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Fabrication and Characterization of Borosilicate Glasses Containing Alpha-Radionuclides and Silver From Conversion and Mixed-Oxide Facilities Proposed for Russia

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FABRICATION AND CHARACTERIZATION OF BOROSILICATE GLASSES CONTAINING ALPHA-RADIONUCLIDES AND SILVER FROM CONVERSION AND MIXED-OXIDE FACILITIES PROPOSED FOR RUSSIA

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ABSTRACT

Liquid and solid radioactive wastes are formed during conversion of plutonium metal to oxide and during fabrication of weapons-grade plutonium into mixed-oxide (MOX) fuel. In Russia, these wastes are to be processed for disposition by immobilization in either borosilicate glass or cement matrices depending upon the waste stream-specific radionuclide contents.

Vitrification is planned for the liquid high-level waste raffinate stream containing the bulk of the Am-241 produced from Pu-241 decay. Previous work on the Russian MOX Fuel Fabrication Facility (R-MFFF) by the Public Joint Stock Corporation (TVEL) [1] showed that this waste stream may contain significant amounts of silver derived from the electrochemical dissolution of PuO_2 using a Ag(II) catalyst. The work reported here further investigated silver solubility limits, which, if exceeded in a production glass melter, allow discrete silver grains to form in the glass and also deposit over time on the bottom of a joule-heated ceramic melter. In melters with immersed electrodes, such as the Russian EP-100 for phosphate glasses or the US Duratek DP-100 type melters for borosilicate glasses that are being considered for use at the Siberian Chemical Combine (SCC) Tomsk site, the undissolved silver could cause a short circuit and an unacceptable production melter failure.

The silver solubility limit of 3.85 wt% Ag_2O in liquid, alpha-bearing wastes determined in this work will guide the production scale use of borosilicate glass compositions, and effectively increase the capacity of the ceramic melters and reduce the total volume of solidified vitrified wastes at SCC Tomsk that require storage prior to geologic disposal.

INTRODUCTION

Equipment and techniques previously developed by the V. G. Khlopin Radium Institute (KRI) for the production and characterization of homogeneous borosilicate glass compositions with Pu-239 were used to synthesize and characterize various borosilicate glass compositions loaded with variable amounts of silver and Am-241. The expected compositions of liquid wastes generated annually at the R-MFFF containing large amounts of silver, zirconium, and americium (Am-241) were studied. Americium’s chemical analog, europium, was used in some, but not all, vitrification tests as a substitute to simulate the liquid radioactive waste. The composition by wt% of simulated alpha-bearing waste (Eu_2O_3, 13.80; Ag_2O, 62.96; ZrO_2, 22.31; Al_2O_3, 0.78) suggested that waste load in the glass matrix would be limited by the solubility of silver.

Glasses were either synthesized in aluminum crucibles in an electric resistance furnace or, for batches weighing over 0.5 kg, in a bench melter facility at KRI. Extrapolating from previous work that established the effects of glass melting temperatures on the carry-over of radionuclides including Pu-238-239-240 and Am-241-242-243 as gas or fine particulates, twenty-two simulated borosilicate glass compositions (Ag1-Ag22) were selected and then melted at 1150°C in oxidizing conditions to minimize any carry-over and to study the homogeneity of the glass [2-4]. In our previous work, we studied plutonium carry-over as gases or aerosols and found that in melting borosilicate glasses at 1000–1300°C, plutonium carry-over was lower than 10^{-4} %. The other work on synthesizing and melting ceramics doped with Pu-238 and Am-243 showed that at 1300–1600°C, there was no aerosol carry-over of these nuclides [5]. As shown in [6], Pu-238 to Pu-240-241 do not form any volatile compounds at temperatures below 1200°C.

The plutonium solubility limit was shown in previous KRI work to depend on glass composition and the chemical form of plutonium used in lab tests. The earlier work achieved homogeneous incorporation of 2.67 wt% Pu-239 in the form of dioxide and 4.67 wt% in the form of nitrate at 1150°C in borosilicate glass [7].

In the follow-on stages reported here, KRI studied borosilicate glass compositions with higher waste loads of 0.30–0.88 wt% Am_2O_3 and 1.35–3.97 wt% Ag_2O incorporated into borosilicate glasses. Eight samples of different borosilicate glass compositions were spiked with Am-241 for detailed study of the chemical durability by the Standard Method of static and dynamic leaching using the MCC-1 test at 25°C and 90°C and the MCC-5 test at 90°C [8-10].

Batches were prepared by mixing nitrates of simulated waste components with appropriate quantities of glass formers and fluxing additives, such as SiO_2, H_3BO_3, sodium and lithium nitrates, and manganese and antimony oxides. Glasses were kept molten for 2 h at 1150°C and then poured from crucibles onto a metal plate heated to 250–300°C. Viscosity and leach rate measurements were made.

Physical and chemical properties of the samples in the form of pellets or granules were studied by x-ray diffraction analysis (XRDA), x-ray spectral microanalysis (XRSMA), and scanning electron microscopy (SEM) to determine homogeneity, establish maximum waste loads (which are dependent primarily on the silver content), and develop recommendations for the practical use of these compositions at the SCC.

