APPLICATION OF SPENT CRT GLASS FOR LOW-LEVEL, MIXED, AND HAZARDOUS WASTES CONDITIONING

F.A. LIFANOV, S.V. STEFANOVSKY, T.N. LASHTCHENOVA, O.A. KNYAZEV,
O.V. TOLSTOVA, S.V. CHIZHEVSKAYA
SIA "Radon", 7th Rostovskii per. 2/14, Moscow 119121 RUSSIA

ABSTRACT

Recent results of R&D work on joint vitrification of radioactive and hazardous wastes are described. Glasses containing spent cathode ray tube (CRT) glass and low-level Nuclear Power Plant (NPP) wastes were produced and examined. Various natural raw materials (eudialyte, datolite concentrates, loam clay, sandstone) were added to NPP wastes to obtain glasses and glassy slags (glass crystalline materials) with low leachability. The NPP waste oxide content in the products reached 30 wt.% for RBMK and institutional wastes and 40 wt.% for boron-containing VVER waste. Joint vitrification of NPP waste, incinerator ash (slag), and CRT glass has also been demonstrated. Ash content in the glassy slags may reach 50-70 wt.%. The materials with appropriate compositions had low leaching of waste elements like conventional borosilicate glasses. The structure of the materials obtained was examined with X-ray diffraction (XRD), optical microscopy, infra-red (IR) spectroscopy, and electron-probe microanalysis (EPMA). Liquid-liquid phase separation and crystallization effects were observed. Two of the glassy compositions were produced by cold crucible melting. Process parameters depend strongly on batch particles distribution in sizes. Milling of CRT glass breakage is required. The best results are reached by treatment of milled batch in an apparatus with a rotating magnetic field.

INTRODUCTION

In Russia currently just minor part of spent TV sets is processed to recover glass and valuable components, but major part of them is buried at garbage sites or usual rubbish heaps. Spent cathode ray tube (CRT) glass contains toxic components (Sb, Pb, Ba, F, etc.) and it is potentially dangerous to the environment. Institutional radioactive waste, mainly low- and intermediate-level, is collected at the Radon governmental system sites to be treated and conditioned. Radioactive wastes formed at Nuclear Power Plants (NPP) are stored at NPP territories. Low salt low level waste is subjected to cementation. Intermediate-level liquid waste is concentrated, followed by storage in barrels. Recently, vitrification of liquid intermediate-level waste as well as incinerator ash (solid waste formed at incinerators) has been proposed [1-3].

A major index of waste treatment efficiency is the waste volume reduction factor (VRF). Comparison of various waste treatment processes (cementation, bituminization, ceramization, and vitrification) has shown that the highest VRF (ranged between 3 and 7) is reached by vitrification. It is clear, that the most efficient way is joint vitrification of various radioactive and hazardous wastes providing the lowest volume of final product to be disposed. We proposed to use spent CRT glass as a glass forming agent for intermediate-level waste vitrification [4]. Waste vitrification provides production of waste form with lower volume and higher chemical durability than cemented waste form. This paper describes recent advances in mixed waste conditioning.

EXPERIMENTAL

Glasses were produced from blended dry waste salts, incinerator ash, spent CRT glass, and natural rocks (eudialyte concentrate, datolite concentrate, loam clay) in alumina crucibles in a resistive furnace at temperatures 1150-1350 ^{0}C. Some tests were carried out using a bench-scale unit based on a cold crucible [5]. The unit included batch preparation and feeding systems, the cold crucible in a process box, and an off-gas system.

Typical compositions of Russian low- and intermediate level wastes are given in Table I. Taking into account that VVER (Russian reactor designed very similar to Pressurized Water Reactors – PWR) and RBMK (Russian channel-type fast neutron reactor) are two of the typical reactors operating at Russian NPPs, in the present work actual wastes from the Kalinin (Tver) NPP with a VVER reactor and the Leningrad NPP with a RBMK reactor were used. Compositions of CRT glass and other glass forming agents are given in Table II. A CRT consists of a screen, a taper, and a throat. The average composition of CRT glass is given assuming that the whole CRT is crushed and ground to be used.

