

## Product consistency test of fully radioactive high-sodium content borosilicate glass K-26

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

<sup>1</sup>Scientific and Industrial Association "Radon", Moscow, Russia.

<sup>2</sup>Immobilisation Science Laboratory, Department of Engineering Materials, University of Sheffield, UK.

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

### ABSTRACT

Chemical durability of fully radioactive, high-sodium borosilicate glass K-26 was evaluated using the product consistency test PCT-A. Examination revealed normalised leaching rates as high as  $5.93 \cdot 10^{-2}$ ,  $4.05 \cdot 10^{-2}$  and  $2.93 \cdot 10^{-2}$  g/m<sup>2</sup>•day for sodium, boron and silicon respectively. Data on chemical durability of glass K-26 are consistent with similar composition glasses. These are of particular interest for performance assessment models.

### INTRODUCTION

Waste forms disposed of in a near-surface wet repository eventually come into contact with groundwater. Engineered structures used or designed to prevent or postpone such contact and the subsequent radionuclide release, are complex and often too expensive. Development of vitrification technologies by the beginning of the 1970s provided waste forms with excellent durability and gave the basic possibility of maximal simplification of engineered barrier systems. The most simple disposal option is to emplace the waste form packages directly into earthen trenches provided the host rock has the necessary sorption and confinement properties. Such an approach has been implemented on an experimental scale as part of the research program of SIA 'Radon' on the immobilisation of radioactive waste in a glass matrix. The program was initiated in the mid-70s. Since then pilot and industrial vitrification plants have been constructed based on the use of a ceramic Joule-heated melter, plasma melter, and induction cold-crucible melting process. Vitrification techniques were applied to liquid and solid LILW received by the site from various sources including the Moscow wastewater purification plant, nuclear power plants and minor producers. Among the glasses used as waste forms for radionuclide immobilization, borosilicate glass is the most frequently used. The high sodium content borosilicate glass K-26 has been designed to immobilise intermediate level operational waste from nuclear power plants. Some tons of this glass were produced in the 1980s during a pilot vitrification campaign of radioactive waste from the Kursk nuclear power plant, which uses uranium-graphite channel type reactors. The glass K-26 had a density 2.46 g/cm<sup>3</sup> with target composition on the oxide basis (wt.%): 48.2SiO<sub>2</sub>-7.5B<sub>2</sub>O<sub>3</sub> - 2.5Al<sub>2</sub>O<sub>3</sub> - 15.5CaO - 16.1Na<sub>2</sub>O - 1.7Fe<sub>2</sub>O<sub>3</sub> - 1.2NaCl - 1.1Na<sub>2</sub>SO<sub>4</sub> - 6.2Misc. The main radioactive contaminant of waste was <sup>137</sup>Cs with the resulting concentration in the vitrified product as high as  $C_0 = 3.7 \cdot 10^6$  Bq/kg. The content of Na<sub>2</sub>O in the K-26 glass makes it relevant to the glass formulations being considered at Hanford site in the USA and hence data on chemical durability of this glass can be useful in the performance assessment of disposal facilities [1, 2].

Examination of fully radioactive nuclear glasses gives reliable data on performance of these materials and enhances our confidence in available performance assessment models [3, 4]. One of important questions is whether fully radioactive glasses behave in the same way as non-radioactive simulating glasses of similar composition. This work evaluates the chemical durability of fully radioactive high-sodium borosilicate glass K-26 using the product consistency test C 1285-02, PCT Method A [5]. This method was selected as it allows to evaluate the chemical durability of glasses rapidly using elevated leaching temperatures (90 °C) and large contacting surface [5]. Although such temperatures are not expected in a disposal environment obtained data are important for comparison with non-radioactive samples. Data on chemical durability of glass K-26 are of particular interest because they may aid validation of performance assessment models [1, 2].