PRODUCTION AND CHARACTERIZATION OF BOROSILICATE GLASS COMPOSITIONS

This study used the techniques and equipment developed previously at KRI for production and characterization of Pu-239-bearing borosilicate glass compositions [7]. Table I shows the compositions of glasses loaded with higher waste loads of americium and silver ranging from 0.30–0.88 wt% Am_2O_3 and 1.35–3.97 wt% Ag_2O.

In earlier work, compositions Ag1–Ag5 were based on a borosilicate glass matrix suggested for conditioning of high-level waste [11]. The polyvalent elements such as manganese and antimony were introduced in compositions Ag6–Ag22 to create oxidizing conditions in glass melts and prevent silver oxide reduction to silver metal [12]. Manganese dioxide, MnO_2, for example, has been shown by differential thermal analysis (DTA) to dissociate at 460–590°C yielding Mn_2O_3 with further formation of gaussmanite, Mn_3O_4, at 895-1205°C. The liberated oxygen creates oxidizing conditions over the whole temperature interval of the synthesis from 460°C to 1203°C. In comparison with manganese dioxide, antimony pentoxide releases oxygen only in the range of 380–930°C; therefore, its oxidizing ability is somewhat lower. Having this in mind, we excluded antimony pentoxide from compositions Ag18, Ag20, Ag21, and Ag22 to increase the percentage of manganese dioxide (Table I). Lithium oxide was introduced in the compositions to reduce viscosity and facilitate glass discharge.

Table I. Formulations of Model Borosilicate Glass Compositions to Incorporate Alpha-bearing Wastes (0.30-0.88 wt% Am_2O_3 and 1.35-3.97 wt% Ag_2O)

Oxide	Ag16	Ag17	Ag18	Ag19	Ag20	Ag21	Ag22
Eu_2O_3	0.30	0.40	0.45	0.55	0.55	0.70	0.88
Ag_2O	1.35	1.80	2.02	2.47	2.47	3.13	3.97
Na_2O	18.75	18.50	18.75	18.00	18.00	18.00	18.00
B_2O_3	16.00	16.25	16.40	17.00	17.00	16.50	17.00
SiO_2	48.25	47.45	47.48	45.20	46.70	46.76	47.00
ZnO	2.50	2.50	2.00	2.00	2.50	2.00	1.50
Fe_2O_3	1.50	1.50	1.25	1.00	1.50	1.25	1.00
Al_2O_3	2.62	2.71	2.86	2.90	2.90	3.00	3.16
ZrO_2	1.48	1.64	1.79	1.88	1.88	1.92	1.99
MnO_2	3.50	3.50	5.50	4.00	5.00	5.25	5.50
Li_2O	1.25	1.25	1.50	1.50	1.50	1.50	-
Sb_2O_5	2.50	2.50	-	3.50	-	-	-
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

STUDY OF HOMOGENEITY OF BOROSILICATE COMPOSITIONS

All the borosilicate compositions obtained were studied by XRDA. Samples Ag1–Ag15 were found to be amorphous and contained neither crystalline inclusions nor segregations of silver metal or crystalline europium dioxide. SEM was used to evaluate the homogeneity of compositions Ag1–Ag15, and XRSMA was used to study the distribution of the main constituents over the volume of the samples.

Glass compositions Ag1–Ag5. Electron microphotographs (*not shown*) and data (Table II) show that compositions Ag1-Ag5 are chemically heterogeneous due to the nonuniform distribution of aluminum and sodium over the volume of the samples. The dark regions on the photographs correspond to the zones enriched in aluminum. The relative deviation in the content of the elements in Table II exceeds 5%. The most homogeneous sample was Ag4.

Glass compositions Ag6-Ag10. Microphotographs (*not shown*) and data in Table III show that glasses Ag6-Ag10 are practically homogeneous and do not have any liquation zones or

Table II. Target and Averaged Experimental Data on Borosilicate Glass Compositions Ag1-Ag5 (wt%)

	Ag1		**Ag2**		**Ag3**		**Ag4**		**Ag5**	
	Target	**Anal.**	**Target**	**Anal.**	**Target**	**Anal.**	**Target**	**Anal.**	**Target**	**Anal.**
Ag_2O	0.45	0.50	0.63	0.71	0.77	0.66	0.90	0.99	0.99	1.07
Eu_2O_3	0.10	0.20	0.14	0.21	0.17	0.22	0.20	0.25	0.22	0.30
Na_2O	20.0	18.31	19.90	18.10	19.84	14.95	19.79	15.97	19.74	15.78
SiO_2	51.00	47.90	50.85	51.65	50.70	43.70	50.55	50.83	50.40	50.81
ZnO	4.00	4.03	4.00	4.21	4.00	3.12	4.00	4.38	4.00	4.50
Fe_2O_3	3.00	2.84	3.00	3.12	3.00	2.73	3.00	3.10	3.00	3.10
Al_2O_3	3.29	9.11	3.36	4.00	3.40	16.82	3.45	6.50	3.55	6.50
ZrO_2	1.16	0.93	1.22	1.09	1.27	0.95	1.31	1.18	1.35	1.18
B_2O_3[1]	17.00	n/m	16.90	n/m	16.85	n/m	16.80	n/m	16.75	n/m

[1] Was not measured.

