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# Waste glass behavior in a loamy soil of a wet repository site

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**Abstract**

Intermediate-level operational waste from a nuclear power plant was immobilized in borosilicate (BS) glass in a pilot vitrification plant. Glass blocks weighing in average 30 kg with a waste loading of 35 wt% and total α-, β-activity of about $3.75 \times 10^6$ Bq/kg were prepared and placed for testing in a near-surface repository and on an open site. Results of 12 years of exposure are presented. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Research on the encapsulation of radioactive waste in a glass matrix was initiated at the SIA 'Radon' in the mid-1970s. Pilot and industrial vitrification plants based on the use of a ceramic Joule-heated melter, plasma melter, and induction cold-crucible melting process have been constructed. Vitrification techniques have been applied to liquid and solid low- and intermediate-level waste collected from the Moscow wastewater purification plant, nuclear power plants and minor producers.

Vitrification implies incorporation of radionuclides in the form of oxides in the matrices of borosilicate (BS), aluminosilicate, aluminophosphate and other glasses. Among them, the BS glass is the most frequently used. This paper aims to describe and mathematically process the data generated during the 12-year testing of BS waste glass under conditions of a near-surface repository (glass K-26) and open testing site (glass Bs-10) to predict the waste form behavior over extended time periods. The testing approach envisages the possibility of implementation of a near-surface disposal concept based on the direct disposal of low-level vitrified wastes into the earth trenches. The tests may be also regarded as simulating the waste form behavior in certain repository evolution scenarios developed for ISAM safety cases, such as scenarios of degradation of engineered barriers (protective covering, overpacks and containers), denudation and weathering scenarios. These are the cases when glass matrix emerges as the only barrier to the release of radionuclides into the environment.

When selecting a modeling approach, we took into account that a number of well developed theoretical models to predict the long-term behavior of waste glass materials were existing [1]. However, in our case of a proposed relatively short-term (300 years) storage of LILW glasses under conditions of the shallow ground repository, we considered preferable to use a conceptually straightforward model that may be easily adjusted to varying environmental conditions. Here we use a two-parameter semiempirical model, which include terms to account for the major processes of radionuclide release from the glass: (i) diffusion of radionuclides and (ii) glass matrix dissolution. Parameters, characterizing the rates of these two processes, were derived from 12-year field tests and used to calculate the radioactive inventory fraction that will be released into the environment throughout the entire storage period.

## 2. Experimental

Real intermediate-level operational waste from the Kursk NPP (with the RBMK reactor) representing sludge with a salt content of about 340 g/l and $NaNO_3$ as the main waste component (86 wt% of dry weight) was used. The main radionuclides in the waste were $^{137}Cs$ (82%), $^{134}Cs$, and $^{90}Sr$. Technical grade or naturally occurring materials such as quartz sand, loam and

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Table 1
Composition of waste glass by oxides, wt%

| $SiO_2$ | $Na_2O$ | $B_2O_5$ | $Al_2O_3$ | $K_2O$ | CaO | Other |
|---|---|---|---|---|---|---|
| 48.2 | 16.1 | 7.5 | 2.5 | 0.5 | 15.5 | 9.7 |

datolite concentrate were used for the glass batch preparation. The molten waste glass was produced in a pilot plant 'EPOS' with a single-stage slurry-fed Joule-heated ceramic glass melter (the process temperature was below 1150°C) and poured into containers of carbon steel. Annealing was not applied. The product density was 2.46 $g/cm^3$. The composition of glass is showed in Table 1. The activity in the waste form was for total β ($^{90}Sr + ^{90}Y$), $3.74 \times 10^6$ Bq/kg, and for total α ($^{239}Pu$) $1.3 \times 10^4$ Bq/kg.

Static leaching experiments conducted at room temperature using IAEA methodology, resulted in a mass leach rate of $2.6 \times 10^{-5}$ $g/cm^2$ day (average for the first 294 days). Other product characteristics and test conditions are reported in detail elsewhere [2,3].

