

16-YEARS FIELD TESTS OF VITRIFIED OPERATIONAL NPP RADIOACTIVE WASTE

N.V. Ojovan, S.A. Dmitriev, A.S. Barinov, Z.I. Golubeva, I.A. Sobolev, S.V. Stefanovsky
Scientific and Industrial Association “Radon,”
Moscow, 119121, Russian Federation

M.I. Ojovan
Immobilisation Science Laboratory,
Department of Engineering Materials,
University of Sheffield, United Kingdom

ABSTRACT

We examined the 16-years field test data on environmental behaviour of vitrified NPP operational radioactive waste revealing that radionuclide losses during 16 years obey a square root time dependence, which indicates on a prevailing diffusion-controlled release mechanism. The main parameters controlling the corrosion of waste glass K-26 in the near-surface repository are determined by the cesium effective interdiffusion coefficient $D_{Cs} = 4.5 \cdot 10^{-12} \text{ cm}^2/\text{d}$ and rate of glass hydrolysis $r_h = 0.1 \text{ } \mu\text{m}/\text{y}$. We found that the total release of radionuclides from 190 kg of buried radioactive glass K-26 will not exceed 20 kBq over 300 years.

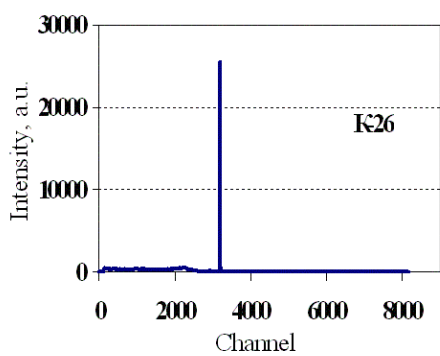
INTRODUCTION

Vitrification is currently attracting great interest for immobilisation of operational radioactive wastes from nuclear power plants as well as radioactive and toxic legacy wastes [1-4]. New types of melters such as cold-crucible induction melters [2] and thermochemical reactors [3] make vitrification competitive to conventional low-temperature immobilisation methods such as cementation and bituminisation. Moreover large-scale vitrification programmes are underway in a number of countries and new applications can be expected in the future [1-4]. Glass as one of the most durable wastefrom minimises the environmental impact of radionuclides and enables utilisation of simplest and hence less expensive waste disposal facilities. One of possible disposal options for vitrified radioactive waste is emplacement in a non-saturated wet environment such as near-surface repositories. Waste glasses in near-neutral water solutions have minimal corrosion rates. Analysis of their behaviour in such conditions requires long duration tests. Herein we examine the 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 [5, 6].

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 48.2 SiO₂-7.5 B₂O₃-2.5 Al₂O₃-15.5-CaO-16.1 Na₂O-1.7 Fe₂O₃-1.2 NaCl 1.1-Na₂SO₄-6.2

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 [7]. The main radioactive contaminant of K-26 glass is ^{137}Cs which is present in the waste glass at a level of up to $3.73 \cdot 10^6$ Bq/kg. Figure 1(a) shows a gamma-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 ^{137}Cs is the only gamma emitter present in the glass. Moreover from XRD patterns it was revealed that K-26 glass remains an X-ray amorphous material after 12 years. Figure 1(b) shows a view of experimental repository, which was opened after 12 years of tests for inspection and sample analyses.



(a)



(b)

Fig. 1. Gamma-spectrum of waste glass K-26 (a) and a view of opened experimental repository with groundwater sampling tube (b).

Field tests of K-26 glass have been run since 1987 to evaluate the behaviour of the glass near surface disposal conditions [7]. 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 (0.7m). 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. Testing conditions have been described in detail in [7]. The conditions may be considered as water saturated with an average pH of 7.6 and mineralization of 600 mg/L. 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). Overall measurement errors were not higher than 10%. Table I gives data on

volume and specific radioactivity of the groundwater batches that had contacted the waste glass. The effects of waste glass leaching on groundwater chemistry are summarised in Table II.