Table III. Target and Averaged Experimental Data on Borosilicate Glass Compositions Ag6-Ag10 (wt%)

	Ag6		**Ag7**		**Ag8**		**Ag9**		**Ag10**	
	Target	**Anal.**	**Target**	**Anal.**	**Target**	**Anal.**	**Target**	**Anal.**	**Target**	**Anal.**
Ag_2O	0.45	0.42	0.63	0.70	0.77	0.79	0.90	1.04	0.99	0.98
Eu_2O_3	0.10	0.15	0.14	0.16	0.17	0.22	0.20	0.22	0.22	0.27
Na_2O	19.00	16.58	18.9	17.38	18.84	17.38	18.79	16.92	18.74	15.92
SiO_2	50.00	45.37	49.60	45.94	49.20	45.68	48.80	45.40	48.40	47.06
ZnO	4.00	3.92	4.00	3.72	4.00	3.63	4.00	3.66	4.00	3.79
Fe_2O_3	3.00	2.84	3.00	2.96	3.00	2.86	3.00	3.04	3.00	2.93
Al_2O_3	3.29	11.46	3.36	9.22	3.40	9.88	3.45	10.92	3.55	8.89
ZrO_2	1.16	1.18	1.22	1.37	1.27	0.98	1.31	0.89	1.35	1.25
MnO_2	3.00	2.32	3.25	2.64	3.50	2.74	3.75	2.97	4.00	3.17
B_2O_3[1]	16.00	n/m	15.90	n/m	15.85	n/m	15.80	n/m	15.75	n/m

[1] Was not measured.

crystalline inclusions. The target and averaged experimental concentrations of basic elements in all glasses are practically equal within experimental error. The smallest standard and relative deviations are observed for the composition of glass Ag 9, which is chemically the most homogeneous.

Glass compositions Ag11-Ag15. The compositions Ag11-Ag15 (Table IV), as determined by XRSMA and SEM, are homogeneous. The matrix and polyvalent elements are distributed over the volume of the samples uniformly. The discrepancies between the experimental and target glass compositions are due to corrosion of the alundum crucible with aluminum passing into the melt. Nevertheless, the relative deviations in the content of the main glass components do not exceed the permissible 5%.

Table IV. Target and Averaged Experimental Data on Borosilicate Glass Compositions Ag11-Ag15 (wt%)

	Ag11		**Ag12**		**Ag13**		**Ag14**		**Ag15**	
	Target	**Anal.**	**Target**	**Anal.**	**Target**	**Anal.**	**Target**	**Anal.**	**Target**	**Anal.**
Ag_2O	0.45	0.53	0.63	0.69	0.77	0.84	0.90	0.98	0.99	0.98
Eu_2O_3	0.10	0.14	0.14	0.17	0.17	0.20	0.20	0.21	0.22	0.29
Na_2O	19.00	15.66	18.80	15.82	18.64	16.91	18.49	15.12	18.24	16.35
SiO_2	50.00	50.24	49.55	49.15	49.15	49.29	48.75	48.51	48.40	47.52
ZnO	3.00	3.16	3.00	3.17	3.00	3.18	3.00	2.67	3.00	2.98
Fe_2O_3	2.00	2.29	2.00	2.16	2.00	2.03	2.00	1.84	2.00	1.98
Al_2O_3	2.29	5.65	2.36	6.25	2.40	4.64	2.45	4.59	2.55	7.15
ZrO_2	1.16	1.02	1.22	1.04	1.27	1.13	1.31	1.07	1.35	1.15
MnO_2	2.75	2.49	3.00	2.68	3.25	2.83	3.50	2.58	3.75	2.97
Sb_2O_5	1.75	1.41	2.00	1.56	2.25	1.86	2.50	1.53	2.75	2.05
B_2O_3[1]	16.00	n/m	15.80	n/m	15.60	n/m	15.40	n/m	15.25	n/m
Li_2O[1]	1.50	n/m	1.50	n/m	1.50	n/m	1.50	n/m	1.50	n/m

[1] Was not measured.

Glass Compositions with Silver Oxide Load Over 1 wt%

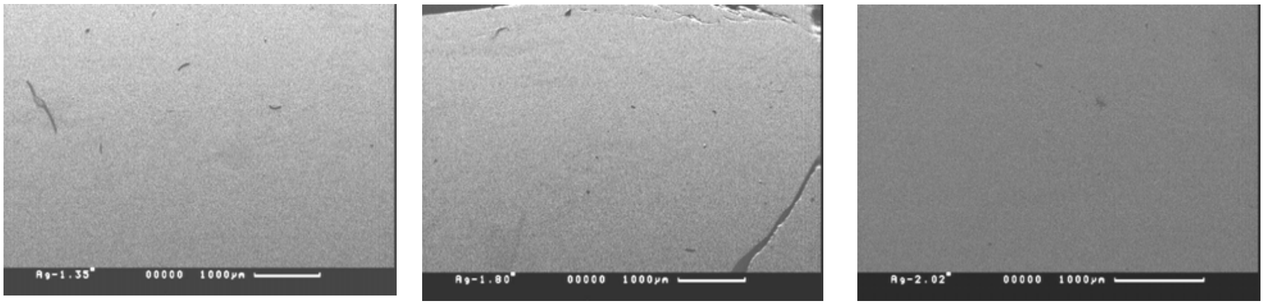
Table V shows the target and experimental compositions of the synthesized glasses. Boron and lithium are not included in the total amount of oxides calculated from the experimental data, for they cannot be determined by electron probe microanalysis (EPMA).