Table I. Low- and intermediate level liquid waste compositions

Parameters		Institu-ional waste	NPP wastes from RBMK			NPP wastes from VVER		
	Ions		Leningrad	Kursk	Chernobyl	Kalinin	Kola	Novo-Voronezh
Chemical composition, kg·dm^{-3}	Na^+	50-150	71.0	82.0	15.0	104-130	70	20-30
	K^+	1-10	3.1	2.4	1.5	7-30	48	5-15
	NH_4^+	n.m.*	2.1	-	n.m.	0.1	0.1	n.m
	Ca^{2+}	5-20	<0.1	0.9	n.m.	0.6	-	-
	Mg^{2+}	1-10	-	0.4	-	-	-	-
	Al^{3+}	0.5-2	0.3	-	-	-	-	-
	Fe^{3+}	3-15	<0.1	0.9	5-10	-	4.2	<0.1
	NO_3^-	100-350	150-180	195.0	35.0	100-200	155	80-100
	Cl^-	5-20	28-32	11.8	-	2-9	5.5	<0.1-5
	SO_4^{2-}	3-35	3-6	9.2	n.m.	0.5-10	26	n.m.
	PO_4^{3-}	1-5	0.1	0.7	n.m.	-	-	-
	BO_3^{3-}	<0.1-2	0.5	-	-	70.8	74	40-70
	MnO_2	<0.1-0.5	-	-	3.5	-	-	-
Total, kg·dm^{-3}		250-600	300-350	332	60-65	450-500	520	150-230
Radio-nuclide compo-sition, Bq·m^{-3}	^{137}Cs	10^7-10^{10}	$5·10^6$	$4.8·10^9$	$3.7·10^8$	$1.9·10^{10}$	$7.5·10^{10}$	$1.2·10^{10}$
	^{134}Cs	10^6-10^9	-	$6.8·10^7$	$1.0·10^7$	$6.5·10^9$	$8.0·10^9$	$9.0·10^8$
	^{60}Co	10^5-10^7	$2.8·10^7$	$2.7·10^7$	n.m.	$2.7·10^8$	$1.5·10^9$	$2.6·10^7$
	^{54}Mn	10^5-10^6	n.m.	n.m.	n.m.	n.m.	$1.5·10^8$	n.m.
	^{239}Pu	10^3-10^5	n.m.	$5.0·10^6$	n.m.	$1.5·10^6$	n.m.	n.m.
PH		9-12	12.9	12.0	~7	9-11	7-8	10-11.5

n.m. – not measured

Table II. Compositions of CRT glasses, raw materials, and ash (in wt.%)

Glass	SiO_2	Al_2O_3	B_2O_3	CaO	MgO	SrO	BaO	PbO	Li_2O	Na_2O	K_2O	others
CRT[1]	66.8	4.4	-	4.0	1.0	2.0	6.1	5.4	0.6	4.5	4.5	0.7[2]
Datolite	35.5	1.0	20.0	41.0	-	-	-	-	-	-	-	2.5[3]
Eudialyte	49.5	7.7	-	6.8	0.7	-	-	-	-	13.4	1.8	20.1[4]
Loam clay	70.0	13.0	-	3.0	1.5	-	-	-	-	2.5	1.5	8.5[5]
Ash (slag)	33.0	7.0	-	13.5	7.5	-	-	-	-	4.4	7.0	27.6[6]

[1]average, screen to tube ratio is 2:1, [2] 0.1 Sb_2O_3, 0.6 F, [3]$FeO+Fe_2O_3$, [4]8.3 ZrO_2, 5.1 $FeO+Fe_2O_3$, 1.6 TR_2O_3, 0.8 TiO_2, 0.6 HfO_2, 0.6 Nb_2O_5, 1.8 MnO, [5]7.0 $FeO+Fe_2O_3$, 1.5 the balance, [6] 0.6 MnO, 1.4 CuO, 0.8 Cr_2O_3, 5.5 $FeO+Fe_2O_3$, 0.4 TiO_2, 14.8 P_2O_5, 0.8 S (total), 1.8 Cl (total), 1.9 others.

CRT glass and other additives, including ash, contain typical glass forming oxides (SiO_2, Al_2O_3), whereas intermediate-level wastes are composed mainly of alkali salts. Such a combination provides formation of glasses at relatively low temperatures.

Specific activities of NPP waste salts for $\beta-\gamma$-, and α–emitters are 10^5-10^6 Bq/kg and ~10^2 Bq/kg, respectively, and incinerator ash for $\beta-\gamma-$ and α–emitters are about 10^5-10^6 Bq/kg and 10^7-10^8 Bq/kg, respectively. Major $\beta-\gamma$–emitters are ^{137}Cs, ^{134}Cs, ^{90}Sr, and ^{60}Co (Table I). Major α–emitters are ^{235,238}U and ^{238,239}Pu. Traces of ^{152}Eu, ^{210}Po, ^{226}Ra, ^{237}Np, and natural thorium may be also present.

The samples obtained were examined with X-ray diffraction (XRD, diffractometer DRON-4, Cu K_α - radiation), optical microscopy (POLAM L-213), replica electron microscopy (REM, EMV 100L unit, etching of polished surface in 0.1 M HCl), electron-probe microanalysis (EPMA, Camebax micro-beam system), and selective leaching of Cs, Sr, total α-emitters, Na, and Pb (if present) in 0.1 M HCl and deionized water. Leach rates of elements were measured using IAEA test [6]. Viscosity and electric resistivity of melts were measured using a combined system designed at SIA Radon based on the vibrational viscosimeter VRT-3 (designed at State Institute of Glass, Moscow, Russia).

