

## Corrosion mechanisms of low level vitrified radioactive waste in a loamy soil

M.I. Ojovan<sup>1</sup>, W.E. Lee<sup>1</sup>, A.S. Barinov<sup>2</sup>, N.V. Ojovan<sup>2</sup>, I.V. Startceva<sup>2</sup>, D.H. Bacon<sup>3</sup>, B.P. McGrail<sup>3</sup>, J.D. Vienna<sup>3</sup>

<sup>1</sup>Immobilisation Science Laboratory, Department of Engineering Materials, University of Sheffield, UK;

<sup>2</sup>Scientific and Industrial Association "Radon", Moscow, Russia;

<sup>3</sup>Pacific Northwest National Laboratory, Richland, Washington, US.

### ABSTRACT

Field experiments have run for over 14 years to evaluate the behaviour of the same high-sodium content radioactive waste borosilicate glass buried in a loamy soil (glass K-26) and in an open testing area (glass Bs-10). Processing of field data for glass Bs-10 tested in an open area has resulted in a dissolution rate  $r = 0.42 \mu\text{m/y}$  and caesium diffusion coefficient  $D \approx 1.8 \cdot 10^{-20} \text{ m}^2/\text{s}$  at testing temperatures up to 19 °C. Both ion-exchange and hydrolysis control the corrosion of this glass. Processing of field data for K-26 glass revealed an insignificant role of glass dissolution. The caesium diffusion coefficient was estimated as  $D \approx (3.4\text{-}5.1) \cdot 10^{-21} \text{ m}^2/\text{s}$ . Due to the relatively low storage temperatures (4.5 °C) used the leaching behaviour of glass K-26 is believed to be controlled by ion exchange processes. This mechanism is likely to remain dominant until the decay of <sup>137</sup>Cs in the glass is below exemption levels.

### 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 including Russia and the USA. 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 the 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<sup>3</sup> and theoretical composition on an oxide basis of (wt.%): 48.2 SiO<sub>2</sub>-7.5 B<sub>2</sub>O<sub>3</sub> 2.5 Al<sub>2</sub>O<sub>3</sub> 15.5 CaO 16.1 Na<sub>2</sub>O 1.7 Fe<sub>2</sub>O<sub>3</sub> 1.2 NaCl 1.1 Na<sub>2</sub>SO<sub>4</sub> 6.2Misc [2]. The Na<sub>2</sub>O 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 <sup>137</sup>Cs at a level in the waste glass as high as  $C_0 = 3.7 \cdot 10^6 \text{ Bq/kg}$ . The normalised leach rate of glass K-26 measured following the IAEA test procedure was  $2.6 \cdot 10^{-5} \text{ g/cm}^2\text{d}$  averaged over 294 days.

## 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].

The amount of radionuclides leached from the glass was quantified by measuring the volume and radioactivity concentrations of the contacting waters. Water sampling was performed periodically, usually twice a month (except in winter). At each sampling time, the volume of water batch was recorded. Water aliquots were retained for analysis. Standard radiometrical, radiochemical, and chemical analytical techniques were applied [4]. The main results of field tests are presented in Table I.