Table V. Calculated and Experimental Glass Compositions, Ag16-Ag22 (wt%)

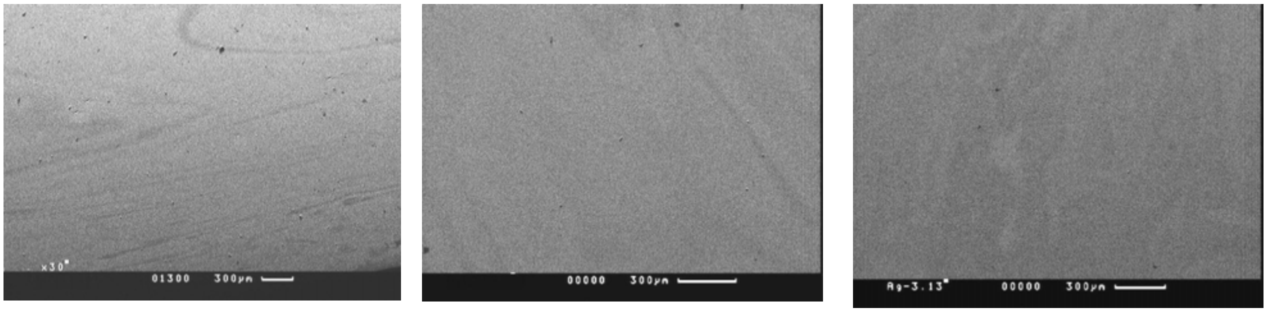
Oxide	**Ag 16**		**Ag 17**		**Ag18**		**Ag 19**		**Ag 20**		**Ag 21**		**Ag22**	
	Target	Anal.	Target	Anal.	Target	Anal.	Target	Anal.	Target	Anal.	Target	Anal.	Target	Anal.
Eu_2O_3	0.30	0.14	0.40	0.25	0.55	0.35	0.70	0.44	0.88	0.62	0.45	0.30	0.55	0.30
Ag_2O	**1.35**	**1.62**	**1.80**	**1.74**	**2.47**	**2.47**	**3.13**	**3.12**	**3.97**	**3.30**	**2.02**	**2.19**	**2.47**	2.50
Na_2O	18.75	17.08	18.50	16.71	18.00	17.71	18.00	16.85	18.00	17.81	18.75	17.99	18.00	16.48
B_2O_3	16.00	n/m[a]	16.25	n/m	17.00	n/m	16.50	n/m	17.00	n/m	16.40	n/m	17.00	n/m
SiO_2	48.25	47.63	47.45	47.57	46.70	45.25	46.76	45.64	47.00	44.43	47.48	46.41	45.20	45.00
ZnO	2.50	2.54	2.50	2.49	2.50	2.61	2.00	1.69	1.50	1.91	2.00	2.15	2.00	1.92
Fe_2O_3	1.50	1.39	1.50	1.23	1.50	1.29	1.25	0.83	1.00	0.88	1.25	1.20	1.00	1.05
Al_2O_3	2.62	7.37	2.71	6.49	2.90	6.05	3.00	7.84	3.16	7.88	2.86	5.83	2.90	6.42
ZrO_2	1.48	1.32	1.64	1.42	1.88	1.76	1.92	1.57	1.99	1.80	1.79	1.77	1.88	1.84
MnO_2	3.50	2.07	3.50	2.59	5.00	4.01	5.25	4.01	5.50	4.37	5.50	4.26	4.00	3.28
Li_2O	1.25	n/m	1.25	n/m	1.50	n/m	1.50	n/m	-	-	1.50	n/m	1.50	n/m
Sb_2O_5	2.50	1.59	2.50	2.05	-	-	-	-	-	-	-	-	3.50	2.71
Total	100.0	82.75	100.0	82.88	100.00	81.50	100.0	82.00	100.0	83.00	100.00	82.10	100.00	81.50

[1] Was not measured.

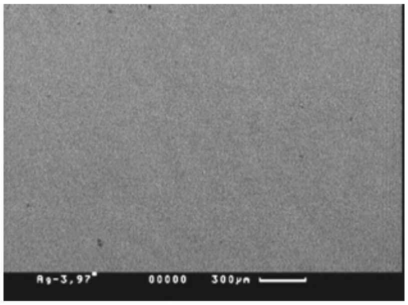
The SEM analysis of glasses Ag16–Ag22 (Fig. 1) did not reveal any inclusions of silver metal. The dark regions in the photographs of the glasses correspond to the regions enriched in aluminum. The study of composition and distribution of elements over the volume of the glass samples loaded with increased amount of silver showed that the glasses did not have any crystalline inclusions. The chemical nonuniformity of the glasses was attributed to corrosion of the alundum crucible.



(a) Ag 16 **(b) Ag 17** **(c) Ag 18**



(d) Ag 19 **(e) Ag 20** **(f) Ag 21**



(g) Ag 22

Fig. 1. SEM microphotographs of glasses Ag16 –Ag22.