RESULTS

Vitrification of VVER waste

Boron-containing VVER waste forms glassy products easily in the presence of silica and alumina. Loam clay, bentonite, and sandstone can be used as glass forming agents [1,2]. Experimental data on joint vitrification of VVER waste salts and CRT glass are presented in Table III and IV.

Table III. Properties of glasses and glassy slags containing VVER waste and CRT glass

Composition, wt.%	Density, g/cm^3	Viscosity, Pa·s	Resistivity, Ω·cm
VVER waste oxides – 10-40; Ash oxides – 60-90	2.6-2.8	3.8-15.6 (1300 ^{0}C); 2.3-9.5 (1400 ^{0}C)	4.8-18.4 (1300 ^{0}C); 2.7-8.6 (1400 ^{0}C)
VVER waste oxides – 10-40; CRT glass – 60-90	2.7-2.9	6.7-26.3 (1200 ^{0}C); 2.5-10.7 (1300 ^{0}C)	3.2-12.3 (1200 ^{0}C); 2.4-7.7 (1300 ^{0}C)
VVER waste oxides – 10-40; Ash oxides – 40-70; CRT glass – 10-30	2.6-2.8	5.0-15.0 (1200 ^{0}C); 3.2-10.5 (1300 ^{0}C)	6.8-17.5 (1200 ^{0}C); 4.0-11.2 (1300 ^{0}C)
VVER waste oxides – 10-40; CRT glass – 40-70; Loam clay – 10-30	2.7-2.8	4.5-9.8 (1200 ^{0}C); 3.0-7.7 (1300 ^{0}C)	5.8-14.7 (1200 ^{0}C); 3.7-11.6 (1300 ^{0}C)
VVER waste oxides – 10-40; SiO$_2$ – 60-90	2.5-2.6	4.6-13.2 (1200 ^{0}C); 3.1-9.7 (1300 ^{0}C)	8.7-35.0 (1200 ^{0}C); 5.0-22.0 (1300 ^{0}C)
VVER waste oxides – 10-40; CRT glass – 40-70; SiO$_2$– 10-30	2.6-2.7	3.7-11.1 (1200 ^{0}C); 2.4-8.6 (1300 ^{0}C)	6.5-18.7 (1200 ^{0}C); 3.7-10.5 (1300 ^{0}C)
VVER waste oxides – 20-40; CRT glass – 40-70; Eudialyte oxides – 10-20	2.7-2.9	4.6-19.4 (1200 ^{0}C); 3.0-10.8 (1300 ^{0}C)	5.3-13.7 (1200 ^{0}C); 3.3-9.5 (1300 ^{0}C)

Table IV. Leaching of waste elements from glasses and glassy slags
containing VVER waste and CRT glass

Composition, wt.%	Leach rate, g/(cm^2·day)				
	^{137}Cs	^{90}Sr	(α-emitters	Na	Pb
VVER waste oxides – 10-40; Ash oxides – 60-90	10^{-4}-10^{-6}	10^{-6}-10^{-7}	10^{-7}	10^{-5}-10^{-6}	-
VVER waste oxides – 10-40; CRT glass – 60-90	10^{-5}-10^{-6}	10^{-7}-10^{-8}	10^{-8}	10^{-5}-10^{-6}	~10^{-6}-10^{-7}
VVER waste oxides – 10-40; Ash oxides – 40-70; CRT glass – 10-30	10^{-5}-10^{-6}	10^{-6}-10^{-7}	10^{-8}	10^{-5}-10^{-6}	~10^{-7}
VVER waste oxides – 10-40; CRT glass – 40-70; Loam clay – 10-30	10^{-6}-10^{-7}	~10^{-7}	10^{-8}	10^{-5}-10^{-6}	~10^{-7}
VVER waste oxides – 10-40; SiO$_2$ – 60-90	10^{-5}-10^{-6}	10^{-6}-10^{-7}	~10^{-8}	10^{-5}-10^{-6}	-
VVER waste oxides – 10-40; CRT glass – 40-70; SiO$_2$– 10-30	~10^{-6}	~10^{-7}	~10^{-8}	10^{-5}-10^{-6}	~10^{-6}
VVER waste oxides – 20-40; CRT glass – 40-70; Eudialyte oxides – 10-20	10^{-6}-10^{-7}	10^{-6}-10^{-7}	~10^{-8}	10^{-5}-10^{-6}	~10^{-6}

All the batches containing VVER waste were fully melted at 1200 ^{0}C and produced homogeneous materials. However, melts containing ≤20 wt.% VVER waste oxides were too viscous causing problems during pouring. The electric resistivity of these materials were also too high to allow a glass to be produced by electric melting. To reduce viscosity and resistivity, the melting temperature should be raised to at least 1300 ^{0}C. Melt viscosity and resistivity were reduced, when VVER waste oxide content becomes higher than 20 wt.%. Such melts may be produced at 1200 ^{0}C by electric melting, including cold crucible melting. Leach rates of waste elements increases as VVER waste oxide content in glasses increases. The most appropriate VVER waste oxide content in glass ranges between 25 and 35 wt.%. The leach rate of the most leachable element – cesium from such glasses is about $(1-5) \cdot 10^{-6}$ g/(cm$^2 \cdot$day). Leach rates of Sr, Pb, and α–emitters are lower by 1-2 orders of magnitude (Table IV).