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

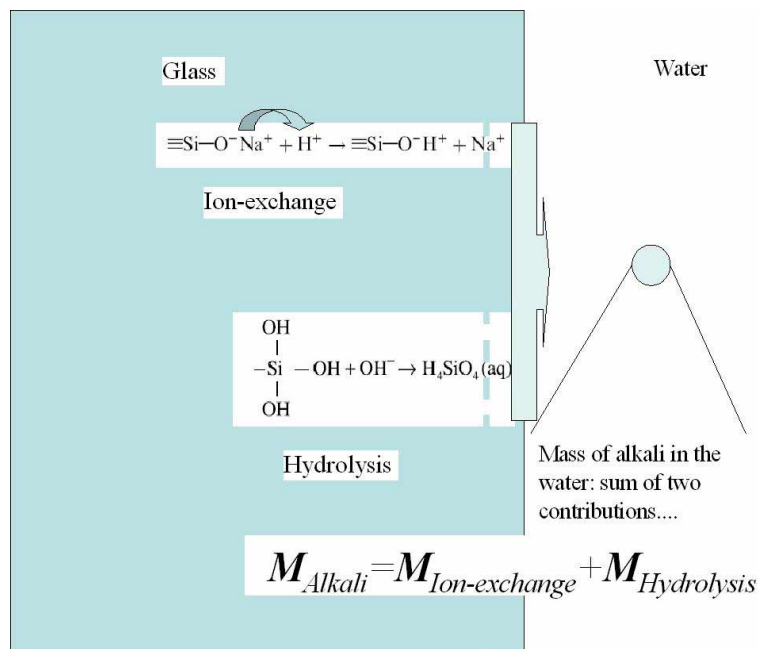
Waste glass	Leach rate $R$ , g/cm <sup>2</sup> day,		Leached inventory fractions $f$ , %	
	For 1 <sup>st</sup> year	Over 14 years	For 1 <sup>st</sup> yr.	Total for 14 years
K-26 (loamy soil)	$1.3 \cdot 10^{-6}$	$5.8 \cdot 10^{-7}$	$4 \cdot 10^{-4}$	$1.36 \cdot 10^{-3}$
Bs-10 (open area)	$3.0 \cdot 10^{-6}$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

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  $r_{Bs-10} \approx 0.42 \mu\text{m/y}$  and caesium interdiffusion coefficient  $D_{Cs} \approx 1.8 \cdot 10^{-20} \text{ m}^2/\text{s}$ . 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 °C. A rough estimate based on the experiments suggested that the dissolution rate is at least an order of magnitude less than that for the same glass tested in open area conditions, e.g.  $0.002 \mu\text{m/y} < r_{K-26} < 0.42 \mu\text{m/y}$ . The  $^{137}\text{Cs}$  interdiffusion coefficient was estimated as  $D_{Cs} = (0.34-0.51) \cdot 10^{-20} \text{ m}^2/\text{s}$ . 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.

## ANALYSIS OF CORROSION

Release of alkali elements from the alkali-borosilicate glasses into water is controlled by two basic mechanisms: ion-exchange and hydrolysis [1, 6]. 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. Depending on the degree of polymerisation up to three silanol groups must be formed before the last anchoring bond is broken, releasing a silicic acid molecule into solution (Fig. 1).



**Figure 1.** Schematic of alkali-borosilicate glass corrosion in water.

Ion-exchange and hydrolysis reactions are not separated in space or in time and both contribute to the release of alkali ions into the water although at different rates. Hence the total mass of alkali released into the water is the sum of releases via ion exchange and hydrolysis (Fig. 1). The release of alkali ions into the water via ion-exchange mechanisms from nuclear waste glasses was quantified by Doremus and co-workers [7, 8] whereas the release of alkali via hydrolysis was quantified by Grambow [9]. In the simplest form the normalised leached mass of an alkali via Doremus' ion-exchange mechanism  $NLx_i(t)$  can be expressed as:

$$NLx_i = \frac{2\rho}{\sqrt{\pi}} \sqrt{D_i t} \quad (1)$$

where  $\rho$  is the density of glass,  $D_i$  is the effective interdiffusion coefficient for  $i$ -th alkali and  $t$  is time. The release of species by ion-exchange is incongruent. We accounted in (1) that the concentration of alkali in water is negligible comparing the glass. Note that, in fact  $D_i$  is the effective interdiffusion coefficient as it depends on the diffusion coefficients of both alkali and hydrogen ions [7-10]. A more complex form of  $NLx_i(t)$ , 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  $D_i$ . The effective interdiffusion coefficient depends on temperature:

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

where  $D_{0i}$  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 leached mass of an alkali via hydrolysis mechanism  $NLh_i(t)$  can be expressed as:

$$NLh_i = \rho r t \quad (3)$$

where  $r$  is the hydrolysis (dissolution) rate of the glass revealing that releases via hydrolysis are congruent. In the simplest form the hydrolysis rate is given by:

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

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  $\sigma$  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. The temperature dependence of the initial hydrolysis rate is:

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

where  $r_{0c}$  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 [11]. Glass K-26 (Bs-10) has  $E_a = 68$  kJ/mol [3].