Determination of Solubility Limit of Silver in the Borosilicate Glass Melt

To determine the solubility of silver in the melt, glass Z was synthesized with high silver content in the batch. The target composition of glass Z (converted to oxides) is given in Table VI. The initial silver oxide content was 5.03 wt%. In the course of synthesis, the melt stratified in two glassy phases with a Phase1/Phase2 volume ratio of 15/1. Phase 2 formed in the bottom part of the crucible. The composition of the phases, as determined by EPMA, is given in Table VI. Phase 2 is significantly enriched in aluminum (~18 wt%). Figure 2 shows the microphotograph of glass Z. The dark area corresponds to phase 2.

Table VI. Target Composition of Glass Z vs. Actual Phase Composition

Oxide	**Content, wt%**		
	Glass Z (target)	**Phase 1**	**Phase 2**
Eu_2O_3	1.11	0.87	0.58
Ag_2O	**5.03**	**3.85**	**2.99**
Na_2O	17.40	16.45	15.72
B_2O_3	16.30	n/m	n/m
SiO_2	46.55	46.21	38.05
ZnO	1.00	0.81	0.00
Fe_2O_3	0.75	0.62	0.92
Al_2O_3	2.27	6.64	18.21
ZrO_2	2.09	1.99	1.73
MnO_2	5.75	4.51	3.74
Li_2O	1.75	n/m	n/m
Total	100.00	81.95	81.95

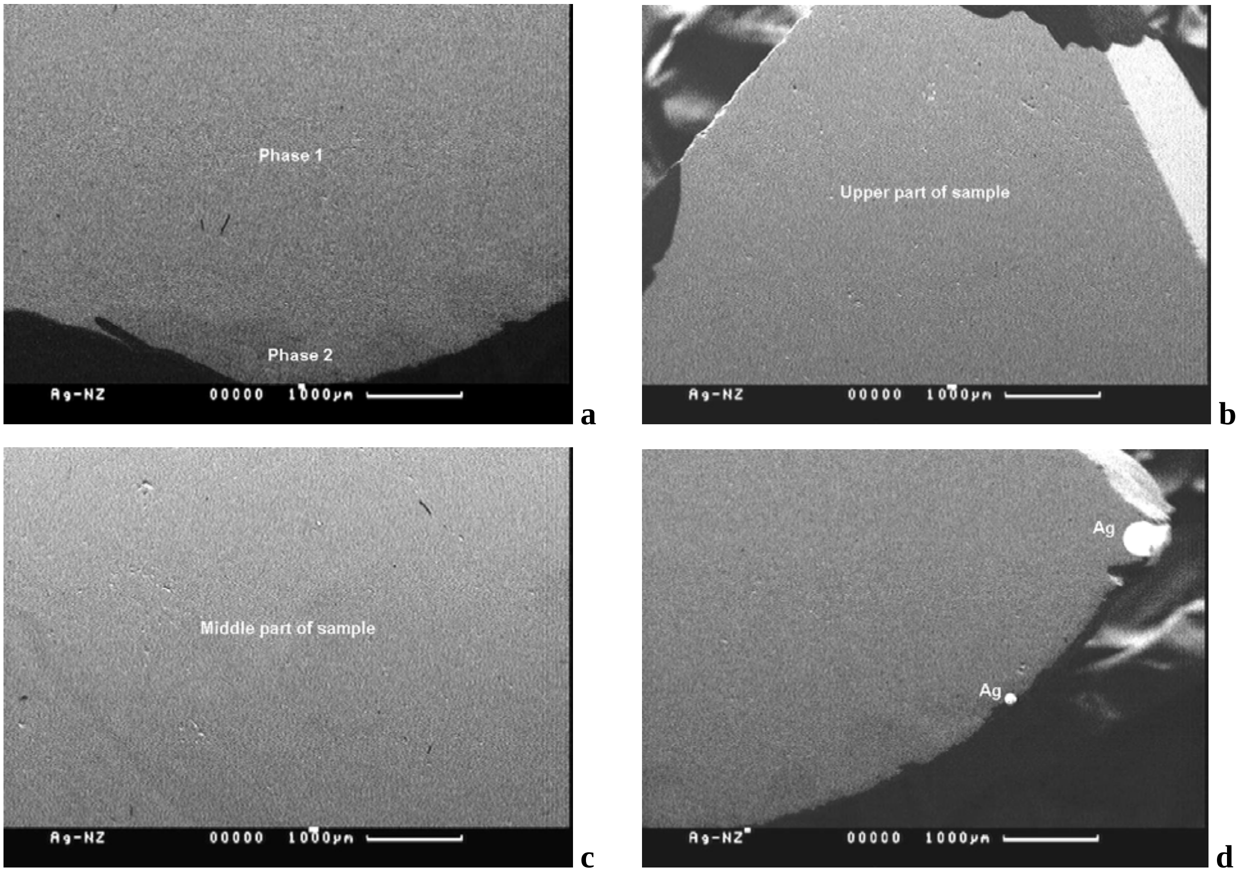


Fig. 2 (a-d). Microphotographs of glass Z in reflected electrons.

Silver was distributed within both phases uniformly. No sedimentation was observed over the volume of the samples, yet they differed in silver content: 3.85 wt% in phase 1 and 2.99% in phase 2. Figure 3 shows waste oxide content in the sample vs. distance from its bottom part. The excess silver settled to the bottom of the crucible in the form of metal beads (Fig. 1(g)), which was confirmed by X-ray analysis and EPMA.

