CORROSION OF NUCLEAR WASTE GLASSES IN NON-SATURATED CONDITIONS: TIME-TEMPERATURE BEHAVIOUR

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This paper examines corrosion behaviour of radioactive borosilicate glasses intended for nuclear waste immobilisation based on experimental data obtained during long term natural tests. These demonstrated diminishing of release rates of radionuclides by time. Corrosion of glasses is analysed assuming non-saturated conditions of leaching. It is suggested to characterise the corrosion of nuclear waste glasses in terms of time-temperature (t, T) parameters. A linear (non-coupled) approximation is used to give quantitative description of leaching rates. This enables identification of main corrosion mechanisms depending on disposal conditions and exposure time. The initial stage of glass corrosion is controlled by the incongruent ion exchange/interdiffusion mechanism, which is followed by the congruent dissolution of glass controlled by hydrolysis. The transition from one mechanism of corrosion to another may take from several days to many thousands years. This demonstrates that nuclear waste glasses may corrode in actual conditions both via ion exchange/interdiffusion and dissolution depending on the temperature of the disposal environment.

(Key words: nuclear waste, borosilicate glasses, corrosion, disposal conditions)

1. Introduction

Vitrification of low and intermediate level radioactive waste (LILW) is attracting great interest and large programmes are currently underway or planned in a number of countries. Utilisation of glass as a waste form for LILW requires appropriate performance assessment support for waste disposal facilities, which presumes an understanding of the main glass corrosion mechanisms. The corrosion of LILW glass has not been as intensively studied as that of high-level vitrified waste. Studies of actual vitrified radioactive waste in conditions similar to those expected in the disposal environment give realistic data diminishing many of the uncertainties, and enabling validation of computer code simulation to improve the confidence of mathematical models [1]. This paper examines corrosion behaviour of radioactive borosilicate glasses intended for nuclear waste immobilisation based on experimental data obtained during long term natural tests. These demonstrated diminishing of release rates of radionuclides by time. Our analysis is based on corrosion behaviour of identical radioactive high-sodium content borosilicate glass in a loamy soil (glass K-26) and in an open testing area (glass Bs-10). The borosilicate glass K-26 (Bs-10) has been designed to immobilise intermediate level operational nuclear power plant (NPP) radioactive waste. Some tonnes of this glass were produced in the 1980-s using radioactive waste from the Kursk NPP in Russia (with a channel type reactor RBMK) and a number of glass blocks have been disposed of in an experimental shallow land facility for long-term corrosion tests. K-26 waste glass has a density 2.46 g/cm^3 and theoretical composition on an oxide basis of (wt.%): 48.2 SiO_2-7.5 B_2O_3 2.5 Al_2O_3 15.5 CaO 16.1 Na_2O 1.7 Fe_2O_3 1.2 NaCl 1.1 Na_2SO_4 6.2Misc [2]. The Na_2O content in K-26 glass (16.1) makes it relevant to the glass formulations being considered at the Hanford site in the USA [3]. The main contaminant is ^{137}Cs at a level in the waste glass as high as C_0 =3.7 10^6 Bq/kg. The normalised leach rate of glass K-26 measured following the IAEA test procedure was 2.6·10^{-5} g/cm^{2}d averaged over 294 days.

2. Field tests

Field experiments have run for over 14 years to evaluate the behaviour of waste glass buried in a loamy soil (K-26) and in an open testing area (Bs-10). The two glasses are the same but tested in different environments: Bs-10 is tested on the surface of the ground whereas K-26 is tested in a near surface repository. 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 was 1.7 m deep which is below the freezing depth of soil (0.7m). 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. The test conditions for K-26 may be considered as saturated. Data on ground water showed an average pH = 7.59 and mineralization 600 mg/l. Testing conditions have been described in detail in [4]. Resulting leaching rates measured for ^{137}Cs are presented in Table I where leached inventory fractions are given as measured for 1-st and after 14 years as well as calculated for the suggested institutional period time 300 years.

Table I. Annual means for normalized leach rates of radionuclides (R, ^{137}Cs) and leached inventory fractions (f) for 1 year, 14 years and calculated for 300 years exposure.