As both ion exchange and hydrolysis occur simultaneously, the total mass of alkali ions released into the water will be the sum of two contributions, e.g. the sum of equations (1) and (3) as schematically shown in Fig. 1:

$$NL_i = NLx_i + NLh_i \quad (6)$$

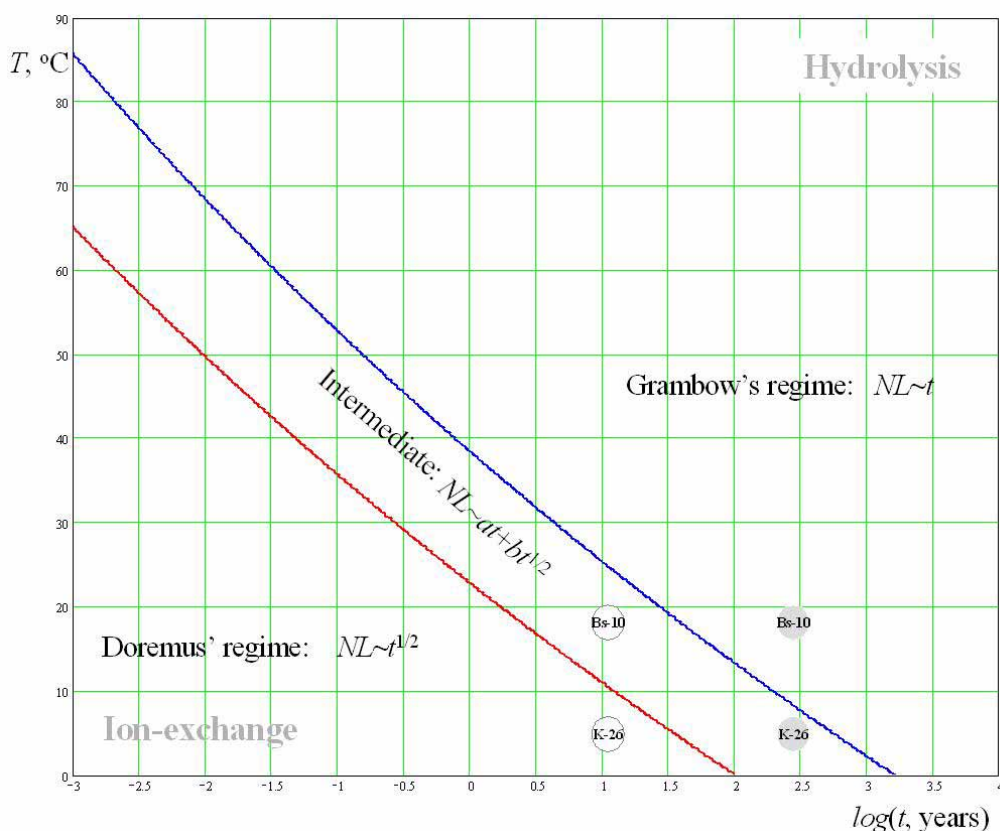
At the initial stage of leaching ion-exchange prevails as the rate of ion exchange is high. However, since the hydrolysis has a stronger dependence with time ( $\propto t$ ) compared to ion-exchange ( $\propto t^{1/2}$ ) it will eventually dominate, except under saturated conditions when the rate of hydrolysis is zero. The higher the temperature the sooner hydrolysis becomes dominant as it has a significantly higher activation energy compared to ion-exchange:  $E_a \gg E_{di}$ . Defining the characteristic time as:

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

$E_{di}$  can be neglected in this equation as it is much smaller than  $2E_a$ . 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]. For  $t \geq 16\tau$  the glass dissolves through Grambow's mechanism as the contribution into the mass release of alkali from the ion exchange becomes less than 1/3 of the total mass. Within time intervals of  $\tau \leq t \leq 16\tau$  the contribution of both mechanisms to the released inventory is of the same order of magnitude and the normalised leached mass will be:

$$NL_i = a_i t^{1/2} + bt, \quad (8)$$

where  $a_i$  and  $b$  are constants. Such leaching behaviour is seen in many corrosion experiments [12, 13] 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. Equation (7) hence allows identifying the actual corrosion mechanism of glass depending on temperature and exposure time. Fig. 2 shows the mechanisms of corrosion for the glass K-26 (Bs-10) as a function of temperature and time.