The dark area in Fig. 2(a) corresponds to phase 2. Both glass phases are x-ray amorphous and essentially homogeneous. Figure 2(b) shows the upper part of the sample and 2(c) the middle part of the sample. Figure 2(d) shows white spheres that are beads of silver metal. From the data obtained, the silver solubility limit was determined as 3.85 wt% at the given temperature and duration of the synthesis.

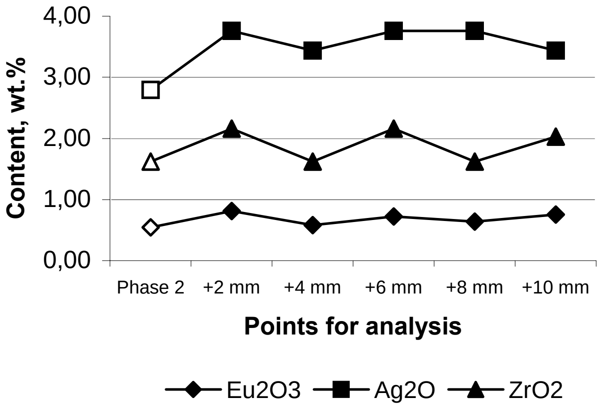


Fig. 3. Distribution of waste oxides over glass volume vs. distance from lower part of sample.

VISCOSITY

The viscosity of glass samples Ag16 and Ag18 was determined at temperatures between 850°C and 1250°C. Logarithmic viscosity against inverse temperature is shown in Fig. 4.

The viscosity parameters are essential for evaluating convection currents and tracking glass melt homogenization in direct heated ceramic melters. Viscosity of the melt also determines the conditions of glass discharge and time needed for filling the storage containers.

As reported in earlier work, analysis of compositions Ag1–Ag4 shows that at temperatures between 1100 and 1150° C, their viscosity falls within 6.0–8.0 Pa·s, which would cause problems with glass discharge. This indicates that the temperature in the discharge zone of the melter should be increased at least by 50 degrees [13].

After introduction of manganese oxide, the viscosity of samples Ag4, Ag9, Ag14, Ag 18, Ag 20, and Ag 21 was reduced to 3.0–5.0 Pa·s, which had a positive effect on the discharge conditions. Compositions Ag11–Ag14, Ag16, Ag17, and Ag 19 with additional lithium and antimony had a viscosity as low as 2.0 Pa·s and lower, which caused a beneficial effect on characteristics of the glass melt due to active convection in the melt zone and better glass homogenization. [8,14].

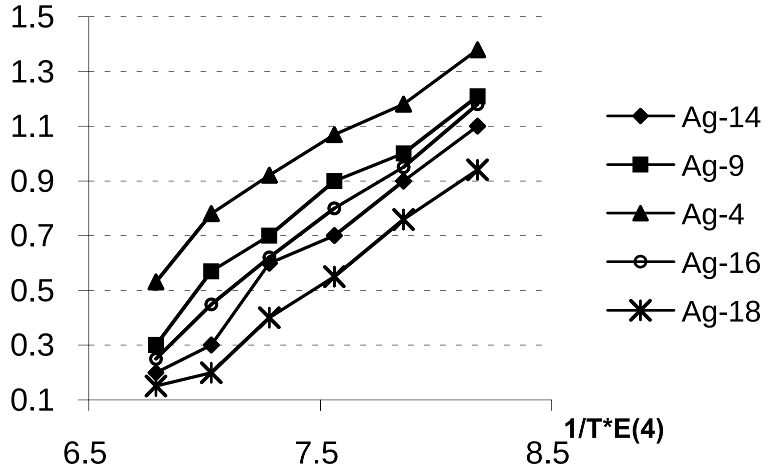


Fig. 4. Logarithmic viscosity vs. inverse temperature for samples Ag4,Ag9, Ag14, Ag16, and Ag18 (Pa·s).

CHEMICAL DURABILITY OF AMERICIUM- AND SILVER-BEARING BOROSILICATE GLASSES

Eight samples of borosilicate glass (Ag6, Ag7, Ag9, Ag12, Ag14, Ag18, Ag19, and Ag21) were spiked with Am-241 for detailed study of chemical durability by MCC-1. The glasses were selected on the grounds of characteristics measured by x-ray pulse height analysis (XRPHA), SEM and XRSMA, with regard to their viscosity and water resistance. The water resistance of glasses was roughly estimated by a rapid method of boiling small, disk-shaped samples in demineralized water for 5 h. Americium-241 was added to the powder-like batch mixture prior to melting as a volumetric nitrate solution in the amount equal to its mass percentage in the corresponding glass composition. Americium concentrations and specific activities of the glasses are in Table VII.

Static Leaching by the Standard Test Method MCC-1

The glass compositions selected were tested for chemical durability by the standard test method MCC-1 at 25°C and 90°C. The tests were conducted in demineralized water with an initial pH of 5.6 [8,9]. The samples tested were glass granules with 0.005 m base diameter, 0.004 m in height. The surface area-to-leachate volume ratio was 0.1 cm^{-1}.