## EXPERIMENTAL

Field experiments are running at the industrial site of Moscow SIA “Radon” to evaluate the behaviour of waste glass buried in a loamy soil. Six blocks of waste glass K-26 each weighing about 30 kg, 30 cm in height, have been emplaced in the experimental repository at 1.7 m depth in a single 40 cm high stainless steel tray supplied with a water trap and a tube for water extraction by pumping. 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 tray was filled with host loamy soil up to the ground surface. The average temperature at the disposal depth is 4.5 °C. Product characteristics and test conditions were given in more detail elsewhere [6]. Effects of waste glass dissolution on groundwater chemistry are shown in Table I.

**Table I.** The composition of groundwater contacting with glass K-26 (concentrations in mg/L).

Ions	1st year	8th year	12th year	Background
pH	7.53	7.80	7.93	7.61-7.72
Na <sup>+</sup>	34.64	54.55	63.40	13.11
K <sup>+</sup>	3.70	3.82	3.72	1.26
Ca <sup>2+</sup>	78.93	54.26	46.30	48.74
Mg <sup>2+</sup>	32.30	30.26	27.75	20.91
Fe	9.33	2.64	2.02	1.16
Cl <sup>-</sup>	33.11	26.49	24.08	13.17
NO <sub>3</sub> <sup>-</sup>	2.22	4.18	4.23	2.30
HCO <sub>3</sub> <sup>-</sup>	435	390	373	258.03
SO <sub>4</sub> <sup>2-</sup>	13.93	12.45	10.62	4.73
B		24.75	27.72	
Mineralization	710	830	810	600

Water mineralization altered from  $(\text{HCO}_3^- - \text{Ca}^{2+})$ - type to  $(\text{HCO}_3^- - \text{Na}^+ - \text{K}^+ - \text{Na}^{2+} - \text{NO}_3^- - \text{Cl}^-)$ - type, being numerically higher than background by a factor of about 1.35. Progressive decrease in concentration with time was observed for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and TDS. For boron,  $\text{Na}^+$  and  $\text{NO}_3^-$ , the opposite concentration trends were maintained throughout the experiment. Enhanced leaching of alkaline ions resulted in progressive pH change to slightly alkaline.

In summer 1999, after 12 years of exposure, the experimental repository was unsealed and the samples of waste glass K-26 were taken for analyses. Fig. 1 shows an extracted container with glass K-26 from the experimental burial.



**Figure 1.** A view of a container with glass K-26 (left) and the glass surface interfacing with backfill (right).

Samples for PCT-A tests were taken from the bulk of glass blocks from different places. Surface alteration of glass K-26 was minor and described in [7] nevertheless samples from the surface were avoided for PCT-A analysis. For comparison non-radioactive reference glasses EA and ARM were also analysed. The composition of these glasses is described in [8].

The results of chemical analysis of samples used for PCT-A tests are shown in Table II. The analysis revealed a higher content of sodium compared to the target composition and a lower content of both silicon and boron. The mismatch between target and real glass compositions could arise from technological reasons and probably was caused by a higher waste loading at waste immobilisation stage.

**Table II.** Average content of Na, B and Si in analyzed samples, wt.%.

Oxide	$\text{SiO}_2$	$\text{B}_2\text{O}_3$	$\text{Na}_2\text{O}$
Target content	48,2	7,5	16,1
Measured	46,1	5,8	24,7

PCT-A tests were carried out in 3 parallel series for all samples, including 9 stainless steel test vessels with samples of radioactive glass K-26, 3 with samples of reference glass EA, and 3 with samples of reference glass ARM. Additionally, two blank test vessels filled with pure water were tested as recommended by PCT procedure C 1285-02. Glass samples were prepared according to PCT procedure C 1285-02 requirements. The ASTM Type I water for PCT was obtained by water purification system Elix (3) and Milli-Q of Millipore SAS. The water had a resistivity of 19 MΩ•cm at 25 °C. Test vessels were placed in a pre-heated oven and the temperature was maintained at 90±0.5°C for the 7 days test duration. After 7 days test vessels were gradually cooled over 2 hours and checked for eventual loss of mass as requested by ASTM test protocol C 1285-02. The pH of leachates was measured with probes of 3-4 mL volume using the Ph-meter Piccolo (Hanna Instruments) with an error of ±0.01. The specific radioactivity of leachates from glass K-26 was about 990 Bq/L (measured by gamma spectrometry for <sup>137</sup>Cs). The leachates were diluted and acidified using 8 mL of high purity 0.4M HNO<sub>3</sub>. The concentrations of Si, B and Na in the leachates were measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES JY24).

