

Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Mechanisms of Phase Formation in the Vitrification of High-Ferrous Savannah River Site SB2 HLW Sludge Surrogate - 9300

O.I. Stefanovsky, S.V. Stefanovsky
SIA Radon, 7th Rostovskii lane 2/14, Moscow 119121 RUSSIA

A.A. Akatov
Institute of Technology, Moskovskii av. 26, St-Petersburg 198013 RUSSIA

J.C. Marra
Savannah River National Laboratory, Building 773-42A, Savannah River Site, Aiken, SC 29808
USA

ABSTRACT

Phase formation mechanisms associated with the vitrification of high-ferrous Savannah River Site (SRS) Sludge Batch 2 (SB2) high level waste surrogate were studied by infrared spectroscopy (IRS) and X-ray diffraction (XRD). Two mixtures at 50 wt% waste loading with commercially available Frit 320 ($\text{Li}_2\text{O} - 8 \text{ wt } \%$, $\text{B}_2\text{O}_3 - 8 \text{ wt } \%$, $\text{Na}_2\text{O} - 12 \text{ wt } \%$, $\text{SiO}_2 - 72 \text{ wt } \%$) and batch chemicals ($\text{LiOH}\cdot\text{H}_2\text{O}$, H_3BO_3 , NaNO_3 , SiO_2) to represent the frit formulation were prepared as slurries with a water content of $\sim 50 \text{ wt } \%$. The mixtures were air-dried at a temperature of $115 \text{ }^\circ\text{C}$ and heat-treated at 500, 700, 900, 1000, 1100, 1200, and $1300 \text{ }^\circ\text{C}$ for 1 hr at each temperature. Infrared spectra and XRD patterns of the products produced at each temperature were recorded. In both mixtures prepared using frit and batch chemicals to represent the frit, phase formation reactions were completed within the temperature range between 900 and $1000 \text{ }^\circ\text{C}$. However, residual quartz was still present in glass produced from the mixture with batch chemicals even at $1100 \text{ }^\circ\text{C}$. Although, the phase composition and structure of the glassy products obtained from both mixtures at temperatures over $1000 \text{ }^\circ\text{C}$ were similar, the products obtained from the mixture using actual frit were more homogeneous than those from the mixture with batch chemicals. Thus, the use of frit rather than batch chemicals reduced the temperature range of phase formation and provided for production of higher quality glass.

INTRODUCTION

The DOE-EM Office of Engineering and Technology is responsible for implementing EM's international cooperative program. In the framework of this program The State Unitary Enterprise of the City of Moscow – United Ecology, Technology, Research & Development Center on RAW Management and Environmental Remediation (SIA Radon) and Savannah River National Laboratory (SRNL) are performing collaborative work on development and testing of the cold crucible inductive melter (CCIM) and its application to high level waste (HLW) vitrification at the US DOE sites. Specifically, the cold crucible is considered as an alternative to Joule heated ceramic melter (JHCM) currently being used at Defense Waste Processing Facility (DWPF) [1,2].

The main objectives of the collaborative work are to achieve maximized waste loading in glass and increase of throughput for the vitrification facility. Application of the CCIM process

with an active hydrodynamic regime and vigorous melt agitation by eddy currents strongly increases melting rate and improves rheological properties of glassmelts. The latter provides for higher waste loading and content of crystalline phase (if present) in glass. This is particularly of importance in the vitrification of high-ferrous HLW where there is a tendency for crystallization of iron-bearing spinel structure phases. The maximum waste loading for vitrification of high-ferrous sludge batch 2 (SB2) waste using a JHCM is limited to ~40 wt.% [3]. In the cold crucible, SB2 waste loading may reach ~55 wt.% [4,5] while still maintaining good flow and viscosity properties to facilitate pouring into canisters through the pouring unit.

In addition to increasing waste loading, another aspect to increase throughput is lowering temperature ranges for completion of phase formation reactions and achieving melt homogeneity faster, thus, improving the rate of melting. From this point of view, a study of phase formation mechanisms is required for mixtures of waste and glass formers. Understanding the phase formation mechanisms in reaction mixtures may allow for a better control of the vitrification process. In the present work we studied phase formation mechanisms in the batches containing high-ferrous SRS SB2 surrogate.

EXPERIMENTAL

Chemical composition and some properties of the SB2 waste are given in Table I. Waste surrogate was prepared according to SRT-ITB-2004-00027 procedure [6] including precipitation of MnO₂ and Fe, Ni and sodium-uranyl hydroxides from nitrate solutions. Two mixtures at 50 wt% waste loading with commercially available Frit 320 (Li₂O – 8 wt %, B₂O₃ – 8 wt %, Na₂O – 12 wt %, SiO₂ – 72 wt %) and batch chemicals (LiOH·H₂O, H₃BO₃, Na₂CO₃, SiO₂) to represent the frit formulation labeled as glass frit (GF) and glass chemicals (GC) were prepared as slurries with a water content of ~50 wt%.