It should be noted that the glasses Bs-10 (see Fig. 1) and K-26 (see Fig. 2) are prepared from the same waste glass batch. Glass blocks were placed for testing into stainless steel welded trays (designed for contact water collection) at the open site and in the experimental near-surface repository K-26, respectively. In total, six containers with six blocks of waste glass, weighing together about 180 kg were placed with open top surfaces in the tray (40 cm deep, 60 cm wide, and 65 cm long) at a depth of 1.7 m in the repository K-26. Pure coarse sand was used to backfill the glass blocks in order to prevent the glass from direct contact with soil and to facilitate water infiltration to blocks and its accumulation in the water trap. Repository test conditions throughout the warm year seasons may be considered as water-saturated or very close to saturated.

Fig. 1. Block of waste glass Bs-10 in a carbon steel container placed on the stainless steel tray at the open testing site.

## 3. Analytical procedures

Samples of rainwater, groundwater, backfill and soil as well as drill cores of intact host rock were collected for analyses using specially developed methodologies providing reliability of results. Water samples were taken periodically, typically twice a month, throughout the overall testing period. Samples of solids were received during the unsealing of the SIA 'Radon' experimental repositories, performed in July 1999. Fill-up soil samples were taken at 4 depth levels, 0–0.3, 1.2–1.45, 1.70–2.15, and 2.65 m below the ground surface, at three distances from the object of testing. Drill cores of undisturbed host rock were sampled at the depths of 1.90–2.90 m below the surface. 104 samples of soil, rock and backfill were analyzed. Standard techniques of radiometric, γ-spectrometric, radiochemical and chemical analyses were applied to samples of water, soil and glass.

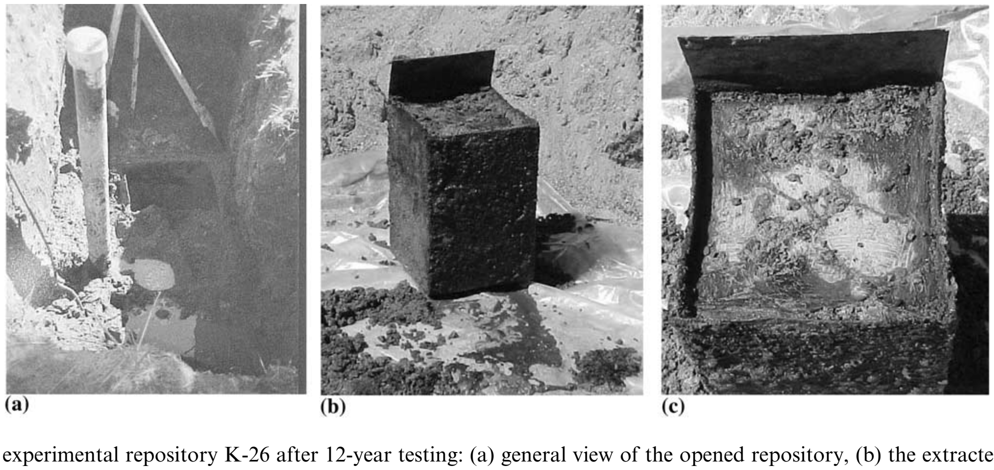

Fig. 2. The experimental repository K-26 after 12-year testing: (a) general view of the opened repository, (b) the extracted container, (c) surface of the waste glass block.

Clay-type minerals in the backfill contacting the waste blocks and in the surrounding soil were detected and analyzed using electron microscopy and X-ray analysis. Physical and physicochemical parameters of rock samples (grain-size composition, density, humidity, sorption capacity, etc.) were determined.