Activity of glass samples and liquid samples of leachates placed in standard vials was measured with a Schlumberger model EG PC 20P 11A well-type HPGe detector connected to a Canberra Accu SpecA PC-built MCA. To improve accuracy in activity determination, data for solid samples were corrected for self-absorption. The total error in activity measurements did not exceed 6%.

Matrix elements and silver in leachates were determined using glasses of the same compositions with europium added (Table VII). The leachates were analyzed by atomic emission spectroscopy with inductively-coupled plasma and by the mass-spectrometric method with inductively-coupled plasma. The total error in the measurement of concentrations did not exceed 10%.

Table VII. Composition and Characteristics of Borosilicate Glasses (wt%)

Oxide	**Ag6**	**Ag7**	**Ag9**	**Ag12**	**Ag14**	**Ag18**	**Ag19**	**Ag21**
Am_2O_3	0.10	0.14	0.20	0.14	0.20	0.45	0.55	0.70
Ag_2O	0.45	0.63	0.90	0.63	0.90	2.02	2.47	3.13
Na_2O	1.00	18.90	18.79	18.80	18.49	18.75	18.0	18.0
B_2O_3	16.00	15.90	15.80	15.80	15.40	16.4	17.0	16.5
SiO_2	50.00	49.60	48.80	49.55	48.75	47.48	45.2	46.76
ZnO	4.00	4.00	4.00	3.00	3.00	2.0	2.0	2.0
Fe_2O_3	3.00	3.00	3.00	2.00	2.00	1.25	1.0	1.25
Al_2O_3	3.29	3.36	3.45	2.36	2.45	2.86	2.9	3.0
ZrO_2	1.16	1.22	1.31	1.22	1.31	1.79	1.88	1.92
MnO_2	3.00	3.25	3.75	3.00	3.50	5.50	4.0	5.25
Li_2O	-	-	-	1.50	1.50	1.50	1.5	1.5
Sb_2O_5	-	-	-	2.00	2.50	-	3.5	-
Spec. activity (Bq/g) 10^{-8}	1.11±0.07	1.52±0.07	2.21±0.07	1.56±0.07	2.25±0.07	4.69±0.07	6.11±0.07	7.81±0.07

At 25°C, samples were tested in Teflon vials with screw caps and at 90°C, in stainless steel autoclaves with 20-ml Teflon capsules. Water was replaced at 3, 14, and 28 days. Visual examination of the glasses tested at 25°C did not reveal any significant change of their surface caused by leaching. Table VIII gives the pH values of leachates and normalized mass release for glass samples after 28-day leaching at 25°C. The data in Table VIII show that after leaching, the normalized mass release values are close for the elements studied irrespective of glass composition. The calculated leaching rate values [10] fall within the following ranges (g/cm^2 day): Eu: (1–2) $\cdot 10^{-8}$; Am:(1–2) $\cdot 10^{-8}$; Ag: (2–4) $\cdot 10^{-7}$, Zr: (5–7) $\cdot 10^{-7}$, Na: (6–7) $\cdot 10^{-6}$; B: (5–6) $\cdot 10^{-6}$; and Si: (5–6) $\cdot 10^{-6}$, which are in agreement with previous values [15,16].

Table VIII. Chemical Durability of Glasses (MCC-1, 25°C, 28 days)

Sample	**Na/Si(sol):Na/Si(liq)**	**pH**	**Normalized mass release by the 28th day, g/m**				
			Eu	**Am**	**Na**	**B**	**Si**
Ag6	1:5.7	5.84	0.0039	0.0048	0.379	0.354	0.254
Ag7	1:5.1	5.91	0.0056	0.0071	0.412	0.297	0.201
Ag9	1:3.1	5.73	0.0033	0.0036	0.197	0.189	0.164
Ag12	1:4.4	5.77	0.0035	0.0042	0.302	0.207	0.189
Ag14	1:3.7	5.75	0.0036	0.0038	0.225	0.194	0.175
Ag18	1:2.9	5.62	0.0030	0.0035	0.179	0.179	0.156
Ag19	1:4.1	5.71	0.0033	0.0041	0.278	0.197	0.175
Ag21	1:5.9	5.89	0.0041	0.0082	0.487	0.389	0.271

Glasses Ag6, Ag7, Ag9, Ag12, Ag14, Ag18, Ag19, and Ag21 were tested according to MCC-1 at 90°C for 28 days. The normalized mass release of basic components of the glasses as well as mass loss of the samples after boiling for 5 h is given in Table IX.