Waste glass	Leach rate R, g/cm^{2}day,		Leached inventory fractions f, %		
	For 1st year	Over 14 years	For 1st yr.	For 14 years	Calculated for 300 years
K-26 (loamy soil)	$1.3 \cdot 10^{-6}$	$5.8 \cdot 10^{-7}$	$4\ 10^{-4}$	$1.36 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$
Bs-10 (open area)	$3.0 \cdot 10^{-6}$	$9.9 \cdot 10^{-7}$	$2\ 10^{-3}$	$7.75\ 10^{-3}$	$2.1 \cdot 10^{-2}$

Both at the initial and final stages of the testing period, the activity release rates per unit area of contact surface were greater at the open site (Bs-10). 14 years field testing data for glass Bs-10 averaged in a dissolution rate $r_{Bs-10} \approx 0.42$ µm/y and caesium interdiffusion coefficient $D_{Cs} \approx 1.8\ 10^{-20}$ m^2/s. This value for diffusion coefficient is consistent with reported data on the leaching behaviour of alkali-borosilicate glasses [5]. The experimental data for K-26 glass revealed that glass dissolution played an insignificant role at this stage of the tests. Moreover, it was difficult to assess numerically the glass K-26 dissolution rate based on just 14 years in the loamy soil conditions at an average soil temperature of 4.5 ^{o}C. A rough estimate based on the experiments suggested that the dissolution rate is at least an order of magnitude less that for the same glass tested in open area conditions, e.g. 0.002 µm/y $< r_{K-26} < 0.42$µm/y. The ^{137}Cs interdiffusion coefficient was estimated as $D_{Cs} = (0.34-0.51)\ 10^{-20}$ m^2/s. Hence the leaching behaviour of glass K-26 is still controlled by interdiffusion and ion exchange, consistent with the results of [6] on the major role of ion-exchange in leaching of low-level vitrified wastes.

3. Corrosion mechanisms

Release of alkali elements from the alkali-borosilicate glasses into water is controlled by two basic mechanisms: ion-exchange (termed also leaching) and hydrolysis [1, 6, 7]. The alkali ion-exchange reaction releases alkali ions which are then transported by interdiffusion processes to the water. This reaction also produces a silanol group and increases the local pH, thus catalysing the hydrolysis reaction. Hydrolysis of the glass network leads to practically glass-congruent release of ions into the water solution. Hydrolysis is suppressed in saturated conditions hence the glass corrodes basically via leaching. In non-saturated conditions later or soon the corrosion of silicate glasses is determined via hydrolysis [7]. The time required for silicate glasses to get into hydrolysis regime depends first of all on glass composition and temperature. More polymerised glasses require a longer time to become hydrolysed. At higher temperatures the time required to achieve hydrolysis regime is shorter. Fig. 1 shows the transition from leaching (ion-exchange) to hydrolysis during 1 hour exposure of different composition glasses at different temperatures.
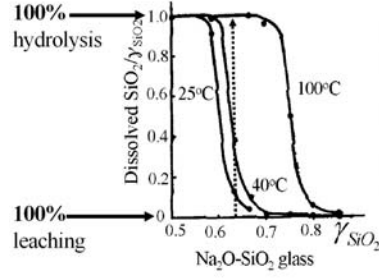
Fig. 1. Mechanisms of sodium-silicate glasses corrosion in water at 25, 40 and 100 $^{\circ}$C (adapted from [7]).

As can be seen the same composition glass depending on temperature shows different mechanisms of corrosion from almost 100% leaching at 25 $^{\circ}$C to about 40% at 40 $^{\circ}$C to practically 100% hydrolysis at 100 $^{\circ}$C. Glasses with higher silica content require a longer time to become hydrolysed comparing high sodium content glasses.

4. Corrosion rates

To quantify the time necessary to achieve the hydrolysis regime it is necessary to determine the contribution in the released ions into water from the two basic mechanisms. The total release rate of alkali into the water is the sum of release rates via ion exchange and hydrolysis. The release of alkali ions into the water via ion-exchange mechanisms from glasses was quantified by Doremus and co-workers [8, 9] whereas the release of alkali via hydrolysis is based on the approach of Agaard and Helgeson [10] which was adapted for waste glasses by Grambow [11]. In the simplest form the normalised leaching rate of an alkali via Doremus' ion-exchange mechanism $NRx_i(t)$ can be expressed as:

$$NRx_i = \rho\sqrt{\frac{D_i}{\pi t}} \quad (1)$$

where ρ is the density of glass, D_i is the effective interdiffusion coefficient for i-th alkali and t is time. We accounted in (1) that the concentration of alkali in water is negligible comparing the glass. In fact D_i is the effective interdiffusion coefficient as it depends on the diffusion coefficients of both alkali (i) and hydronium ion (h) through Nernst-Plank equation [8, 9, 12]. A gel layer is formed on the surface of glasses which corrode preferentially via leaching. A more complex form of $NRx_i(t)$, accounting for formation of a gel layer on the leached glass surface, was given by [5]. This, however, does not change the $t^{1/2}$ time dependence of mass releases and can be included into the value of the D_i. As the leaching rates depend on D_i which are different for different species (i) the release of species by ion-exchange is incongruent. The effective interdiffusion coefficient is expressed as an Arrhenius type function of temperature:

$$D_i = D_{0i}\exp(-\frac{E_{di}}{RT}) \quad (2)$$

where D_{oi} is the pre-exponential coefficient, R is the gas constant, T is absolute temperature and E_{di} is the activation energy of interdiffusion, which for nuclear waste glasses is of the order of several tens of kJ/mol. The values of E_{di} can be calculated using the structural energy barrier model [6]. The normalised leaching rate of an ion via hydrolysis mechanism NRh_i can be expressed as:

$$NRh_i = \rho r \quad (3)$$

where r is the hydrolysis (dissolution) rate of the glass. As the leaching rate does not depend on the specie i, e.g. is the same for all ions, the releases via hydrolysis are congruent. The hydrolysis of glass

occurs directly from the contacting surface hence the hydrolysis rate does not depend on time. In the simplest form the hydrolysis rate is given by equation [1, 10]:

$$r = r_0 \left(1 - \left(\frac{Q}{K} \right)^{\sigma} \right) \quad (4)$$

where r_0 is the initial hydrolysis rate, Q is the ion-activity product of the rate controlling reaction, K is the equilibrium constant of this reaction and σ is the net reaction order. The affinity term 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. Therefore in saturated conditions the hydrolysis rate $r \rightarrow 0$. The initial hydrolysis rate depends mainly on the glass composition, temperature and pH. We will assume conditions not very far from neutral which is the case for most nuclear waste glasses. The temperature dependence of the initial hydrolysis rate is:

$$r_0 = r_{0c} \exp(-\frac{E_a}{RT}) \quad (5)$$

where r_{oc} is the pre-exponential coefficient and E_a is the apparent activation energy of dissolution, which for nuclear waste glasses is of the order of 70–90 kJ/mol [13]. Glass K-26 (Bs-10) has $E_a = 68$ kJ/mol [3]. As both ion exchange and hydrolysis occur simultaneously in the linear approximation the total rate of ions releases into the water will be the sum of two contributions:

$$NR_i = NRx_i + NRh_i \quad (6)$$

5. Evolution of corrosion

Ion-exchange (leaching) prevails at the initial stage of leaching as the rate of ion exchange is high. However by time the rate of ion-exchange diminishes (see eq. (1)), whereas the rate of hydrolysis though small in neutral conditions remains constant. Hence hydrolysis will eventually dominate, except under saturated conditions when the rate of hydrolysis is close to zero. The higher the temperature the sooner hydrolysis becomes dominant as it has a significantly higher activation energy compared to ion-exchange: $E_a \gg E_{di}$. To find out the transition time from one mechanism to another define the characteristic time as:

$$\tau = \max\{\frac{D_{oi}}{r_{oc}^2} \exp(\frac{2E_a - E_{di}}{RT})\}, \quad (7)$$

In this equation E_{di} can be neglected as it is much smaller than $2E_a$. We can identify three areas in the field of time-temperature $\{t, T\}$ parameters (Fig. 2). **First** (Doremus' regime), if $t \leq \tau$ the glass releases alkalis through Doremus' mechanism as the contribution to alkali mass release via hydrolysis is always less than 1/3 of the total released mass. Note that in saturated conditions $\tau \rightarrow \infty$, which reflects the negligible role of hydrolysis [6]. In this area the normalised leaching rate can approximately be determined by equation (1) and is proportional to square root of reciprocal time: $NR_i \propto t^{-1/2}$. **Second** (intermediate), within time intervals of $\tau \leq t \leq 16\tau$ the contributions of both ion-exchange and hydrolysis mechanisms to the released inventory are of the same order of magnitude. The normalised leaching rate is determined by equation:

$$NR_i = \rho \sqrt{\frac{D_i}{\pi t}} + \rho r \quad (8)$$

Such leaching behaviour is seen in many corrosion experiments [14, 15] and thus the mechanism of waste glass leaching depends on time, e.g. what stage of corrosion it is at, as well as on temperature. **Third** (Grambow's regime), for $t \geq 16\,\tau$ the glass dissolves through hydrolysis as the contribution into the mass release of alkali from the ion exchange becomes less than 1/3 of the total mass. In this area the normalised leaching rate does not depend on time: $NR_i \propto const$. Hence equation (7) allows identifying the actual corrosion mechanism of glass depending on temperature (T) and exposure time (t). Fig. 2 shows the mechanisms of corrosion for the glass K-26 (Bs-10) as a function of temperature and time.
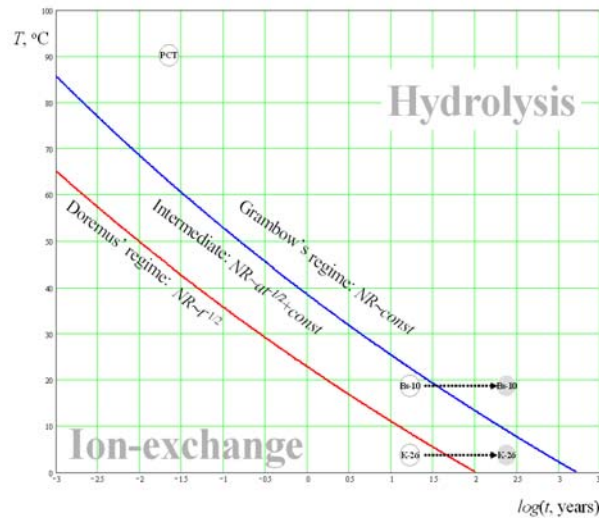

Fig. 2. Corrosion mechanisms for alkali-borosilicate glass K-26 (repository) and Bs-10 (open area) as a function of exposure time and temperature. Circles are glasses after 14 years of testing and grey circles – where glasses will be after~260 years. PCT-circle is the glass under PCT-A test [18].

As can be seen currently the corrosion of Bs-10 occurs via both ion-exchange and hydrolysis. This glass will be corroded by almost pure hydrolysis presumably after ~40 years. Corrosion of K-26 at the 4.5 ^{o}C temperature of the disposal environment occurs almost entirely through ion-exchange. This will occur for more than 30 years followed by an intermediate regime, where both mechanisms will play an important role. Since the waste radionuclides are short-lived (e.g. ^{137}Cs) ion-exchange will remain important for the release of radionuclides until their decay below the exemption levels (about 260 years) [16]. This conclusion is consistent with the results of [6] on dominant role of ion-exchange for low-level high-alkali glasses. Note that self-irradiation of glass will not change these conclusions as it leads to a higher ion-exchange rate particularly at low temperatures [17].

6. Vapour hydration and performance consistency tests

Vapour hydration test (VHT) is intended to study the reaction between waste forms and water [19]. VHT uses enhanced temperatures (150-300°C) to accelerate the corrosion of glasses. Such enhanced temperatures in fact do not occur in disposal systems. Nevertheless it relies on the fact that VHT generates alteration products similar to those that would be created by natural ageing [19, 20]. For example alteration products from naturally altered Hawaiian basaltic glasses are same to those from the VHT conducted at temperatures ranging from 70 to 240°C [20]. The time-temperature (t, T) map of glass corrosion processes (such as in Fig. 2) enables explanation of identity of corrosion products from VHT carried out at very high temperatures unexpected within disposal environment and extremely old naturally altered Hawaiian basaltic glasses. As can be seen from Fig. 2 the patterns for VHT glasses would be within the hydrolysis area as well as old glasses, which are also within hydrolysis regime but because of very long exposure time not high temperatures.

Performance consistency test (PCT) uses both enhanced surfaces and temperatures to accelerate corrosion processes [21]. The circle PCT in Fig. 2 shows the glass K-26 under conditions of PCT-A test (T=90 ^{o}C, t=7 days) carried out recently for glass samples extracted from the experimental burial

[18]. It demonstrated normalised leaching rate for sodium ions NR_{Na}=5.93 10^{-2} g/m^2 day. As seen from Fig. 2 due to the enhanced temperature of water the corrosion of glass under PCT-A conditions was practically controlled by hydrolysis.

Hence ensuring that corrosion mechanisms are the same one can conclude on what accelerated tests are predicting. E. g. for non-saturated and close to neutral conditions both VHT and PCT are characterised as tests correctly predicting corrosion of glasses in the regime of hydrolysis.

7. Conclusions

Corrosion of nuclear waste glasses is determined by leaching (ion exchange/interdiffusion) and hydrolysis. In non-saturated conditions corrosion is initially controlled by ion exchange/interdiffusion whereas late stages of glass corrosion are controlled by hydrolysis. The time necessary to achieve the regime of pure hydrolysis depends exponentially on environmental temperature. The higher temperature the lesser time is required for the transition from practically pure ion exchange/interdiffusion to practically pure hydrolysis. Nuclear waste glasses may corrode in actual conditions both via ion exchange/interdiffusion and hydrolysis depending on the temperature of the disposal environment.

8. References

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