## 4. Results and discussion

A SEM study of the waste glass Bs-10 demonstrated that a compact and smooth layer of a few micrometer thick has formed with time on the glass surface. SEM and X-ray diffraction analyses as well as visual examinations of contact glass surfaces showed no evidence for the formation of secondary alteration phases in any considerable amount throughout the 12-year exposure time. The activity of the glass surface layer has decreased by a factor of about 1.7 due to leaching. SEM and X-ray studies of the bulk glass samples (Bs-10, K-26) showed there was little or no difference in microstructure and amorphous structure of the waste glass at various testing stages. Compression strength measured on samples split off the glass blocks, was in the range of 30–80 MPa.

Graph representations of the changes in the annual radioactivity concentration means and in other parameters characterizing the radionuclide release from the glass into contacting rainwater (Bs-10) and contacting groundwater (K-26) are given in Figs. 3–6.

As an example, numerical values for total β, total α and activity levels for $^{137}$Cs, $^{90}$Sr, $^{238}$Pu, $^{238}$U, $^{226}$Ra in contact waters are given in Table 2.

It should be noted that the activity concentrations of $^{137}$Cs in waters contacting the waste glass were in average below the allowable level for radioactive cesium in water (96 Bq/l in Russia till 01.01.2000) over the test duration, while exceeding background values by factors of about 30 and 5 at the open and repository sites, respectively.

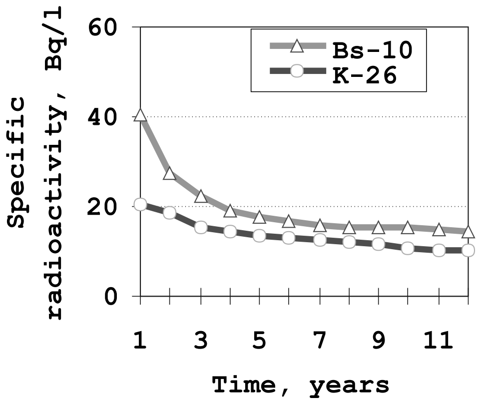

Fig. 3. Annual concentration means for radionuclides in water contacting vitrified waste.

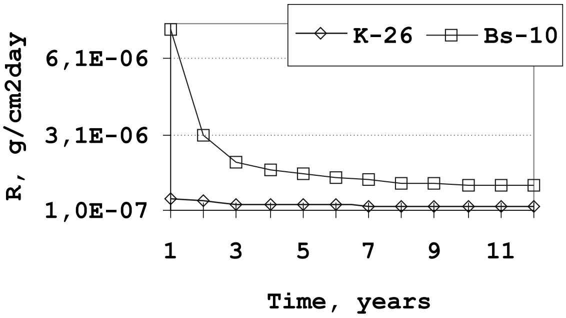

Fig. 4. Changes in $^{137}$Cs average annual leach rate with time.

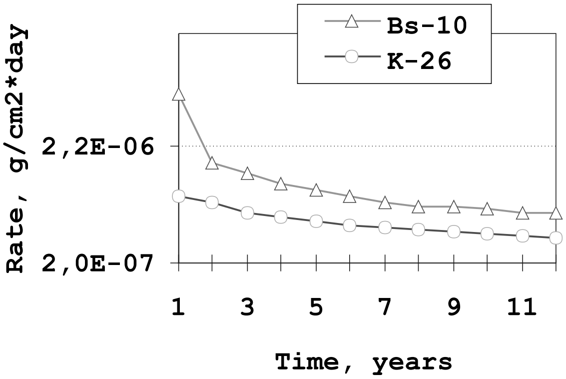

Fig. 5. Changes in average annual radioactivity leach rate with time.

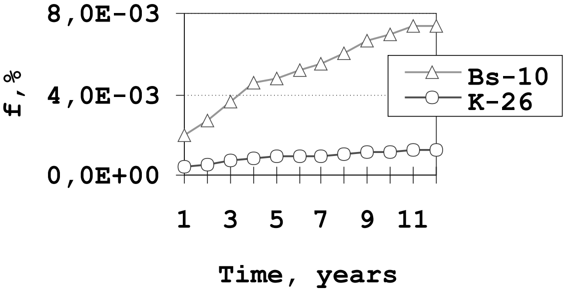

Fig. 6. Inventory fractions released from Bs-10 and K-26 glass samples as a function of time.