## RESULTS

Table III gives data on measured pH and concentrations of Si, B and Na in the initial (non-diluted) solutions averaged for tested samples.

**Table III.** Average pH and concentrations of elements in PCT-A leachates, mg/L.

Glass	pH	Si	B	Na
<b>K-26</b>	11.27	88.5	10.2	152.0
<b>EA</b>	11.66	108.4	90.3	175.1
<b>ARM</b>	10.29	46.0	18.5	35.9

Measured concentrations were used to calculate normalized leaching rates of Si, B and Na. The normalized leaching rate  $NR_i$  was calculated using the expression:

$$NR_i = \frac{c_i}{f_i \cdot (SA/V) \cdot t} \quad (1)$$

where  $NR_i$  is normalized rate (g/m<sup>2</sup>•day),  $c_i$  is the concentration of element "i" in the solution (g/L),  $f_i$  = weigh fraction of element "i" in the initial glass, (SA/V) is surface area of the glass SA (m<sup>2</sup>) divided by the leachate volume V (L),  $t$  is the time duration of test in days, e.g.  $t=7$  days. The resulting normalized leaching rates are given in Table IV. It shows data calculated for target composition of glass K-26 and for glass K-26 of measured composition. E.g. leaching rates for the glass K-26 are from the same test results but calculated for theoretical (target) and measured glass composition. The table also shows, for comparison, published data on two US DOE glasses with similar compositions to K-26, e.g. HLP-30 and HLP-51 which were designed for LILW immobilisation [8].

**Table IV.** Measured PCT-A normalized leaching rates ( $\text{g/m}^2 \cdot \text{day}$ ) of Si, B and Na from glasses K-26 and literature data for glasses HLP-30 and HLP-51 [8].

Glass	Si	B	Na
<b>K-26</b> , for target composition	$2.81 \cdot 10^{-2}$	$3.13 \cdot 10^{-2}$	$9.09 \cdot 10^{-2}$
<b>K-26</b> , for measured composition	$2.93 \cdot 10^{-2}$	$4.05 \cdot 10^{-2}$	$5.93 \cdot 10^{-2}$
<b>HLP-30</b>	$2.43 \cdot 10^{-2}$	$2.00 \cdot 10^{-2}$	$3.57 \cdot 10^{-2}$
<b>HLP-51</b>	$2.14 \cdot 10^{-2}$	$4.85 \cdot 10^{-2}$	$5.86 \cdot 10^{-2}$

## DISCUSSION

PCT-A data on leaching of Si, B and Na from the radioactive glass K-26 are similar to those obtained for non-radioactive glasses of similar composition HLP-30 and HLP-51 [8]. Comparison of obtained data show that the leaching of Na from the glass K-26 is slightly faster than from HLP-30 and close to that of HLP-51. The leaching of Si is the fastest from the glass K-26 although leaching rates are of the same order of magnitude. The leaching of boron from the glass K-26 is faster than from the glass HLP-30 but slower than from glass HLP-51. Such differences in the leaching behaviour can be explained by the difference in compositions of these glasses. The approximate compositions of the HLP glasses are as follows (wt.%) [8]: glass HLP-30  $52\text{SiO}_2 - 6\text{B}_2\text{O}_3 - 12\text{Al}_2\text{O}_3 - 16\text{Na}_2\text{O} - 14\text{Misc.}$ , glass HLP-51:  $42\text{SiO}_2 - 9\text{B}_2\text{O}_3 - 10\text{Al}_2\text{O}_3 - 20\text{Na}_2\text{O} - 19\text{Misc.}$  Both HLP-30 and HLP-51 have a higher content of  $\text{Al}_2\text{O}_3$  which improves their water durability compared to K-26 (see [4]). In addition the glass HLP-30 has a higher content of  $\text{SiO}_2$  which results in a more polymerised structure and hence a better performance.