**Figure 2.** Corrosion mechanisms for alkali-borosilicate glass K-26 (Bs-10) as a function of exposure time and temperature. Circles are glasses after 14 years of testing and grey circles – glasses after ~260 years.

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 °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.  $^{137}\text{Cs}$ ) ion-exchange will remain important for the release of radionuclides until their decay below the exemption levels (about 260 years) [14]. 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 [15].

## CONCLUSIONS

The corrosion mechanisms of the same high-sodium content radioactive waste borosilicate glass in field conditions depend on the environment conditions. In open area tests at relative higher temperatures after 14 years the glass is corroded via both ion-exchange and hydrolysis. In burial conditions at relative lower temperatures after 14 years the glass is corroded only via ion-exchange and this mechanism will remain significant until almost complete decay of  $^{137}\text{Cs}$  in the glass. Authors acknowledge P. Van Iseghem and R.H. Doremus for valuable comments.

## REFERENCES

1. P. Van Iseghem ed. *J. Nucl. Mat.*, **298**, N. 1, 2 (2001).
2. I.A. Sobolev, F.A. Lifanov, S.V. Stefanovsky, S.A. Dmitriev, N.D. Musatov, A.P. Kobelev and V.N. Zakharenko. *Atomic Energy*, **69**, 233-236 (1990).
3. D.H. Bacon., M.I. Ojovan, B.P. McGrail, N.V. Ojovan, I.V. Startceva. *Proc. Int. Conf. ICEM '03*, 21–25.09.03, Oxford, England, CD ROM 4509.pdf. (2003).
4. M.I. Ojovan, N.V. Ojovan, I.V. Startceva, G.N. Tchuikova, Z.I. Golubeva., A.S. Barinov *J. Nucl. Mat.* **298**, 174-179 (2001).
5. M. Aertensen, K. Lemmens, P. Van Iseghem. *Mat. Res. Soc. Symp. Proc.*, **757**, II5.8.1-8 (2003).
6. B.P. McGrail, J.P. Isenhower, D.K. Shuh, P. Liu, J.G. Darab, D.R. Baer, S. Thevuthasen, V. Shutthanandan, M.H. Engelhard, C.H. Booth, P. Nachimuthu. *J. Non-Cryst. Solids*, **296**, 10-26 (2001).
7. R.H. Doremus. *J. Non-Cryst. Solids*, **19**, 137 (1975).
8. R.H. Doremus. *J. Non-Cryst. Solids*, **25**, 261 (1977).
9. B.E. Grambow. *Mat. Res. Soc. Symp. Proc.*, **44**, 15 (1985).
10. R.W. Douglas, J.O. Isard. *J. Soc. Glass Techn.* **33**, 289-335 (1949).
11. D.M. Strachan. *J. Nucl. Mat.*, **298**, 69-77 (2001).
12. M.I. Ojovan, N.V. Ojovan, I.V. Startceva, G.N. Chuikova and A.S. Barinov. *Mat. Res. Soc. Symp. Proc.*, **663**, 837-842 (2001).
13. S. Portal, R. Sempere. *Phys. Chem. Glasses*, **44**, 303-307 (2003).
14. M.I. Ojovan, R. Burcl. *Proc. 2003 EPRI Int. Conf. in Conj. with IAEA*, 16-18.07.03, New Orleans, LA, USA, CD ROM EPRI-S08-P7.pdf (2003).
15. M.I. Ojovan, W.E. Lee. *Mat. Res. Soc. Symp. Proc.*, **792**, R2.5.1-6 (2004).