**Solubility of Sulfate and Chloride Ions in Borosilicate Melts at
Vitrification of Intermediate-Level Radioactive Wastes - 10348**

Natalia S. Ilyukhina, Irina Y. Ponomaryova, Tatiana N. Lashchenova, Sergey V. Stefanovsky
SUE SIA Radon, 7th Rostovskii lane 2/14 Moscow 119121 Russia

ABSTRACT

Solubility limit of sulfate ions (introduced as Na_2SO_4) in simulated borosilicate waste glass with a target composition of (in wt.%) 20 Na_2O, 17 CaO, 4 Fe_2O_3, 7 B_2O_3, 5 Al_2O_3, 45 SiO_2, 2 others was found to be ~1.0 wt.% (recalculated to SO_3). Addition of V_2O_5 in amount of 5 wt.% (over 100 wt.%) in glass increased SO_3 solubility to 2.4 wt.%. Solubility limits of chloride ions (introduced as NaCl) in borosilicate glass not containing and containing V_2O_5 were found to be 1.3 wt.% and 2.7 wt.%, respectively. Simultaneous introduction of SO_3 (as Na_2SO_4) and Cl (as NaCl) in glass reduced solubility limits to ~0.8 wt.% each of them in vanadia free and ~1.3 wt.% each of them in vanadia-bearing glasses, respectively. Heat-treatment of glasses nearby glass transition temperature resulted in a metastable binodal-type liquid-liquid phase separation. IR and Raman spectra contain weak band at ~615-620 cm^{-1} which may be attributed to stretching modes in sulfate ions with a configuration of nearly regular tetrahedron. Structural role of vanadia consists in loosening of silicon-boron-oxygen network by vanadium-oxygen tetrahedra thus promoting accommodation of sulfate ions and Na-Cl complexes.

INTRODUCTION

Vitrification of radioactive wastes with high concentrations of alkali and alkali earth sulfates, chromates, molybdates and chlorides is accompanied by formation of separate "yellow phase" on the surface of borosilicate melt [1,2]. High concentrations of sulfates and chlorides are the most typical of intermediate-level waste (ILW), where they may be widely varied as well [3]. This phase concentrating Cs and Sr radionuclides is easily evaporated, has low chemical durability, and much higher electric conductivity than the borosilicate glass. The latter is the most negative factor at electric melting of glass [4], including cold crucible melting [5]. Under strongly reduced conditions sulfates may be reduced and deposited as metal sulfides at the melter bottom [6]. They may be also reduced to SO_2 and removed with off-gas.

Solubility limit for sulfate ions (recalculated to SO_3) in silicate and borosilicate glasses does not exceed 0.8-1.2 wt.% [1,2,4]. It increases at 1) increase of melt basicity (alkali oxides content), 2) in the presence of highly polarized cations (in particular, lead – Pb^{2+}), 3) at introduction of oxidizers (MnO_2, SnO_2, V_2O_5), and 4) at transition from silicate to borate and phosphate systems [7-9]. Significant increase of alkali oxides concentration in glass is impossible because at their total content in glass higher than 20-25 wt.% (depending on glass composition) chemical durability of glass decreases strongly. In the system Na_2O-PbO-B_2O_3-SiO_2-SO_3 maximum SO_3 concentration (~19 wt.%) was achieved in sodium free glasses (partial system PbO-B_2O_3-SiO_2-SO_3) at high PbO content [9]. Introduction of Na_2O decreases SO_3 solubility limit to 2-3 wt.% [7]. Sulfate solubility in borosilicate glasses increases markedly at introduction of V_2O_5. However, degree of retention of SO_3 depends strongly on melt keeping time and, if at short-time keeping at 1100-1150 °C SO_3 concentration in glass may reach 5-7 wt.%, then at longer melt keeping it reduces to 2-3 wt.% [7]. Addition of lead or vanadium oxides makes waste vitrification process much more expensive and may be justified at HLW vitrification only. Much higher SO_3 (SO_4^{2-}) concentrations are achieved in phosphate glasses (up to ~7 wt.%) but these glasses are "shorter" and more corrosion aggressive with respect to refractories than borosilicate glasses [10].