Table I. Collected Groundwater Batch Volumes and their Specific Radioactivity.

| Years | t, y | Groundwater batches v_i , L | Specific activity, Bq/L |
|-----------|------|-------------------------------|-------------------------|
| 1987-1988 | 1 | 129.0 | 20.35 |
| 1988-1989 | 2 | 81.7 | 18.51 |
| 1989-1990 | 3 | 103.5 | 15.51 |
| 1990-1991 | 4 | 88.0 | 14.39 |
| 1991-1992 | 5 | 56.0 | 13.58 |
| 1992-1993 | 6 | 45.0 | 13.04 |
| 1993-1994 | 7 | 26.0 | 12.61 |
| 1994-1995 | 8 | 57.0 | 11.96 |
| 1995-1996 | 9 | 97.5 | 11.41 |
| 1996-1997 | 10 | 83.0 | 10.88 |
| 1997-1998 | 11 | 94.0 | 10.37 |
| 1998-1999 | 12 | 76.0 | 10.01 |
| 1999-2000 | 13 | 34.0 | 9.76 |
| 2000-2001 | 14 | 54.0 | 9.48 |
| 2001-2002 | 15 | 30.0 | 9.30 |
| 2002-2003 | 16 | 43.0 | 9.08 |

Table II. Parameters of Groundwater in Contact with the Waste Glass K-26.

| Ions | 1 st year | 8 th year | 12 th year | Background |
|--|----------------------|----------------------|-----------------------|--------------|
| pH | 7.5 | 7.8 | 7.9 | 7.6-7.7 |
| Na ⁺ , (mg/L) | 34.64 | 54.55 | 63.40 | 13.11 |
| K ⁺ , (mg/L) | 3.70 | 3.82 | 3.72 | 1.26 |
| Ca ²⁺ , (mg/L) | 78.93 | 54.26 | 46.30 | 48.74 |
| Mg ²⁺ , (mg/L) | 32.30 | 30.26 | 27.75 | 20.91 |
| Fe, (mg/L) | 9.33 | 2.64 | 2.02 | 1.16 |
| Cl ⁻ , (mg/L) | 33.11 | 26.49 | 24.08 | 13.17 |
| NO ₃ ⁻ , (mg/L) | 2.22 | 4.18 | 4.23 | 2.30 |
| HCO ₃ ⁻ , (mg/L) | 435 | 390 | 373 | 258.03 |
| SO ₄ ²⁻ , (mg/L) | 13.93 | 12.45 | 10.62 | 4.73 |
| B, (mg/L) | Not measured | 24.75 | 27.72 | Not measured |
| Mineralisation, (mg/L) | 710 | 830 | 810 | 600 |

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.*

$$V(t) = \sum_j v_j . \quad (\text{Eq.1})$$

The total amount of groundwater collected that had been in contact K-26 glass during the first 16 years of testing was $V(16y)=1097.7\text{L}$. The amount of radionuclide i leached out from the waste glass $A_i(t)$ (Bq) was calculated using the equation:

$$A_i(t) = \sum_j a_{ij} v_j . \quad (\text{Eq.2})$$

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

$$NM_i = \frac{A_i(t)}{q_i S} , \quad (\text{Eq.3})$$

where $S=2052 \text{ cm}^2$ is the surface area of the glass in contact with groundwater and $q_i =3.73 \text{ kBq/g}$ is the specific ^{137}Cs content in the waste glass K-26. The leached fraction of the radionuclide i , ϕ_i , from the waste glass K-26 was calculated using equation:

$$\phi_i = \frac{A_i(t)}{A_i(0)} , \quad (\text{Eq.4})$$

where $A_i(0)=7.09 \cdot 10^8 \text{ Bq}$ was the initial total content of radioactivity due to radionuclide i in K-26 glass. The average normalised leaching rate of radionuclide i , NR_i , was calculated using

$$NR_i = \frac{NM_i}{t} \quad (\text{Eq.5})$$

where t is the duration of test in days. Figure 2(a) shows the normalised leaching rate as a function of time. It can be seen that, although fluctuating, 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. To reveal the actual tendency we divided the normalised mass losses to the testing time and square root of testing time and plotted results obtained as a function of time. Figure 2(b) which shows the time dependence of the normalised mass losses of ^{137}Cs divided by square root of time (NM_i / \sqrt{t}). As seen this ratio remains almost constant during tests, which demonstrates that the radionuclides are preferentially released from K-26 glass via a diffusion-controlled process. This is consistent with indications of [8] on the major role of ion exchange in leaching of low-level vitrified wastes.