Parameters characterizing the radioactivity release from the waste glass into the environment are given in Table 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.

Changes in groundwater chemistry and radiation effects could lead to irreversible alterations in host rock

Table 2
Radiometry and radiochemistry data for contact waters collected in 1999, in Bq/l

| | | $\sum\beta$ ($^{137}$Cs) | $\sum\alpha$ ($^{239}$Pu) | $^{137}$Cs | $^{90}$Sr | $^{238}$Pu, $^{238}$U, $^{226}$Ra |
|---|---|---|---|---|---|---|
| Bs-10 (open site) | Filtered water | 25 | <0.02 | 24 | 1 | 0.02 |
| | Suspended particles | 1 | <0.02 | – | | |
| K-26 (repository) | Filtered water | 8.3 | <0.02 | 0.7 | 1.7 | <0.02 |
| | Suspended particles | 1.7 | 0.12 | 0.3 | | |

Table 3
Leached inventory fractions ($f$) for exposure duration of 1 year and 12 years, annual means for leach rates ($R$) and activity concentrations in groundwater (K-26) and rainfall (Bs-10) in contact with the waste glass

| Sample | Exposure time (yr) | $f$ (%) | $R$ (g/cm$^2$ d) | $A_{\text{water}}$ (min/max) (Bq/l) |
|---|---|---|---|---|
| K-26 | 1 | $3.75 \times 10^{-4}$ | $1.32 \times 10^{-6}$ | 20.4 (1/66) |
| | 12 | $1.3 \times 10^{-3}$ | $6.35 \times 10^{-7}$ | 10.0 (1/66) |
| Bs-10 | 1 | $1.99 \times 10^{-3}$ | $3.0 \times 10^{-6}$ | 40.3 (10/133) |
| | 12 | $7.39 \times 10^{-3}$ | $1.1 \times 10^{-6}$ | 14.8 (1.6/133) |

that may be considered as a measure of environmental impact of the waste form. Effects of waste glass dissolution on the chemical composition of the contacting groundwater and rainfall water are illustrated in Table 4. Groundwater chemistry altered from ($HCO_3^-$–$Ca^{2+}$)-type to ($HCO_3^+$–$Na^+$–$K^+$)-type, while being numerically higher than the background only by a factor of 1.3 (mineralization after 12 years). Progressive decrease in concentration levels with time was observed for $K^+$, $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, $SO_4^{2-}$ and TDS. For boron, $Na^+$ and $NO_3^-$, the opposite concentration trends were observed throughout the experiment. Enhanced leaching of alkaline ions resulted in a progressive pH change to slightly alkaline. Maximal/minimal radioactivity of the host rock adjacent to the waste glass repository K-26 were 1.7/0.86 kBq/kg for $\sum\beta$, and have varied only by small factors compared to the background levels for the repository loam. The activity concentration profiles in the soil exhibited a maximum at a depth of 1.2 m (the top of the tray), at 40–50 cm distance from the tray wall, and at a depth of 1.7 m (tray bottom level). The velocity of the radionuclide front movement in the direction of watertable determined through measuring the depth of the maximum radioactivity (1400 Bq/kg) is about 4 cm/year. From this rough estimation it follows that it will take 1750 years to reach the first aquifer of the repository site.

Table 4
Concentrations (mg/l) of various ion species in groundwater and rainfall water contacted with the waste glass, and their evolution with time