Reference data on solubility of chloride ions are rather limited. This value in borosilicate glasses is considered to be ≤1 wt.% (as for SO_3) [4]. Phosphate glasses are capable to dissolve more Cl (up to ~5 wt.%) [11].

Among the methods for prevention of the "yellow phase" formation, an increase of solubility of sulfate and chloride ions in borosilicate melts using various chemical additives seems to be the most promising. In the present work we determined solubility of sulfate and chloride ions in borosilicate glass depended on their contents in ILW, studied the mutual effect of these ions and the effect of V_2O_5 on their solubility.

EXPERIMENTAL

Two different sulfate/chloride containing waste stream surrogates were prepared for this study. One of them (LWS1) had chemical composition corresponded to average composition of liquid radioactive waste in SIA Radon tanks. The second waste surrogate had composition typical of waste of Moscow Waste Preparation Plant with variable concentrations of sulfate and chloride ions (LWS2). Batch formulation was as follows (wt.%): dried waste (salt residue) – 40, datolite (CaO – 40, B_2O_3 – 20, SiO_2 – 35, Fe_2O_3 – 2, Al_2O_3 – 3) – 30, loam clay – 15, quartz sand – 15 (base batch), that corresponded to a target composition of glass (in wt.%) 20 Na_2O, 17 CaO, 4 Fe_2O_3, 7 B_2O_3, 5 Al_2O_3, 45 SiO_2, 2 others. Mixtures of these components with Na_2SO_4 and NaCl were placed in 200 cc alumina crucibles and heated in a resistive furnace at a rate of 10 °C/min, kept at a temperature of 400 °C for 1 hr, heated at the same rate to a temperature of 1150 °C, kept at this temperature for 1 hr followed by pouring of melts onto a metal plate. Analytical chemical compositions of glasses are given in Table I. Three series of glasses were prepared with addition of V_2O_5 in amount of 5 wt.% (over 100 wt.%) to the base batch: with SO_3 only (V1), with Cl only (V2), and with both SO_3 and Cl (V3).

Table I. Actual (analytical) chemical compositions of glasses (wt.%).*

Waste	Glass ID	Oxide concentrations, wt.%													
		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	P_2O_5	SO_3	SrO	Cl^-	Cs_2O
LWS1	1	8.27	0.61	7.48	51.74	2.78	16.66	0.23	0.12	2.77	1.07	0.30	0.34	0.05	0.31
	2	8.45	0.62	7.10	52.80	2.81	15.43	0.24	0.11	2.75	1.19	0.55	0.32	0.07	0.31
	3	8.60	0.65	7.28	52.32	2.77	15.13	0.25	0.11	3.07	1.26	0.70	0.31	0.10	0.30
	4	8.61	0.71	6.94	51.94	2.81	15.18	0.24	0.12	3.50	1.26	0.79	0.32	0.14	0.30
	5	8.45	0.61	6.54	53.17	2.77	15.16	0.23	0.11	3.02	1.20	0.80	0.32	0.14	0.29
	6	9.33	0.66	7.02	52.18	2.64	14.89	0.23	0.11	2.89	1.18	0.99	0.32	0.21	0.28
	7	9.45	0.66	6.72	52.09	2.66	15.24	0.24	0.12	2.85	1.17	0.94	0.32	0.27	0.27
	8	9.19	0.62	6.67	52.83	2.59	14.90	0.24	0.11	2.75	1.13	1.03	0.31	0.26	0.25
	9	9.30	0.64	6.80	52.55	2.55	14.86	0.24	0.11	2.79	1.13	1.00	0.31	0.28	0.26
	10	9.90	0.70	6.87	51.16	2.51	14.86	0.24	0.11	3.07	1.13	1.11	0.31	0.34	0.26
LWS2	1	14.91	0.88	3.93	48.02	1.31	16.60	0.23	-	4.75	-	0.86	0.59	0.29	0.38
	2	15.55	0.99	4.17	46.95	1.30	16.63	0.24	-	4.62	-	0.95	0.60	0.35	0.39
	3	15.55	0.91	3.91	47.48	1.29	16.59	0.23	-	4.54	-	0.98	0.59	0.34	0.38
	4	14.97	0.94	3.95	48.27	1.36	17.23	0.24	-	4.75	-	0.08	0.61	0.26	0.44
	5	15.91	0.92	3.83	48.22	1.00	16.42	0.23	-	4.51	-	0.06	0.60	1.18	0.22
	6	16.59	1.05	4.42	47.00	0.95	16.11	0.24	-	4.65	-	0.06	0.60	1.32	0.21