Introduction of alumina-bearing loam clay or zirconia-bearing eudialyte increases the chemical durability of glasses. Addition of up to 30 wt.% of calcined loam clay or up to 20 wt.% of calcined eudialyte to batch lowers leach rate of cesium by approximately one order of magnitude (to 10^{-7} g(cm$^2 \cdot$day)).

As follows from XRD and electron microscopy data, joint vitrification of VVER waste salts and CRT glass yields homogeneous glasses not containing crystalline phases. At the same time materials produced from VVER waste salts and incinerator ash as well from VVER waste salts, incinerator ash, and CRT glass contain crystalline phases (Figure 1 and 2) and may be specified as glassy slags (GS).

Source ash is a non-uniform material containing both amorphous and crystalline constituents (Figure 2, *slag*). Major crystalline phases are silicophosphate close to silicocarnotite $Ca_5(PO_4)_2(SiO_4)$. Actually, the composition of this phase is variable (as is shown by EPMA data) and may be described by general formula $(Ca,Mg,Mn,Fe)_{5-x}(TR,U)_xP_{2-x}Si_{1+x}O_{12-y}$. The other phase occurred is aluminosilicate close on XRD pattern to kalsilite with composition corresponding to general formula $(K,Na,Ca)(Al,Fe)SiO_4$. One more minor aluminosilicate phase with XRD pattern similar to plagioclase is also present. After melting at 1400 ^{0}C the slag is composed of a major vitreous phase, silicocarnotite, and aluminosilicate (Figure 2, *melted slag*).
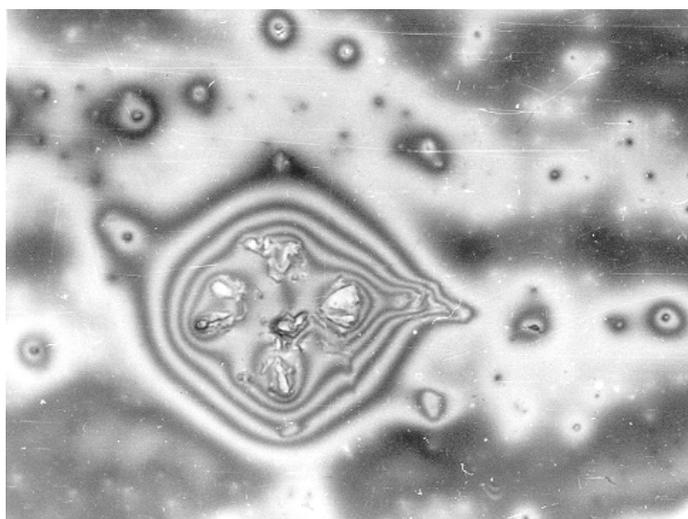

Figure 1. Occurrence of crystals on polished surface of the sample of the glassy slag GS-1. Magnification, x500.

Glasses with high VVER waste oxide content (30-40 wt.%), quite low ash oxides content (40-50 wt.%), and a CRT additive (10-30 wt.%) were almost homogeneous and contained only minor silicophosphate phase with XRD pattern similar to nagelschmidtite $Ca_7(PO_4)_2(SiO_4)_2$ (Figure 2, *GS-1, GS-2*). As in the previous case, actual composition of this phase is very complicated due to isomorphic exchanges $Ca^{2+} \leftrightarrow Me^{2+}$, $Ca^{2+} + P^{5+} \leftrightarrow TR^{3+} + Si^{4+}$, and $Ca^{2+} \leftrightarrow U^{4+}$ + vacancy. As expected, the fraction of vitreous phase becomes higher as CRT content in the product increases (Figure 2 and Table V).

Table V. Compositions of glassy slags (in wt.%)

Nos on Figure 1	VVER waste oxides	RBMK waste oxides	Ash oxides	CRT glass	Loam clay
GS-1	40	-	50	10	-
GS-2	30	-	40	30	-
GS-3	-	30	50	20	-
GS-4	-	30	20	50	-
GS-5	-	30	20	30	20
GS-6	-	30	-	30	40

Investigation of vitreous phase in the glassy slags in more details has shown that glass is phase-separated (Figure 3). Metastable liquid-liquid phase separation is pre-crystallization step following by crystallization itself [7]. It shows that crystallization of glassy slags is incomplete and longer exposure at elevated temperatures (annealing) may yield well-crystallized materials like glass-ceramics.