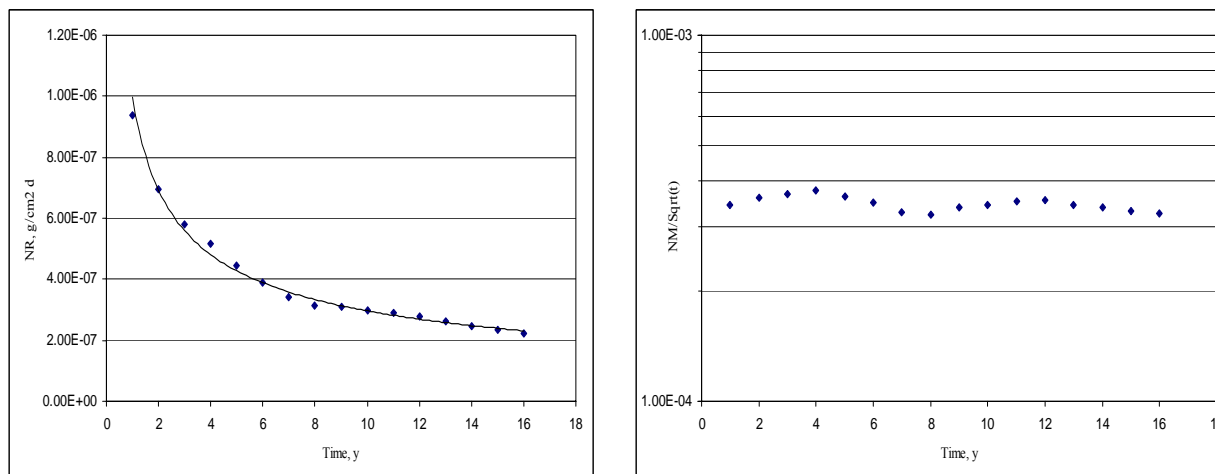


Fig. 2. Average normalised leaching rates (a) and normalised mass losses divided by square root of time (b) for waste glass K-26.

Over time the mineralisation of the water that has been in contact with the glass has altered from (HCO₃⁻ -Ca²⁺)- type to (HCO₃⁺ -Na⁺ -K⁺ - Ca²⁺ -NO₃⁻ -Cl⁻)- type, being numerically higher than background by a factor of about 1.35. Progressive decreases in concentration with time were observed for Ca²⁺, Mg²⁺, Fe, Cl⁻, HCO₃⁻, SO₄²⁻ and mineralisation. For boron, Na⁺ and NO₃⁻, the opposite concentration trends were observed throughout the experiment as well as a small but progressive pH change from 7.5 to 7.9.

THEORETICAL

Define the fraction content f_i of a specie i in the glass as:

$$f_i = \frac{C_i}{\rho} \quad (\text{Eq.6})$$

where C_i is the concentration and ρ is the density of glass (g/cm³). Define the actual release rate for the specie i as r_i , (g/cm² day), then the normalised release rate will be

$$nr_i = \frac{r_i}{f_i} \quad (\text{Eq.7})$$

The average normalised leaching rate NR_i , which is measured in the experiment, can be found calculating the total mass release and dividing to the time of test:

$$NR_i = \frac{\int_0^t r_i dt}{f_i t} \quad (\text{Eq.8})$$

Aqueous corrosion of alkali-silicate glasses such as waste glass K-26 in non-saturated conditions has been described earlier [9 - 12]. Corrosion begins with a transition effect of instantaneous surface dissolution of surface contaminants and near surface layers then is controlled by the diffusion-controlled ion exchange and glass network hydrolysis. The rate of release of species into the water is given by a sum of three terms accounting for these mechanisms:

$$r_i = r_{si} + r_{xi} + r_{hi}, \quad (\text{Eq.9})$$

where r_{si} is the rate of the instantaneous surface dissolution, r_{xi} is the rate of ion exchange and r_{hi} is the rate of glass network hydrolysis.