* B_2O_3 was not determined

Glasses were examined by X-ray diffraction (XRD) using a DRON-4 diffractometer (Fe K$_\alpha$ radiation), Raman spectroscopy (Jobin Yvon spectrometer, excitation wavelength is 514.4 Å), and infrared (IR) spectroscopy (modernized IKS-29 spectrophotometer, compaction of powdered glass in pellets with KBr). Chemical composition of the glasses was determined by X-ray fluorescence using a Philips PW-2400 spectrometer (The Netherlands). Pieces of the glasses obtained were heat-treated at a temperature of 600 °C for 2 hrs and examined by replica electron microscopy using an EMV 100L unit (samples were etched with 0.1 M HCl).

RESULTS AND DISCUSSION

It has been found at vitrification of LWS1 waste surrogate containing equal amounts of SO_4^{2-} and Cl^- ions (each of 0 to 2.5 wt.% over 100 wt.% - series 1) that glasses produced at 1150 °C were non-uniform and highly viscous. Occurrence of "yellow phase" (YP) as a deposit on the glass surface was observed from the sample in which summary content of SO_4^{2-} and Cl^- ions in the surrogate (dried waste) was 2.5 wt.% (target). From the sample containing 3.0 wt.% each of SO_4^{2-} and Cl^- ions the YP was poured separately. Materials balance showed the highest SO_3 concentration in glass (~1.0 wt.%) at SO_4^{2-} content in LWS1 of 1.22 wt.%. Solubility limit for Cl^- ions was found to be 0.27 wt.% (analytical value) that corresponds to their concentration in the surrogate of 1.46 wt.%. For the given type of waste stream maximum summary content of SO_4^{2-} and Cl^- ions in glass is ~1.27 wt.%.