Vitrification of RBMK and institutional wastes

Both RBMK and institutional wastes consist of major sodium nitrate and may also contain significant amounts of sulfates and chlorides (Table I). If the sulfate and chloride ion content is relatively low, no problems during vitrification occur. Sulfate (as SO_3) and chloride ions in silicate-based glass content should not exceed about 1% each [8]. Higher amounts of these ions form a "yellow phase" (yellow color is due to minor chromates and molybdates). In order to avoid phase separation either temperature should be raised or some species should be added to batch. The simplest way is to introduce any carbon-containing agent capable to decompose sulfate ions with formation of SO_2 and CO_2 or CO.
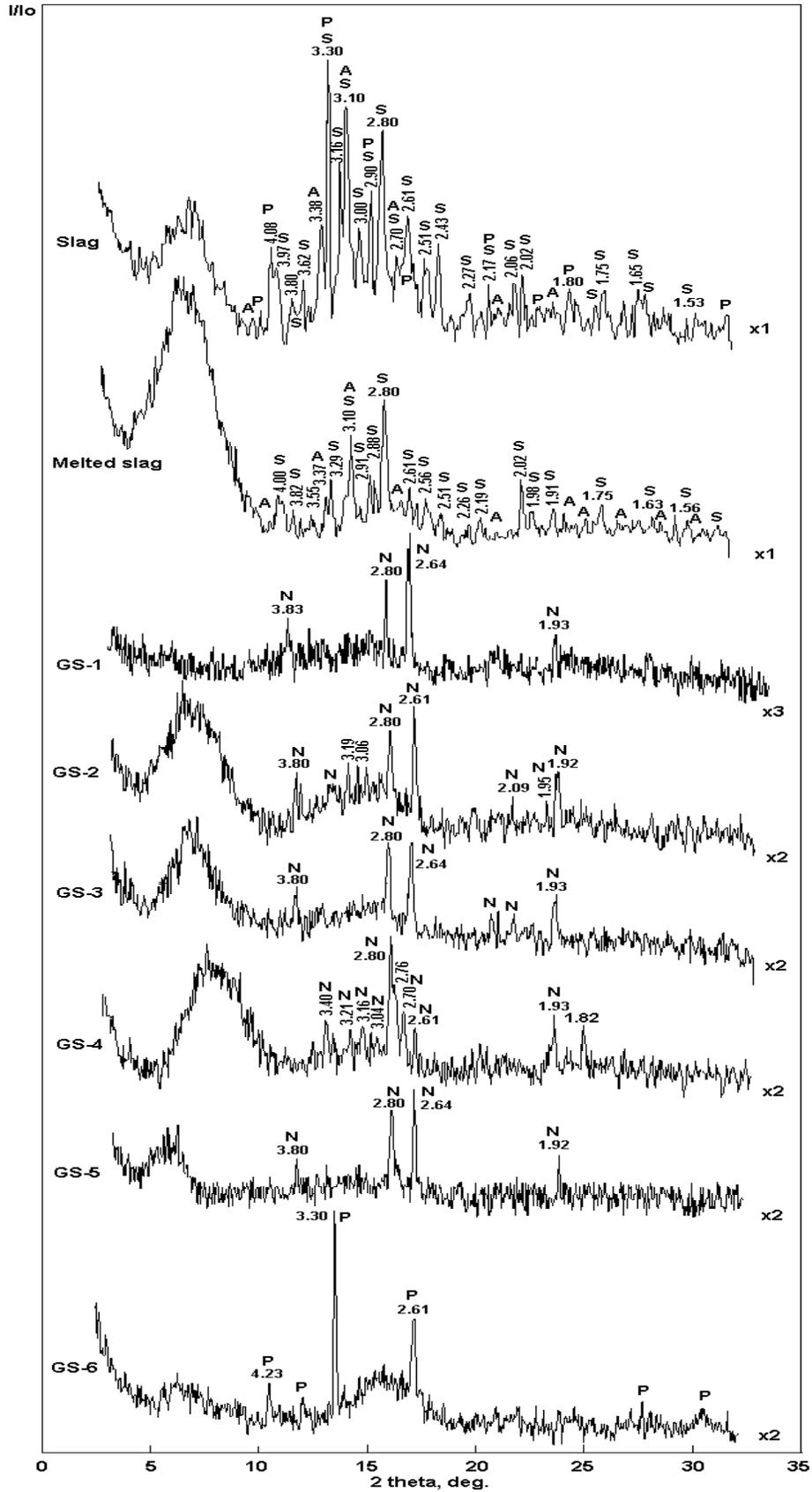
Figure 2. XRD patterns of the incinerator tush (source slag), melted ash (slag), and glassy slags.
A – aluminosilicate similar to kalsilite, N – negelschmidtite, S – silicocarnotite, P – plagioclase.

