ years. Hence for the testing conducted to date (16 years) the corrosion of this glass has been primarily due to diffusion-controlled ion exchange. This would explain why the rate of glass hydrolysis could not be identified in a previous publication based on the data obtained after only 12 years of experiments [62]. The similarity of the predicted transition time to the current test length means that the accuracy of the current prediction has to be treated with caution; confidence in this measurement will increase as the test duration increases still further. However using the values obtained from the current data indicates that from 16 to 262 years K-26 glass will corrode via a mixed mechanism, and only after 262 years will the corrosion of K-26 glass be controlled by hydrolysis. This will however happen after the decay of radioactive ^{137}Cs to concentrations below clearance levels in Russian Federation, i.e. by this stage K-26 glass will no longer be considered as radioactive waste [14,53]. Thus ion exchange in fact fully controls the release of radionuclides, which is consistent with the results of McGrail et al. [20]. Note that self-irradiation of glass will not change the role of ion exchange as it simply leads to a higher ion exchange rate [65].

Cation interdiffusion is often considered as a short duration tertiary process in the general process of glass corrosion [52,66]. However since the first experimental studies it has been clear that the time of change from the first (diffusion-controlled) mechanism to the second (hydrolysis) depends upon the temperature and composition of glass [16,17]. Experimental studies show that this time can really be very long in the case of durable nuclear waste glasses at low and moderate temperatures and in close to neutral conditions. Moreover the longer the transition time τ the more durable is the glass. For example British magnox-waste glass demonstrated incongruent leaching over a period of 28 days at 90 °C indicating that interdiffusion was not a short term process even at a such high temperature [46]. This incongruent dissolution was maximal in the near neutral pH range and increased with decreasing temperature [46]. The values of the effective diffusion coefficients were estimated for French R7T7 glass at 100 °C as below $10^{-18}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ [52]. Typical R7T7 glass dissolution rates were determined experimentally as from 10 to 90 μm years^{-1} at temperatures within the range 80–85 °C [67]. This gives τ = 1d at rate r_h = 100 μm years^{-1} and τ = 0.315 years at rate r_h = 10 μm years^{-1}. Hydrolysis dominated dissolution occurs for $t > 16\tau$ and thus will only occur after somewhere between half of month and 5 years. However, as noted in [63], this is true only for elevated leaching temperatures. Under low (e.g. ambient) temperatures steady-state dissolution is not achieved quickly and persistent selective dissolution will continue for quite extended periods. Analysis of corroded glass profiles demonstrated that in Boom clay the corrosion of nuclear waste glasses is a diffusion controlled process [63]. Similar results have been obtained for French glasses SON68 in silica saturated conditions [68], moreover it has been shown that in such conditions the interdiffusion persists indefinitely and determines the actual rates of radionuclide releases [20]. Table 4 gives some values of the characteristic time τ for a number of glasses in non-saturated conditions.

The longest transition time is for the glass K-26 which is explained by the lowest temperature. Eq. (27) gives transition times at different temperatures assuming similar water solution compositions. For example British magnox-waste glass would show at 4.5 °C a transition time of more than 14.5 years in the same water solution as in the experiments described by Abratis et al. [46], which were carried out at 90 °C.

Table 1 indicates that leaching of species from glass has slightly changed the chemical composition and pH of the groundwater in contact with the glass. As the change in groundwater chemistry is ion-selective, this indicates an important contribution to mass release arising from the ion exchange. It has recently been shown that the ion exchange reactions in glasses are affected by irradiation resulting in a higher release rate of cations at low temperatures [65]. Analysis of the changes in the groundwater chemistry (Table 1) may suggest a potential impact arising from self irradiation of K-26 glass to the release rates of Na^+, however this effect needs further detailed consideration. Borosilicate glasses are extremely durable in near-neutral water solutions so the detected pH change has no significant impact on glass corrosion. It is considered that below a pH $\sim$ 9 ion exchange dominates glass corrosion whereas hydrolysis reactions are significant extent when pH exceeds 9 [23]. Fig. 8 shows caesium normalised leaching rates calculated using Eq. (23) as a function of contacted water pH. The power law coefficient in Eq. (20) was taken as 0.5 [48]. Note that the instantaneous corrosion rates $r_i/f_i = \partial NM_i/\partial t$ are different from the average normalised leaching rates determined by Eq. (5).