As follows from Raman spectroscopy data (Figure 1a) vibrations of S—O bonds in sulfate ions correspond to the ranges of stretching and straining modes of S—O bonds in isolated sulfate ions located in the voids of silicon-oxygen network and having neighboring alkali (Na^+) or alkali earth (Ca^{2+}) ions. This is also in a good agreement with IR spectroscopy data (Figure 1b). However, Raman spectra within the ranges of 850-950 cm^{-1} and 600-650 cm^{-1} contain weak bands (for example, in the spectra of glasses series 2 at 867-887 cm^{-1}), which may be assigned to stretching modes of Si—O—S bridging bonds, but their fraction should be negligible.
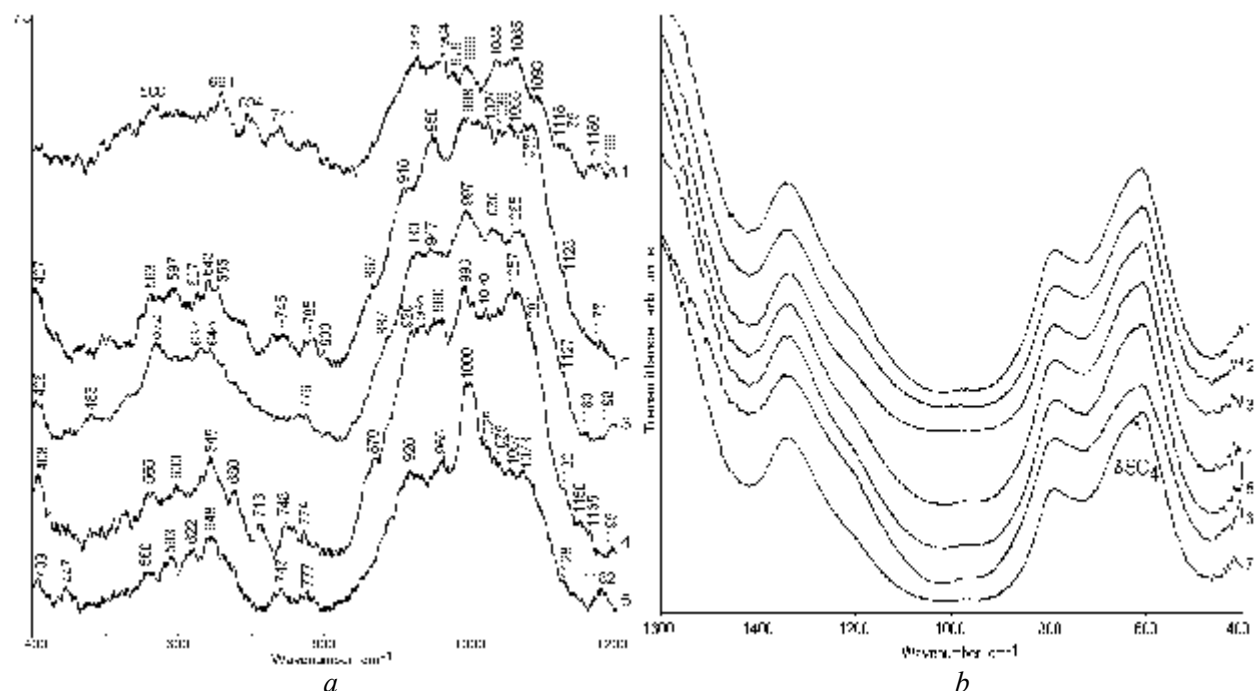

Figure 1. Raman spectra of glasses in series 2 (a) and IR spectra of glasses in series 1 (b). Chemical compositions of glasses are given in Table I.

IR spectra of all the glasses (Figure 1b) consist of the bands within the ranges of 1350-1550 cm^{-1} due to vibrations in carbonate groups, 850-1250 cm^{-1}, 650-750 cm^{-1}, and 400-550 cm^{-1} due to asymmetric and symmetric stretching modes of Si—O bonds in the SiO_4 tetrahedra and in some extent B—O bonds in the units with trigonally coordinated boron, vibrations of Al—O and Fe—O bonds in the AlO_4 and FeO_4 units, preferably incorporated in silicon-oxygen chains, and straining modes in the SiO_4 units. The modes due to S—O bonds correspond to wavenumbers about 980 cm^{-1} (v_1), 450 cm^{-1} (v_2), 1100 cm^{-1} (v_3), and

~610-620 cm^{-1} (ν_4), at that, at a symmetry close to T_d only ν_3 and ν_4 modes are active in IR spectra, whereas in Raman spectra all the modes are active. Reducing symmetry of SO_4^{2-} ion to C_{3v} and, further, to C_{2v} makes active 6 and 9 modes, respectively [12]. However, low concentrations of sulfate ions in glasses do not allow to attributing experimentally observable in IR spectra bands with theoretically predicted modes in the SO_4^{2-} ions with the exception of a weak band at ~620 cm^{-1}, which can be assigned to straining modes of S—O bonds in the isolated sulfate ions (Figure 1b).