| | Repository site | | | Open site | |
|---|---|---|---|---|---|
| | 1st year | 8th year | 12th year | 8th year | 12th year |
| PH | 7.53 (7.40) | 7.80 (7.60) | 7.93 (7.53) | 7.37 | 7.41 |
| TDS[a] | 518 (339) | 412 (270) | 404 (283) | 104 | 93.7 |
| $Na^+$ | 34.64 (13.75) | 54.55 (12.50) | 63.40 (12.84) | 20.46 | 20.00 |
| $K^+$ | 3.70 (0.73) | 3.82 (0.73) | 3.72 (1.47) | 3.83 | 4.23 |
| $Ca^{2+}$ | 78.93 (54.99) | 54.26 (50.62) | 46.30 (50.82) | 7.02 | 5.98 |
| $Mg^{2+}$ | 32.30 (21.00) | 30.26 (20.85) | 27.75 (21.01) | 1.89 | 2.44 |
| Fe | 9.33 (2.24) | 2.64 (1.21) | 2.02 (1.19) | 0.62 | 0.64 |
| $Cl^-$ | 33.11 (18.36) | 26.49 (11.66) | 24.08 (11.32) | 0.98 | 0.84 |
| $NO_3^-$ | 2.22 (2.05) | 4.18 (2.49) | 4.23 (2.31) | 1.58 | 1.73 |
| $HCO_3^-$ | 435 (295) | 390 (264) | 373 (266) | 74.38 | 75.46 |
| $SO_4^{2-}$ | 13.93 (10.59) | 12.45 (10.28) | 10.62 (9.35) | 10.56 | 6.71 |
| B | | 24.75 (0.33) | 27.72 (0.23) | – | 1.78 |
| Mineralization[a] | 710 (350) | 830 (520) | 810 (630) | 259 | 259 |

Background values for groundwater are given in brackets.

[a] Total dissolved salt content.

** Dry residue after water evaporation.

The data in Table 4 show that the concentration levels of most nonradioactive (macro) components which originate from the waste glass are much higher in groundwater than in rainfall contacting with the waste glass, whereas the opposite trends are observed for the radioactive (micro) components of the waste in these waters (see Fig. 3). This can be most readily explained by the accumulation of radionuclides in the clay-size fractions contained in small amounts in the sandy backfill, owing to the retardation/immobilization of radionuclides through adsorption/ion exchange. Analyses of sandy backfill and its fractions have shown that the activity of the sand fractions is not a linear function of their mass content in the sand, partially due to the strong fixation of $^{137}$Cs onto soil minerals (confirmed by analysis of aqueous extracts). An appreciable part of the total leached activity was immobilized in the clayey fractions inside the tray; up to 80 dust-size (0.05–0.005 mm) and clay-size (<0.005 mm) particles, which constitute about 9–10 wt% of the sand.

## 5. Quantitative modeling of waste glass leaching

The radionuclide release is assumed to be controlled by the processes of diffusive limited ion exchange and glass network dissolution. For mathematical modeling the long-term behavior of the nuclear waste glass, we used the glass dissolution model described in [4]. This model is phenomenological and requires the knowledge of experimentally derived parameters. The total radioactivity of a given radionuclide that will be released from the waste glass into the contacting water $Q_{\mathrm{tr}}$ is expressed by the equation representing the integral over time of the radionuclide flux per unit surface area:

$$Q_{\mathrm{tr}} = a(\pi/\lambda)^{1/2}\Phi(\sqrt{\lambda t}) + b[1-\exp(-\lambda t)]/\lambda + nk[1-\exp[-(k+\lambda)t]]/(k+\lambda), \tag{1}$$

where $\lambda_i$ is the decay constant, $t$ is the exposure time, $k$ is the initial surface radionuclide dissolution rate in water, $n$ is the initial concentration of the radionuclides at the glass surface, $a$ and $b$ are the constants depending on glass composition and experimental conditions, determined experimentally, and $\Phi(\sqrt{\lambda t})$ is the error function integral expressed as

$$\Phi(x) = 2/\sqrt{\pi}\int_0^x \exp(-t^2)\,\mathrm{d}t. \tag{2}$$

The constant $a$ depends on the effective diffusion coefficient $D_{\mathrm{eff}}$ of the radionuclide in the glass matrix as follows

$$a = 2Sq_0(D_{\mathrm{eff}}/\pi)^{1/2}, \tag{3}$$

where $S$ is the glass surface area, and $q_0$ is the initial radioactivity of a volume unit. The constant $b$ is related to the glass dissolution rate $R$ through the relationship

$$b = Sq_0R. \tag{4}$$

The constants $a$ and $b$ are defined from processing experimental data. Both efficient diffusion coefficient and dissolution rate can be find out from formulae (3) and (4).