Figure 3. Phase separation of the vitreous phase in the glassy slag GS-1. Magnification, x50000.

All the melts produced from RBMK waste and CRT glass at 1200 ^{0}C were phase-separated (Figure 4). Increasing the temperature to 1250-1300 ^{0}C resulted in decomposition of the "yellow phase". In the Leningrad NPP waste samples taken for these experiments, the major component of the "yellow phase" was sodium chloride rather than sodium sulfate and, therefore, this "yellow phase" is easier to vaporize.

Melts produced from institutional waste containing lower concentrations of sulfates were fully homogeneous. If sulfate ions were present in amounts ≥10 wt.%, melts were also phase-separated.
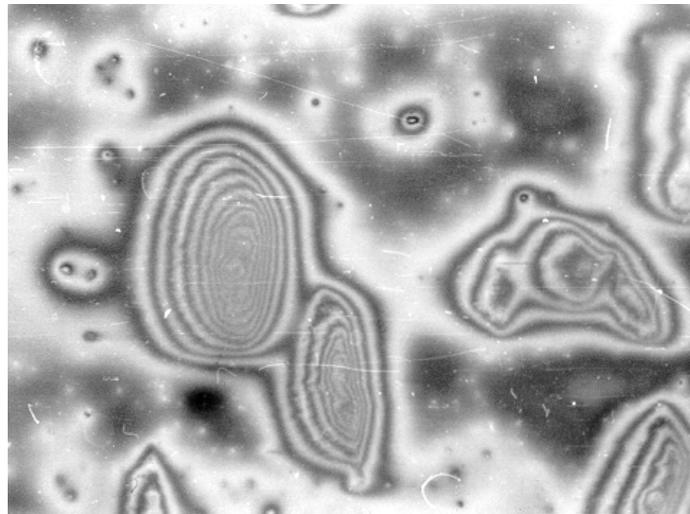

Figure 4. Occurrence of "yellow phase" drops on polished surface of the sample of the glass 30 wt.% RBMK waste oxides, 70 wt.% CRT glass. Magnification, x500.

Melts produced at 1250-1300 ^{0}C from just RBMK or institutional wastes and CRT glass are too viscous (Table VI). To reduce viscosity addition of a boron-containing agent, for example datolite, is required. This reduces the viscosity, whereas the electric resistivity is maintained at a level suitable for electric melting (Table VI).

Table VI. Properties of glasses and glassy slags containing RBMK waste and CRT glass

Composition, wt.%	Density, g/cm^3	Viscosity, Pa·s	Resistivity, Ω·cm
RBMK waste oxides – 10-30; CRT glass – 70-90	2.5-2.6	8.5-50 (1200 ^{0}C); 5.3-17.8 (1300 ^{0}C); 2.6-7.5 (1400 ^{0}C)	>10 (1200 ^{0}C); 4-10 (1300 ^{0}C); 2.8-5.2 (1400 ^{0}C)
RBMK waste oxides – 10-30; Datolite oxides – 20-40; CRT glass – 40-60	2.5-2.7	4.4-12.1 (1200 ^{0}C); 2.2-6.8 (1300 ^{0}C)	5-15 (1200 ^{0}C); 3.2-7.7 (1300 ^{0}C)
RBMK waste oxides – 10-30; CRT glass – 20-50; Ash oxides – 20-70	2.6-2.7	7.5-35.5 (1300 ^{0}C); 4.7-15.3 (1400 ^{0}C)	5.5-14.0 (1300 ^{0}C) 4.0-8.3 (1400 ^{0}C)
RBMK waste oxides – 10-30; CRT glass – 30-70; Loam clay – 20-40	2.6-2.8	5.8-40.0 (1300 ^{0}C); 3.4-20.0 (1400 ^{0}C)	4.7-20.0 (1300 ^{0}C) 3.5-9.1 (1400 ^{0}C)
Institutional. waste oxides* – 10-30; CRT glass – 70-90	2.6-2.7	4.8-14.5 (1300 ^{0}C)	3.7-9.8 (1300 ^{0}C
Institutional waste oxides* – 10-30; CRT glass – 30-50; Datolite oxides – 10-40; Loam clay – 10-20	2.6-2.7	3.5-8.9 (1300 ^{0}C)	2.6-4.7 (1300 ^{0}C)

* low sulfate-chloride waste

Table VII. Leaching of waste elements from glasses and glassy slags containing RBMK waste and CRT glass