Because glasses with the LWS1 surrogate were inhomogeneous, further study was performed using the LWS2 surrogate in which alkali and nitrate ion contents in dry residue were 23.0 wt.% and 65.9 wt.%, respectively (series 2). All the glassmelts were easily poured after melting at a temperature of 1150 °C, visually homogeneous, transparent, X-ray amorphous and had brown color. Trace of the YP was observed on the surface of glass at a content of 0.77 wt.% each of SO_4^{2-} and Cl$^-$ (1.54 wt.% in total) in waste surrogate or at 0.95 wt.% SO_3 and 0.35 wt.% Cl in glass. Amount of the YP increases with the increase of sulfate and chloride contents in waste surrogate. Saturation of glass with sulfate and chloride ions (~1.30 wt.%) was achieved at their summary concentration in the LWS2 surrogate of 1.54 wt.% (Figure 2a). At that, at their mass ratio in the waste surrogate of 1:1 they are present in glass at a ratio of 2.7:1 corresponding to SO_4:Cl molar ratio.

Glasses with the LWS2 surrogate at various concentrations of SO_4^{2-} ions were homogeneous after melting at a temperature of 1150 °C, easily poured, transparent and had brown color. Trace of the YP was observed from the sample prepared from waste surrogate with sulfate ions content in dry residue of 0.95 wt.%. Higher sulfate content in waste surrogate resulted in increase of amount of the YP on the surface of glass. As follows from materials balance saturation of molten glass with SO_3 (0.99 wt.%) takes place at SO_3 content in dry residue of waste surrogate of 0.8 wt.%. Occurrence of Cl$^-$ ions in the waste surrogate nearly does not effect on SO_3 solubility limit in glass (Figure 2b). Losses of Na_2O, K_2O, Cs_2O, MgO, Al_2O_3 increase with the increase of sulfate content in waste surrogate from 5%, 14%, 17%, 8%, and 0% to 12%, 28%, 56%, 19%, and 8%, respectively. At the same time CaO, SrO, Fe_2O_3 and SiO_2 concentrations in glass do not depend on sulfate content in waste surrogate.

Glasses with the LWS2 surrogate at various concentrations of Cl$^-$ ions were homogeneous after melting at 1150 °C and had low viscosity at this temperature. No YP was found on the surfaces of glasses but strong fumes occurred during pouring of glassmelts. Trace of the YP was observed on the surface of glass prepared from waste surrogate contained 7.05 wt.% Cl$^-$ ions in the dry residue of liquid waste surrogate. At higher chlorine content amount of the YP increases. Solubility limit for the chloride ions in borosilicate glass with the given chemical composition is ~1.27 wt.%, but in the presence of sulfate ions it reduces to 0.35 wt.% (Figure 2c), i.e. occurrence of sulfate ions reduces significantly solubility of chloride ions in borosilicate glass.

As follows from materials balance increase of chloride ions content in dry residue of waste surrogate increases volatile losses of K_2O (from 9 wt.% to 40 wt.% of total), Na_2O (from 2 wt.% to 27 wt.%), Cs_2O (from 18 wt.% to 68 wt.%), CaO (from 1 wt.% to 10 wt.%), MgO (from 3 wt.% to 17 wt.%), Fe_2O_3 (from 1 wt.% to 8 wt.% of total) whereas SrO, Al_2O_3 and SiO_2 remain retained in glass. Volatile losses of some elements may be due to high volatility of their chlorides [13]