The near surface layers of any solid including glass are different from the bulk moreover for glasses these differences spread to a depths ~ 100 nm [13-15]. The instantaneous surface dissolution rate is given by equation [9, 10]:

$$r_{si} = n_{si} k_i \exp(-k_i t), \quad (\text{Eq.10})$$

where k_i is the rate of instantaneous dissolution of specie i in water (1/day), and n_{si} is its concentration on the surface of the glass (g/cm^2).

The steady-state 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 [16, 17] whereas the release of alkali via hydrolysis was described by the model of Agaard and Helgeson [18]. 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. The rate of release of species via ion exchange is given by equation:

$$r_{xi} = \rho f_i \left(\frac{D_{0i}}{\pi t} \right)^{1/2} \exp\left(-\frac{E_{di}}{2RT}\right), \quad (\text{Eq.11})$$

where D_{0i} is the pre-exponential term in the effective interdiffusion coefficient of specie in the glass $D_i = D_{0i} \exp(-E_{di}/RT)$, $E_{di} = H_{mH} + H_{fNBO}$ is the activation energy of interdiffusion, H_{mH} is the enthalpy of motion of protons, H_{fNBO} is the enthalpy of formation of non-bridging oxygen (NBO), R is the universal gas constant and T is temperature. Note that the activation energy of interdiffusion holds the same value for all cations because of limiting proton ingress into the glass. As at the water-glass interface concentration of protons significantly exceed that of cations [19] the pre-exponential coefficient of the interdiffusion coefficient can be expressed as a function of pH of contacting water:

$$D_{0i} = \frac{D_{0H}^* \kappa 10^{-pH}}{C_i(0)}, \quad (\text{Eq.12})$$

where D_{0H}^* is the pre-exponential coefficient in the diffusion coefficient of protons in the glass $D_H = D_{0H}^* \exp(-E_{dH} / RT)$, $C_i(0)$ is the concentration of species at the glass surface (mol/L) and κ is a constant, which relates the concentration of protons in water and at glass surface. Relationship (12) reveals that ion exchange occurs preferentially in acidic solutions and diminishes rapidly with the increase of pH.

Glass network dissolution is characteristic of the late phases of corrosion (when ion exchange is substantially diminished) and causes a congruent (to glass composition) 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, these effects however are not considered herein. The rate of release of species via hydrolysis is given by equation:

$$r_{hi} = \rho f_i k a_{H^+}^{-\eta} \left(1 - \left(\frac{Q}{K} \right)^\sigma \right) \exp\left(-\frac{E_a}{RT}\right), \quad (\text{Eq.13})$$

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 $\left(1 - (Q/K)^\sigma\right)$ 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 . The activation energy of network glass dissolution for K-26 glass is $E_a \approx 68 \text{ kJ mol}^{-1}$ [6].

For nuclear waste glasses it is necessary to take into account radioactive decay, which causes an exponential decrease of radionuclide concentrations [7, 10]. Average normalised mass releases of radioactive species such as ^{137}Cs are hence given by equation:

$$NR_i = \frac{NM_{si}}{t} + \frac{\rho}{t} \sqrt{\frac{D_i}{\lambda_i}} \text{erf}\left(\sqrt{\lambda_i t}\right) + \frac{r_h \rho}{\lambda_i t} [1 - \exp(-\lambda_i t)], \quad (\text{Eq.14})$$

where D_i is the effective interdiffusion coefficient (cm^2/d), $r_h = r_{hi}/\rho f_i$ is the linear rate of hydrolysis ($\mu\text{m}/\text{y}$), NM_{si} is a constant accounting for instantaneous surface dissolution, λ_i is the decay constant ($1/\text{y}$), t is the testing time (y) and $\text{erf}(z)$ is the error function