Composition, wt.%	Leach rate, g/(cm^2·day)				
	^{137}Cs	^{90}Sr	α-emitters	Na	Pb
RBMK waste oxides – 10-30; CRT glass – 70-90	10^{-4}-10^{-6}	10^{-6}-10^{-7}	10^{-7}	10^{-5}-10^{-6}	~10^{-6}-10^{-7}
RBMK waste oxides – 10-30; Datolite oxides – 20-40; CRT glass – 40-60	10^{-5}-10^{-6}	10^{-7}-10^{-8}	10^{-8}	10^{-5}-10^{-6}	~10^{-6}-10^{-7}
RBMK waste oxides – 10-30; CRT glass – 20-50; Ash oxides – 20-70	10^{-5}-10^{-6}	10^{-6}-10^{-7}	10^{-8}	10^{-5}-10^{-6}	~10^{-7}
RBMK waste oxides – 10-30; CRT glass – 30-70; Loam clay – 20-40	10^{-6}-10^{-7}	10^{-7}	10^{-8}	10^{-5}-10^{-6}	~10^{-7}
Institutional. waste oxides* – 10-30; CRT glass – 70-90	10^{-5}-10^{-6}	10^{-6}-10^{-7}	~10^{-8}	10^{-5}-10^{-6}	~10^{-7}
Institutional waste oxides* – 10-30; CRT glass – 30-50; Datolite oxides – 10-40; Loam clay – 10-20	10^{-5}-10^{-6}	10^{-6}-10^{-7}	~10^{-8}	10^{-5}-10^{-6}	~10^{-7}

Addition of datolite ($CaBSiO_4OH$) to the RBMK waste-CRT glass batch reduces its melting temperature, its melt viscosity, and leaching of all waste elements. Leach rates of the waste elements from the glasses are reduced in the presence of loam clay as well. But, addition of this component increases the melting temperature. Addition of incinerator ash also increases the melt temperature. In any case, to produce glassy products at moderate temperatures (1200-1300 ^{0}C) the RBMK waste oxide content must be no higher than 20-25 wt.%, and introduction of boron-containing additive is desirable. For example, the amount of calcined datolite (as oxides) should be at least 20 wt.%. For vitrification of institutional waste, datolite oxide content in the glass may be reduced to ~10 wt.%.

As reported earlier [1], good quality glasses with viscosity and electric resistivity suitable for electric melting were designed within the compositional range (in wt.%): 25-35 Institutional or RBMK waste oxides, 25-35 calcined datolite, 15-25 SiO_2, 15-25 calcined loam clay. Melting temperatures of these glasses were 1150-1200 ^{0}C. The CRT glass itself contains components that lower the melting temperature of glass (PbO, alkali oxides), but its fluxing effect is not so efficient as compared to boron-containing agent.

Incinerator ash may also be added to RBMK waste – CRT glass system, but in this case melting temperature, melt viscosity, and resistivity increase (Table VI). The ash-loaded glasses contains crystalline phase of silicophosphate composition (Figure 2, *GS-4, GS-5*). The glass produced from RBMK waste salts, CRT glass, and loam clay and slowly cooled contains minor plagioclase (Figure 2, *GS-6*).

As seen from Table VII, leaching of the waste elements from all the glasses produced is low. The lowest leach rates were found to be from glasses containing ≤30 wt.% of RBMK waste oxides. As follows from infra-red spectroscopy data, increase of high alkali oxide content in glass causes destruction of the silica-oxygen glass network. This is seen from a shift to lower wave numbers of the band due to valency vibrations of bonds in the $[SiO_4]$ tetrahedra (the strongest band in region 1000-1150 cm^{-1} is shifted from 1030 cm^{-1} for glass with 10 wt.% RBMK waste oxides to 975 cm^{-1} for glass with 30 wt.% RBMK waste oxides). Within the same compositional range growth on intensity of the band at ~900-920 cm^{-1} due to Si-O$^-$ bonds (non-bridging oxygen ions) is observed. When the RBMK waste oxide content in glass exceeds ~30 wt.%, the fraction of bridging Si-O-Si bonds is strongly reduced as compared to non-bridging Si-O bonds.

Bench-scale tests on vitrification of VVER and RBMK wastes with CRT glass

Composition of the glass chosen for the cold crucible melting (in wt.%) was: 30 VVER waste oxides, 70 wt.% CRT glass (CC-1) and 30 RBMK waste oxides, 20 calcined datolite, 20 loam clay, 30 CRT glass (CC-2). Process parameters and leach rates of waste elements from the products are given in Table VIII.