Heat-treatment of glasses with low sulfate and chloride contents offers minor effect on their structure whereas glasses in which sulfate and chloride concentrations are close to their solubility limits undergo metastable liquid-liquid phase-separation and acquire the structure typical of phase separation by binodal mechanism (Figure 3). The heat-treated glass is composed of high-sulfate/chloride drop-type phase and matrix glass enriched with SiO_2, Al_2O_3 and depleted with SO_3 and Cl. At that, high-sulfate/chloride phase has lower chemical durability than matrix glass. Longer heat-treatment is expected to result in stable phase separation with segregation of YP as it has been observed earlier [14].
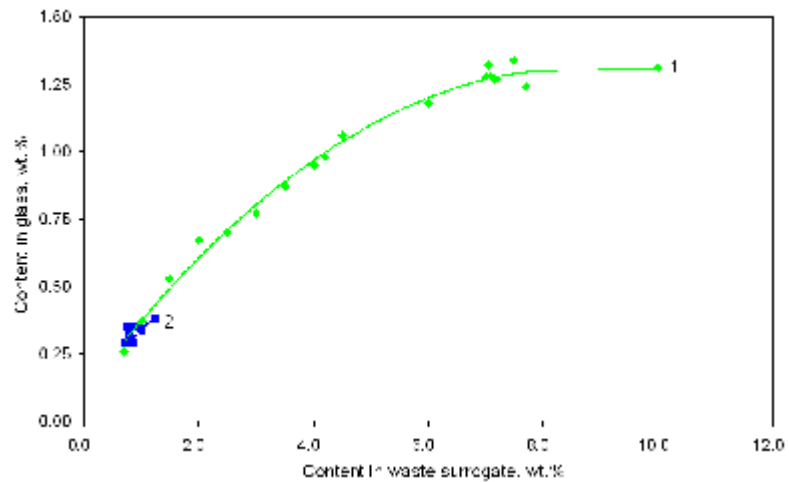
To study the effect of V_2O_5 additive (5 wt.% over 100 wt.% of batch components) on solubility limits of SO_3 and Cl three series of glasses with SO_3 only, Cl only and both SO_3 and Cl were studied (Figure 4).
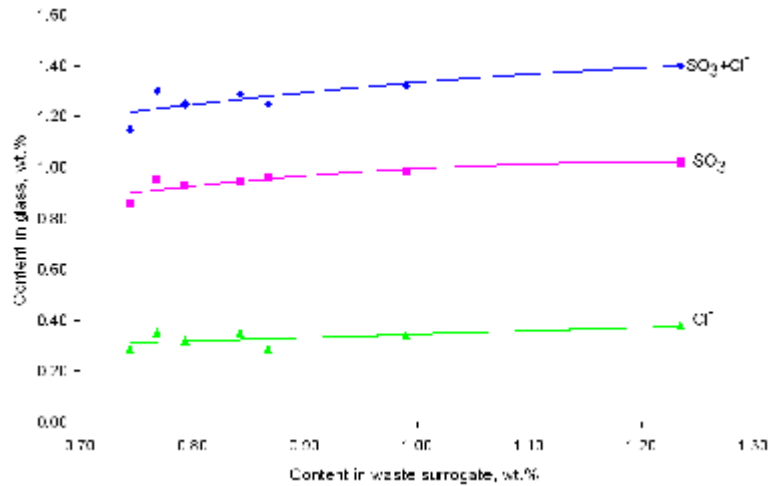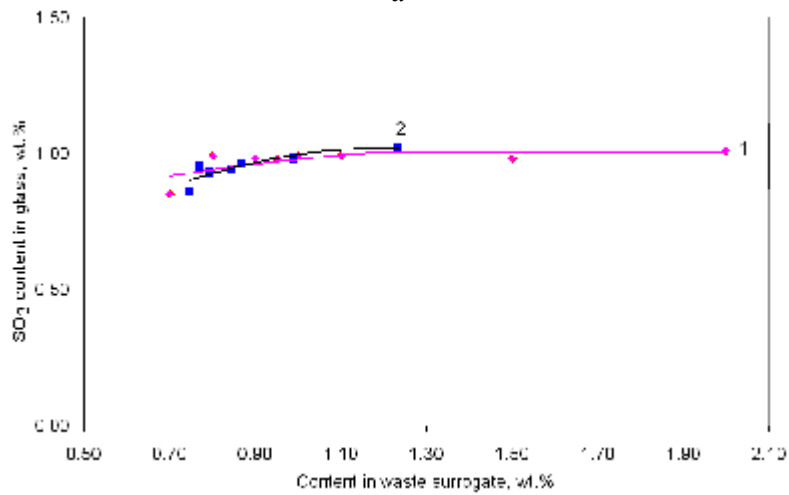
Figure 2. The effect of SO_3 and Cl contents in waste surrogate on their contents in glass.
In waste surrogate: *a*: both SO_4^{2-} and Cl^-; *b*: 1 – SO_4^{2-} only, 2 - both SO_4^{2-} and Cl^- (same concentrations);
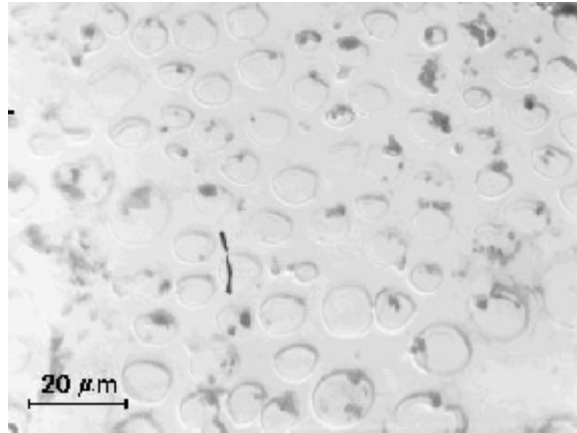*c*: 1 – Cl^- only, 2 – both SO_4^{2-} and Cl^- (same concentrations).