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-x^2) dx. \quad (\text{Eq.15})$$

The fraction of released radionuclides ϕ_i from the glass can be found accordingly as:

$$\phi_i = \frac{S}{\rho V} NM_{si} + \frac{S}{V} \sqrt{\frac{D_i}{\lambda_i}} \operatorname{erf}(\sqrt{\lambda_i t}) + \frac{S}{V} \frac{r_h}{\lambda_i} [1 - \exp(-\lambda_i t)], \quad (\text{Eq.16})$$

where S/V is the waste glass surface to volume ratio, which for the waste glass K-26 is $2.66 \cdot 10^{-2}$ 1/cm.

DISCUSSION

For radioactive samples either equations (14) or (16) can be fitted experimental data to identify both effective interdiffusion 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 $t=300\text{y}$ for the waste glass K-26 as a typical representative of low and intermediate level waste. Figure 3 shows the best fit to experimental data to the normalised leaching rates given by equation (14) and to the fraction of released radionuclides given by equation (16).

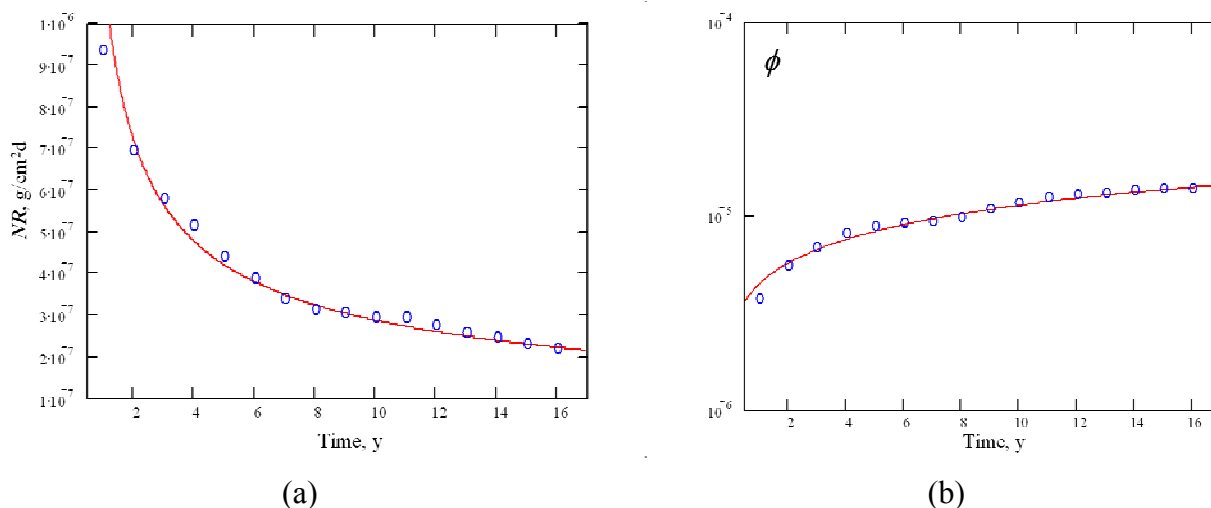


Fig. 3. Best fit to experimental data of the theoretical expressions for average normalised leaching rate (a) and fraction of released radionuclides (b) for the waste glass K-26.

The best fit is achieved for an effective interdiffusion coefficient $D_{Cs} = 4.5 \cdot 10^{-12}$ cm^2/d , and the rate of glass hydrolysis $r_h = 0.1$ $\mu\text{m}/\text{y}$. These data are consistent with the results [20] which reported effective diffusion coefficients from $1.3 \cdot 10^{-23}$ to $2.8 \cdot 10^{-21}$ m^2/s for the nuclear waste glasses SM539 and SON68, as well as [21], which reported diffusion coefficients of boron, sodium and lithium from 10^{-22} to 10^{-20} m^2/s for borosilicate glasses designed to immobilise incineration wastes. Dissolution rates less than $0.3\mu\text{m}/\text{y}$ were reported for nuclear waste glasses in Boom clay at 16°C ambient rock temperature [22].