Table IX. Chemical Durability of Glasses (MCC-1, 90°C, 28 days)

Sample	**Na/Si($_{TB}$): Na/Si$_{()\chi)}$**	**Mass release after boiling (5h, 100^{0}C) %**	**pH**	**Normalized mass release by the 28th day (g/m^2)**					
				Eu	**Am**	**Ag**	**Na**	**B**	**Si**
Ag6	1:1.8	0.047	7.98	0.056	0.063	1.21	31.5	27.8	25.7
Ag7	1:1.4	0.039	7.86	0.049	0.059	1.17	27.3	23.6	21.9
Ag9	1:1.1	0.017	7.37	0.031	0.037	0.98	16.9	14.3	12.9
Ag12	1:1.3	0.031	7.69	0.043	0.051	1.14	21.4	19.8	19.3
Ag14	1:1.2	0.023	7.41	0.045	0.043	1.09	17.3	15.0	14.2
Ag18	1:1.1	0.020	6.51	0.027	0.031	0.84	15.8	13.8	12.1
Ag19	1:1.3	0.031	7.65	0.042	0.053	1.01	20.9	18.9	19.8
Ag21	1:1.9	0.051	8.02	0.059	0.067	1.28	34.5	28.6	27.1

The results of the tests show that europium and americium are confined in the glasses much more securely than silver or elements of the matrix at either 25°C or 90°C. The normalized mass release of matrix elements at 25°C and 90°C differed by 50–100 times, while normalized mass release of europium and americium at 90°C was three orders of magnitude lower than that of silicone and boron [17]. At 90°C, silver is released into the leachate 10–20 times faster than Am and Eu.

Note that normalized mass release of Eu and Am is very similar after either 14 or 28 days of leaching. This may be the result of the formation of slightly soluble Am complexes on the altered glass surface [7]. Comparison of Na^+/Si^{+4} ratios in glasses with ratios in the liquid phase suggests the predominance of the dissolution process for solid samples leached in water at 90°C [18].

Dynamic Leaching in Continuous Water Flow by MCC-5 Tests

The tests were conducted in deionized water for 14 days at 90°C at 0.25 cm^{-1} surface area of the sample-to-leachate volume ratio. Samples Ag6, Ag7, Ag9, Ag12, Ag14, Ag18, Ag19, and Ag21 were tested in the laboratory-scale dynamic test facility MCC-5 with an 8-cm^3 Teflon working cell (16 mm diam, 40 mm height). The cell with the glass samples was kept within the temperature-controlled volume of the MCC-5 at 90°C. The samples tested were 6- to 7-g pieces of glass with up to 20 cm^2 surface area. The average water flow rate was 0.063 ml/min.

The constant flow rate of deionized and deaerated water through the cell was maintained by applying ~0.1 kg/cm^2 constant gage pressure. The water flow rate through the test cell containing glass samples was set after the temperature reached the preset value. This moment was taken as the start time of the experiment. Samples of the leachate were taken daily for 14 days.

The normalized mass release of matrix elements (Na, B, Si) and Am-241 obtained by MCC-1 and MCC-5 at 90°C are given in Table X.

Table X. Normalized Mass Release of Basic Glass Components after 14-day Leaching by MCC-1 and MCC-5 Procedures at 90°C

Element	Glass	Normalized mass release, g/m^2 MCC-1	Normalized mass release, g/m^2 MCC-5
Am-241	Ag6	0.054	0.061
	Ag7	0.049	0.057
	Ag9	0.034	0.036
	Ag12	0.041	0.048
	Ag14	0.039	0.043
	Ag18	0.033	0.034
	Ag19	0.040	0.047
	Ag21	0.055	0.066
Na	Ag6	18.2	44.3
	Ag7	21.4	39.2
	Ag9	11.7	28.1
	Ag12	15.3	32.9
	Ag14	12.9	29.8
	Ag18	10.9	26.2
	Ag19	14.9	32.1
	Ag21	21.5	47.0
B	Ag6	18.1	33.8
	Ag7	16.9	31.01
	Ag9	9.5	22.1
	Ag12	1.8	29.1
	Ag14	1.7	23.9
	Ag18	8.9	20.8
	Ag19	14.3	28.1
	Ag21	19.2	35.9
Si	Ag6	21.0	31.6
	Ag7	19.1	29.8
	Ag9	11.4	17.7
	Ag12	13.5	19.5
	Ag14	11.6	18.9
	Ag18	10.8	16.2
	Ag19	12.9	18.6
	Ag21	22.3	33.4

Upon comparison of static and dynamic leaching process, the following characteristic features in the behavior of basic elements were noted:

- Normalized mass release of Am in the MCC-5 test is close to that obtained in MCC-1.
- Sodium, silicone and boron are leached in dynamic mode 2–3 times more intensively than in static mode of leaching.
- The surface layer of the glass samples is altered after testing at 90°C in both static and dynamic leaching. Both silicone release from the silicone dioxide matrix of the glass and precipitation rate of Me^{n+} cations at 90°C is rather high, which results in precipitation of slightly soluble hydrated compounds on the glass surface and in formation of a protective layer. As determined by XRPHA, the layer is amorphous.

CONCLUSIONS

The physical-chemical characterization conducted shows that borosilicate compositions loaded with 0.10 to 0.22 wt% americium and 0.45 to 0.99 wt% silver oxide are glasses with uniform distribution of the basic elements over the glass volume and they have high chemical durability under static and dynamic conditions.

Glasses formed under oxidizing conditions in the temperature range from 380°C to 1200°C made it possible to reach and exceed the previously published solubility limit of silver in the glass matrices. The solubility limit in the experiments amounted to 3.85 wt% Ag_2O, or approximately twice the published literature value [2, 3, 4].

The glasses developed are recommended for use in further trial melts using the KRI direct heated test melter EP-5 to study the possibility of silver sedimentation in melting large volumes of glass.

Glasses that incorporate up to 3.85 wt% Ag_2O may be recommended for incorporation of liquid alpha-bearing wastes in future work.

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