Figure 3. Phase separation in sulfate-containing borosilicate glass.

All the vanadia-bearing glasses were visually homogeneous, transparent and had brown color. No crystalline phases were found by XRD. In the glasses with SO_3 only (series V1) YP was observed at 5.6 wt.% SO_4^{2-} (over 100 wt.%) in he batch that corresponds to ~5.3 wt.% SO_4^{2-} in dried waste surrogate or ~2.4 wt.% SO_3 in glass (Figure 4a) whereas in vanadia free borosilicate glass solubility limit of SO_3 did not exceed ~1.0 wt.%.

In the glasses with Cl only (series V2) occurrence of Cl^- ions in the batch in amount of ≥ 9.3 wt.% caused opalescence which builds up at growth of Cl concentration. At glassmelt pouring a white fume occurred. YP was observed on the surface of glasses at ~10.3 wt.% Cl^- ions content in the batch or ~9.3 wt.% Cl^- ions in dried waste. Maximum concentration in the vanadia-bearing glass not resulting in phase separation was found to be ~2.7 wt.% whereas in the vanadia free glass it was ~1.3 wt.%.

In the glasses containing both sulfate and chloride ions trace of YP was observed on the surface of glass with total content of these ions of ~10.1 wt.% (over 100 wt.% of major batch constituents) that corresponds to ~9.2 wt.% in dried waste salts. In the absence of vanadia this value was ~3.0 wt.%.

Thus introduction of V_2O_5 increase solubility limit of both sulfate and chloride ions in borosilicate glass by 2-2.5 times. The fact that incorporation of vanadia in glass increases solubility of sulfate ions was revealed about 20 years ago [15] but no satisfactory explanation was done up to now. It has been suggested that vanadium-oxygen tetrahedra loosens borosilicate glass network facilitating accommodation of sulfate ions [7,15]. Attempts to find evidences of direct interaction between sulfate and vanadate structure-forming units were unsuccessful [16,17]. Recently the fact of positive effect of vanadia on dissolution of sulfate ions in borosilicate glass has been confirmed by French researchers [18]. To explain the nature of this effect additional investigations are required.