Equation (16) enables an assessment of the total possible release of radionuclides into the environment assuming preservation of current conditions. Figure 4(a) shows the calculated and measured fractions of released radionuclides from the glass K-26. Figure 4(b) shows an

assessment of contributions to radionuclide releases from the two basic (steady state) mechanisms of glass corrosion– ion exchange and hydrolysis.

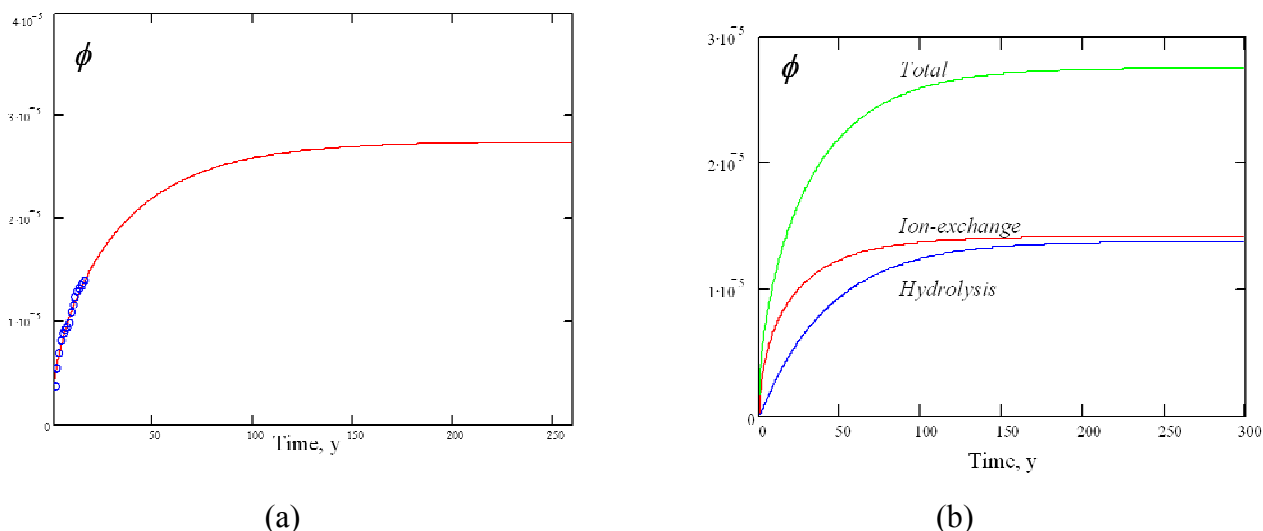


Fig. 4. Measured (circles) and calculated (line) fraction of radionuclides released from K-26 glass (a) and the relative contributions to these releases from ion exchange and hydrolysis (b).

Data obtained herein conform well to STORM computer-code results on Na releases from this glass, which demonstrated a 60% ion exchange contribution to the total mass release [6]. From Figure 4(b) one can see that the fraction of released radionuclides tends to a maximum saturation value. Therefore the total release of radionuclides from 190 kg of radioactive glass K-26 will not exceed this maximal value, which is 20 kBq over 300 years.

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. The analysis of radionuclide release from the radioactive waste glass K-26 tested in a near surface experimental repository over 16 years revealed that the corrosion of this glass is currently dominated by diffusion-controlled ion exchange. Processing of data obtained revealed the effective interdiffusion coefficient $D_{Cs} = 4.5 \cdot 10^{-12} \text{ cm}^2/\text{d}$ ($5 \cdot 10^{-21} \text{ m}^2/\text{s}$) and the rate of glass hydrolysis $r_h = 0.1 \text{ }\mu\text{m}/\text{y}$. This indicates that the total release of radionuclides from 190 kg of radioactive glass K-26 will not exceed 20 kBq over 300 years.

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