The mixtures were air-dried at a temperature of 115 °C and heat-treated in a resistive furnace at 500, 700, 900, 1000, 1100, 1200, and 1300 °C for 1 hr at each temperature followed by removal of crucibles from the furnace, cooling in air and sampling of specimens for analyses. The specimens were milled in an agate mortar and examined by X-ray diffraction (XRD) using a DRON-4 diffractometer (Fe K_α radiation, voltage = 40 KeV, beam current = 30 mA, dwell time = 0.6 s, step size = 0.05 degrees, 2-theta ranged between 10 and 90 degrees, and Si was used as an internal standard) and infrared (IR) spectroscopy using a modernized IKS-20 spectrophotometer (compaction of powdered specimens in pellets with KBr). Specimens obtained at temperatures 1100, 1200 and 1300 °C were also studied by optical microscopy using an OLYMPUS BX51 polarization microscope and selectively by scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) using a JSM-5300+Link ISIS analytical unit (voltage = 25 KeV, beam current = 1 nA, probe diameter is 1 to 3 μm, dwell time = 100 s; metals, oxides and fluorides were used as standards).

RESULTS AND DISCUSSION

XRD patterns of the samples heat-treated at various temperatures (Figure 1, left) demonstrated gradual changes in their phase composition within a temperature range of 115 to 1000 °C. The GC sample air-dried at 115 °C was composed of a complex mixture of compounds

Table I. Concentration of Anion/Cation Content of Sludge SB2 Feed Simulants (air dried at 115° C).

Cations	Content, wt. %	Anions	Content, wt. %
Al ³⁺	6.27	CO ₃ ²⁻	3.59
Ba ²⁺	0.17	F ⁻	0.01
Ca ²⁺	1.89	Cl ⁻	1.06
Cr ³⁺	0.18	I ⁻	0.03
Cu ²⁺	0.11	NO ₂ ⁻	4.10
Fe ³⁺	20.81	NO ₃ ⁻	1.70
K ⁺	0.05	OH ⁻	33.10
Mg ²⁺	0.10	O ²⁻	4.10
Mn ⁴⁺	2.12	PO ₄ ³⁻	0.13
Na ⁺	6.31	SO ₄ ²⁻	0.70
Ni ²⁺	1.20	Properties	
Pb ²⁺	0.21	Specific gravity. g/cm ³	~1.15
Si ⁴⁺	0.65	Total solids. wt. %	~20
Sr ²⁺	0.06		
U ⁶⁺	7.29	Soluble solids. wt. %	~3
Zn ²⁺	0.22	Total organic carbon.	<0.05
Zr ⁴⁺	0.41	wt. %	

mainly α -quartz, SiO₂, hematite, Fe₂O₃, and uranium oxide UO₂. Minor concentrations of sodium sulfate Na₂SO₄ and halite, NaCl, may be also present but their contents were lower than the detection limit. It is of interest that spodumene LiAlSi₂O₆ was formed as a product of reaction between lithium hydroxide and quartz even at such low temperature. After heat-treatment at 500 and 700 °C, quartz remained as a major phase and spinel content began to form. At 900 °C, the amounts of quartz and spinel were comparable and after treatment at 1000 °C and higher, spinel prevailed over quartz until quartz disappeared completely after treatment at 1200 °C. The products heat-treated at 1200 °C and higher were composed of major glass and minor spinel structure phase.

IR spectrum of the GC specimen dried at 115 °C consisted of numerous bands due to vibrations of various bonds in the compounds of the mixture (Figure 2a). The strong bands at 3000-3600 cm⁻¹ due to vibrations of O—H bonds in the water molecules were comparable in intensity with the bands due to C—O vibrations in the CO₃²⁻ ions (maximum at ~1400 cm⁻¹) and vibrations due to Fe—O and, to a less extent, Al—O bonds (400-800 cm⁻¹) [7,8]. Increase of temperature to 700 °C, significantly decreased the concentration of the O—H bonds whereas some hydrogen bonds ≡Me—O···H—O—Me≡ in the compounds were still present. At the same temperature, the band due to C—O vibrations decreased in intensity whereas a broad band at 850-1300 cm⁻¹ due to Si—O bonds was formed. Numerous narrow bands due to vibrations of Fe—O and, to a less extent, Al—O bonds were observable within the range of 400 to 800 cm⁻¹. After heat-treatment at temperatures of 900 °C and higher, the bands due to hydroxyl groups disappeared whereas traces of bands due to hydrogen bonds occurred. After treatment of the batch mixture at temperatures of 1000 to 1300 °C, the IR spectra consisted of four broad structureless bands with maxima at ~1400, ~1000, ~700, and ~460 cm⁻¹ and two shoulders at