CONCLUSION

Solubility limit of sulfate ions in alkali borosilicate glass does not depend nearly on content of chloride ions in liquid radioactive waste and was found to be 0.95-0.99 wt.% (recalculated to SO_3) that is in a good agreement with reference data. Solubility of chloride ions depends on content of sulfate ions in liquid radioactive waste: if waste contains chloride ions only, then their solubility limit is ~1.27 wt.%; if waste contains both chloride and sulfate ions, then solubility limit of chloride ions is much lower – up to ~0.35 wt.%. Raman and IR spectroscopic study showed that vibration modes of S—O bonds in SO_4^{2-} ions correspond to the wavenumber ranges typical of stretching and straining modes of isolated sulfate ions located in voids of silicon-oxygen network. Heat-treatment of sulfate-containing glasses results in metastable phase separation by binodal mechanism.
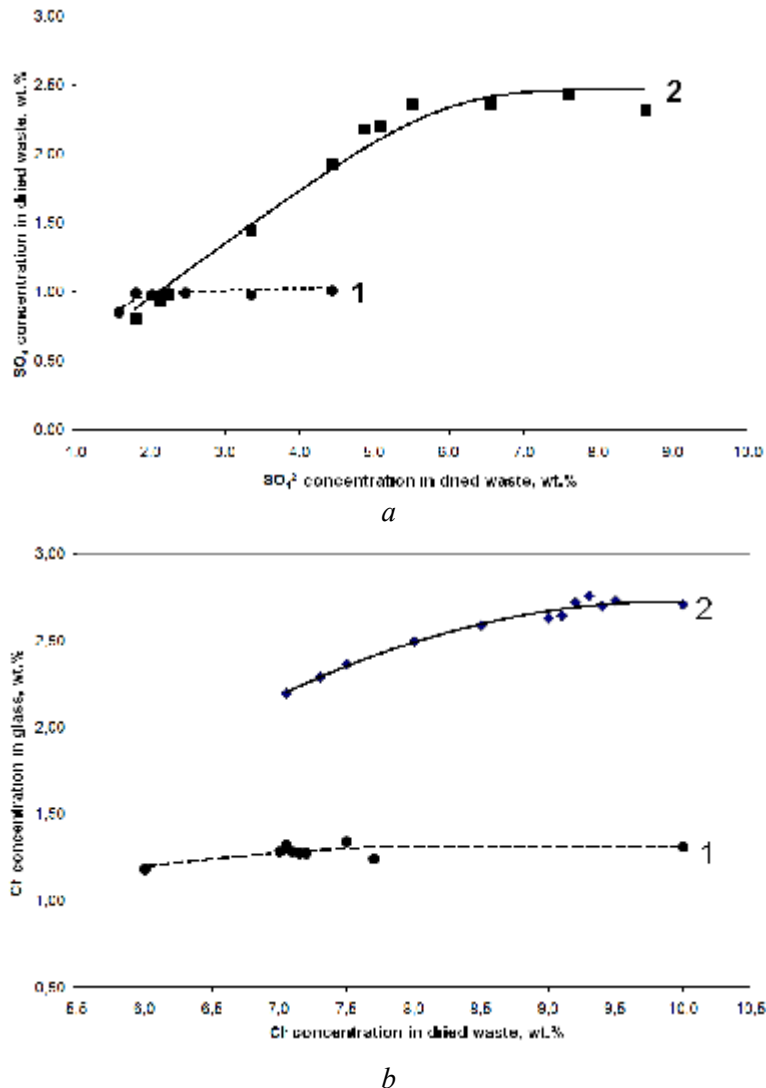
a

b

Figure 4. Effect of SO_4^{2-} (a) and Cl (b) concentration in dried waste on SO_3 (a) and Cl (*b*) solubility limits in glass.
1 – without V_2O_5, 2 – with V_2O_5 (5 wt.% over 100 wt.% of major batch components).

If chloride ions only are present in liquid waste, then yellow phase formation occurs only at high content of chloride ions (≥6 wt.%) in dry residue of liquid waste. Excess of chloride ions is removed with gaseous phase. Occurrence of chloride ions results in elevated losses of some glass constituents (Na, K, Cs, Mg, Ca, Fe).

Addition of V_2O_5 in glass in amout of 5 wt.% over 100 wt.% of major batch constituents increases SO_3 solubility by ~2.4-2.5 times and Cl solubility by ~2 times as compared to vanadia free glasses.

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