Table VIII. The cold crucible melting process parameters and products properties

Glass No.	Batch feeding	Temperature, ^0C	Melt productivity, $kg/(dm^2 \cdot h)$	Leach rate, $g/(cm^2 \cdot day)$			
				^{137}Cs	^{90}Sr	α-emitters	Pb^{2+}
CC-1	Dry waste salts + crushed CRT glass (~1 mm)	1300	3.5	$3.7 \cdot 10^{-6}$	$3 \cdot 10^{-7}$	10^{-8}	$6 \cdot 10^{-7}$
CC-1	Dry waste salts + ball-milled CRT glass (~0.3 mm)	1250	4.5	$3.5 \cdot 10^{6}$	$3 \cdot 10^{-7}$	10^{-8}	$6 \cdot 10^{-7}$
CC-1	Activated mixture of dry waste salts and milled and activated CRT glass (~0.15 mm)	1200	6.2	$3.0 \cdot 10^{-6}$	$3 \cdot 10^{-7}$	10^{-8}	$4 \cdot 10^{-7}$
CC-2	Dry waste salts + ball-milled CRT glass (~0.3 mm) + datolite concentrate + loam clay	1250	4.0	$6.2 \cdot 10^{-6}$	$3 \cdot 10^{-7}$	10^{-8}	$4 \cdot 10^{-7}$

The process was initiated by heating of a conductive material in a high frequency electromagnetic field until a starting melt formed from the initial batch. Three portions of the batch were prepared. At first the mixture of dry VVER waste salts and mechanically crushed CRT glass was fed. The major problems occurred at the cold crucible melting were separation of batch particles due to different specific gravity and preferable melting of waste salts forming very low viscous melt. This effect reduces strongly melt productivity and results in elevated vaporization of the molten salts. After glass sampling the mixture from waste salts and ball-milled CRT glass was fed. Separation was reduced and melt productivity increased (Table VI). The best result was reached at feeding of batch prepared from waste salts and CRT glass ball-milled and activated in the apparatus with a rotating magnetic field (Table VIII). Such treatment produces a fine-grade homogeneous mixture with high reactivity. The apparatus with the rotating magnetic field has been successfully applied to grind and activate natural raw materials before processing [9].

Melting of the batch prepared from RBMK waste salts and ball-milled CRT glass is similar to the process for VVER waste vitrification. Unlike the two component VVER waste batch , the batch with RBMK waste is multicomponent and separation problem is complicated. This problem may be solved using pre-compaction or pre-fritting of the batch.

All the products were examined with XRD and they were found to be vitreous (no crystalline phases have been found). According to replica electron microscopy study, the glassy products were homogeneous and didn't contain inclusions with size more than 50 nm.

CONCLUSION

Broken CRT glass may be used as a glass forming agent to vitrify NPP and institutional wastes. To reach moderate melting temperatures (1200-1300 ^0C) at high chemical durability of glass, the NPP waste oxide content should be limited to ~30 wt.%. Leach rates of waste elements may be some lowered by incorporation of extra silica and alumina with loam clay and sandstone. Joint vitrification of NPP waste salts, incinerator ashes, and CRT glass is also possible. Glasses with ash contain minor crystalline phases predominantly silicophosphates.

Cold crucible melting of glasses containing NPP wastes and CRT glass was performed. Separation problems due to the difference in specific gravity between waste salts and CRT glass grains may be solved using mechanical treatment of the batch in an apparatus with a rotating magnetic field or batch compaction or fritting.

REFERENCES

1.	I.A. SOBOLEV, S.A. DMITRIEV, F.A. LIFANOV, S.V. STEFANOVSKY, and A.P. KOBELEV, Waste Management '95. Proc. Int. Symp., Tucson, AZ (1995), Rep. 11-4. CD Rom.
2.	F.A. LIFANOV, A.P. KOBELEV, S.V. STEFANOVSKY, et al., IT3 Conference. Int. Conf. Incineration & Thermal Treatment Technologies, Salt Lake City (1998), pp. 609-612.
3.	T.N. LASHTCHENOVA, F.A. LIFANOV, and S.V. STEFANOVSKY, Waste Management '97. Proc. Int. Symp., Tucson, AZ (1997), Rep. 13-17. CD Rom.
4.	S.A. DMITRIEV, F.A. LIFANOV, S.V. STRFANOVSKY, et. al. Waste Management '96. Proc. Int. Symp., Tucson, AZ (1996) Rep. 27-3. CD Rom.
5.	O.A. KNYAZEV, B.S. NIKONOV, B.I. OMELIANENKO, et. al., SPECTRUM '96. Proc. Int. Top. Meet. Nuclear and Hazardous Waste Management, Seattle, WA (1996), pp. 2130-2137.
6.	ISO 6961-82, Vienna, 1984.
7.	A.A. APPEN, "Chemistry of Glass" (Russ.), Leningrad (1974).
8.	Glass Technology (Russ.), edited by I.I. Kitaigorodsky (Moscow, 1967).
9.	D.D. LOGVINENKO, and O.P. SHELIAKOV, "Raising the Rate of Technological Processes in Apparatus with Vortex Layers" (Russ.), Kiev, Technika (1976).