For a very long exposure period when $\lambda t \gg 1$, the amount of radioactivity released from a unit glass surface area $Q_{\mathrm{tr}}$, approaches a constant (maximum) value:

$$Q_{\mathrm{tr}} \to a(\pi/\lambda)^{1/2} + b/\lambda + nk/(k+\lambda). \tag{5}$$

The radionuclide release curves were plotted for experimentally derived and calculation results. The curves for waste glass K-26 in a near-surface repository are displayed in Fig. 7.

According to the calculation results, $f_{\max} = 2.3 \times 10^{3}$% of the initial radioactivity will be released from waste glass K-26 into the environment within a proposed institutional control period of 300 years under conditions of a near-surface repository and in the absence of additional engineered barriers.

Thus, knowledge of the waste glass leaching behavior during the first decades of disposal allows the extrapolation of the glass behavior over periods of a few 100 years. To perform this extrapolation, two experimentally derived parameters are needed: effective diffusion coefficient ($D_{\mathrm{eff}}$) and glass dissolution rate ($R$). We determined these two parameters using experimental data derived from 12-year test. In fact, we suppose that the effective diffusion coefficient as well as glass dissolution rate will remain the same over the entire period of storage. This means that we do not expect significant changes to occur in the bulk glass structure (and in groundwater chemistry) during 300-year storage. In assessing whether this hypothesis is reliable or not, we can refer only to available knowledge about glasses. Lifetime of glasses concerning their possible devitrification is much longer than hundreds of years and can approach

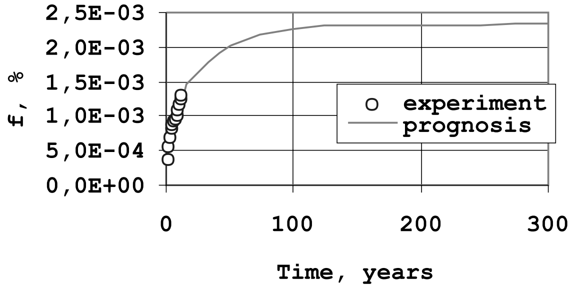

Fig. 7. Curves of radionuclide release from BS waste glass in a humid repository site plotted for experimental and simulation data.

millions of years. The assumption that the geological environment will remain similar to current one is also quite acceptable for a few hundred years. Therefore, in our case of the relatively short time of a few hundred years, the applied two-parameter model could be rather trustworthy.

Field tests with the waste glasses are planned to be continued. That will help validate the accuracy of our estimations and, if necessary, correct the model.

## 6. Conclusions

Unsealing of SIA ‘Radon’ experimental repositories performed on the expiry of a 12-year testing period, revealed there was no conspicuous alteration (cracking or splitting) of BS waste glass blocks during this initial critical stage of storage (when the activity is at a maximum level). XRD patterns of bulk glass demonstrated the absence of crystalline phases and crystallization nuclei. Also, there was no evidence of secondary phase formation in a thin alteration layer developed on the glass surface. The radioactivity level in the groundwater contacting the waste glass blocks decreased on average from initial 20 Bq/l to about 10 Bq/l after 12 years. Both values were lower than the level of radioactive cesium in groundwater authorized in the RF (96 Bq/l till 01.01.2000). An appreciable part (≈80%) of the very insignificant total leached activity is found to be concentrated in dust-size and clay-size fractions constituting 9–10 wt% of the sandy backfill inside the tray containing the waste glass blocks. The radioactivity of the loamy soil surrounding the vitrified waste was close to the background level for the repository site.

There was good agreement between model predictions and available experimental data. Monitoring of the radionuclide leaching will be continued for model testing against experimental data.

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