As seen the pH dependence has a typical U-form curve [46,48,70] with minimal changes in the near-neutral water solutions. This result conforms to Ebert's conclusions about the impact of ion exchange and hydrolysis reactions on the pH scale [23]. In acidic media below pH = 6 the water concentration of protons (or hydronium ions) is high resulting in a high rate of ion exchange. The role of glass network dissolution in this area is insignificant and cation leaching is ion-selective with different leaching curves for different cations. Above pH = 9 the role of ion exchange becomes insignificant due to the high water concentration of hydroxyl ions and thus the glass network commences to dissolve rapidly via reaction (19). In such basic media the release of cations becomes congruent as destruction of glass network results in practically complete dissolution of all glass constituents. Note that the hydrolysis reaction (19) becomes impeded if solutions become silica-saturated [20,23]. As seen from Fig. 7 the total mass release from glass follows simple power laws only below pH = 6 and after pH = 9. In the interval 6 < pH < 9 the dependence is a more complex function with a changing slope when pH changes and with minimal corrosion rates achieved not exactly at pH = 7. Because of the time dependence of ion-exchange rates corroded glasses the minimal rates drift with time to lower values of pH. Therefore attempts to model the pH dependences by simple power laws separated at pH = 7 will inevitably result in smaller values of exponent terms m and η. For example the exponent terms for UK magnox waste glass

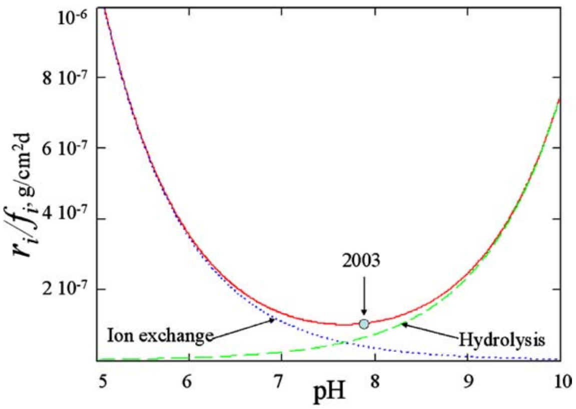

Fig. 8. pH dependence of caesium normalised leaching rate and the contributions to this rate from ion exchange and hydrolysis for the 16-years old glass K-26.

Table 4
Transition times for the onset of the intermediate stage of glass dissolution under non-saturated aqueous solutions

Glass	Temperature (°C)	τ	Reference
British magnox-waste	90	>28 days	[46]
$18.5Na_2O7.4Al_2O_375SiO_2$ (mol%)	80	>300 h	[69]
$15Na_2O10CaO75SiO_2$ (mol%)	60	>4000 min	[16]
SRL131A, SRL202A	25	>240 days	[23]
K-26	4.5	16.4 years	This work

based on data from the pH ranges $2 < \mathrm{pH} < 7$ and $7 < \mathrm{pH} < 10$ were $m = 0.39$ for boron, $m = 0.43$ for silicon, and $\eta = 0.43$ [46]; these are somewhat smaller than those obtained by Knauss et al. [48] and the theoretical value of $m = 0.5$.

6. Conclusions

In contrast to silica-saturated conditions when corrosion of silicate glasses is fully controlled by an ion-exchange mechanism, in non-saturated conditions corrosion occurs in three consecutive steady stages starting with a short-term instantaneous surface dissolution of contaminants, continuing with diffusion controlled ion exchange, followed by a mixed mechanism, which involves both ion exchange and glass network hydrolysis, and ending with a fully hydrolytically-controlled stage. Nuclear waste glasses are durable materials with minimal network hydrolysis rates in near-neutral aqueous solutions. Both ion exchange and hydrolysis are thermally-activated processes with Arrhenius-type temperature dependences, however the activation energies of hydrolysis are significantly higher than those of ion exchange. As a result transition times from one stage to another in the corrosion of glasses at low temperatures can be extremely long. Envisaged temperatures of nuclear waste repositories are relative low indicating that nuclear waste glasses may corrode in actual conditions under various mechanisms. The analysis of radionuclide release from K-26 glass under near surface burial over 16 years indicates that the effective diffusion coefficient $D_{\mathrm{Cs}} = 4.5 \times 10^{-2}\,\mathrm{cm^2\,day^{-1}}$ $(5 \times 10^{-21}\,\mathrm{m^2\,s^{-1}})$ and the rate of glass hydrolysis $r_h = 0.1\,\mu\mathrm{m\,years^{-1}}$. This suggests that glass corrosion for this glass is dominated by diffusion-controlled ion exchange for 16.4 years and that 262 years are required for this glass before hydrolysis dominates in a wet near-surface repository at 4.5 °C storage temperature. Further long term testing is required to increase confidence in the τ value of 16.4 years which is very close to the current test duration.

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