Comparison of normalised rates obtained for target and measured glass compositions shows that the actual normalised leaching rate of sodium glass K-26 is lower than calculated when using the theoretical composition. This however does not change the results of the performance assessment of this glass [9] which were based on really measured losses of radionuclides rather than non-radioactive constituents.

Measurements show that leaching of radionuclides from glass K-26 during 12 years of underground storage occurred practically only through diffusion-controlled ion-exchange, which resulted in a rate diminishing with time as  $t^{-1/2}$  characteristic for initial stages of corrosion [10]. The glass K-26 has been under continuous self-irradiation caused by the decay of incorporated radionuclides. At low temperatures of contacting water and at substantial accumulated doses leaching of radionuclides via ion-exchange can occur faster from actual radioactive glasses in comparison with non-radioactive glasses [11]. The increase in leaching rates due to faster consumption of protons causes an increase of pH of contacting water. A progressive increase in the pH of contacting water can be seen in Table I however this effect cannot exactly be attributed to self irradiation and needs additional studies. At elevated temperatures silicate glasses corrode via hydrolysis [10] thus no effects of irradiation are expected [11]. Hence we

can expect that PCT-A tests will give the same results both for actual and non-radioactive simulating glasses.

## CONCLUSIONS

PCT-A data on leaching of Si, B and Na from the radioactive glass K-26 demonstrated similar leaching rates comparing non-radioactive glasses of similar composition. Testing of fully radioactive glass K-26 both in natural and laboratory conditions gives valuable data for computer modelling and enables validation of computer codes.

## REFERENCES

1. B.P. McGrail, D.H. Bacon, P.D. Meyer, M.I. Ojovan, D.M. Strachan, N.V. Ojovan, I.V. Startceva. *Mat. Res. Soc. Symp. Proc.* **757**, II.2.1.1-13 (2003).
2. D.H. Bacon, M.I. Ojovan M.I., B.P. McGrail, N.V. Ojovan, I.V. Startceva. *Proc. ICEM '03*, Oxford, England, 4509.pdf. (2003).
3. N.E. Bibler. *Advances in Ceramics*, **20**, ACS, Westerville, OH, 619–626 (1986).
4. P. Van Iseghem ed. *J. Nucl. Mat.*, **298**, N. 1, 2 (2001).
5. ASTM Standard C 1285-02 (2002).
6. Long term tests of low and intermediate level waste packages under field and experimental repository conditions. SIA 'Radon', *Report Res. Contr. N 9744/R0*, IAEA, (1998).
7. N.V. Ojovan, I. V. Startceva, A.S. Barinov, A.V. Mokhov, M.I. Ojovan, G. Moebus. *Mat. Res. Soc. Symp. Proc.* **807**, 139-144 (2004)...
8. J.D. Vienna, A. Jiricka, P. Hrma, D.E. Smith. T.H. Lorier, R.L. Schuktz, I.A. Reamer. Hanford immobilized LAW product acceptance testing: tanks focus area results. PNNL-13744 (2001).
9. M.I. Ojovan, N.V. Ojovan, I.V. Startceva, G.N. Chuikova, A.S. Barinov. *Proc. WM'01*, 43c-23.pdf (2001).
10. M.I. Ojovan, R. Burcl. *Proc. 2003 EPRI Int. Conf. in Conj. with IAEA*, 16-18.07.03, New Orleans, LA, USA, EPRI-S08-P7.pdf (2003).
11. M.I. Ojovan, W.E. Lee. *Mat. Res. Soc. Symp. Proc.*, **792**, R2.5.1-6 (2004).