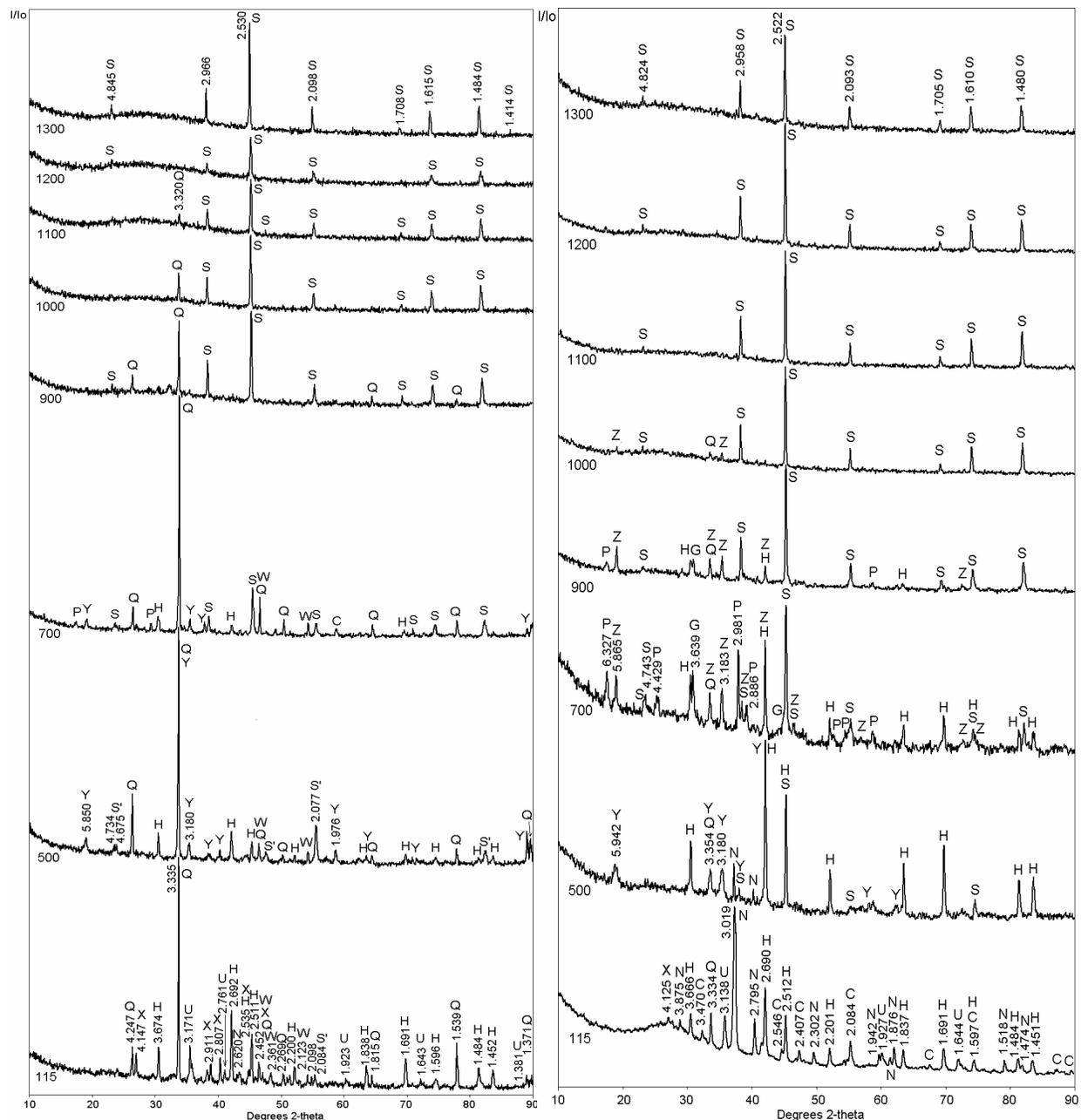


Figure 1. XRD patterns of the mixtures from SB2 waste surrogate and chemicals simulating Frit 320 (left) or actual Frit 320 (right) heat-treated at various temperatures.

C – Al_2O_3 (corundum), G – $\text{Al}_3\text{Fe}_5\text{O}_{12}$ (garnet-structure?), H – Fe_2O_3 (hematite), N – NaNO_3 , P – omphacite-type pyroxene, Q – SiO_2 (α -quartz), S, S' – spinels, U – UO_2 (uraninite), W – $\text{Fe}_{0.95}\text{O}$ (wuestite), X – spodumene, Y – $\text{Na}_2\text{U}_2\text{O}_7$, Z – $\text{Na}_2\text{U}_{2.5}\text{O}_{8.5}$.

~ 1270 and 550 cm^{-1} (Figure 2).

The bands with maxima at $1395\text{-}1410 \text{ cm}^{-1}$ and $\sim 1270 \text{ cm}^{-1}$ were components of twice degenerated asymmetric valence $\nu_3 \text{ O—B—O}$ vibration in the boron-oxygen triangular BO_3 units. The bands at $\sim 720 \text{ cm}^{-1}$ and $\sim 655 \text{ cm}^{-1}$ were components of twice degenerated asymmetric

deformation δ_4 O—B—O vibrations [9]. The strongest band with a maximum at ~ 1000 cm^{-1} was due to asymmetric O—Si—O vibrations in the tetrahedral SiO_4 units. This band is normally a superposition of the bands due to O—Si—O vibrations in the SiO_4 units with various numbers of bridging oxygen ions connecting SiO_4 tetrahedra in the network: four (Q^4) – at ~ 1100 - 1150 cm^{-1} , three (Q^3) – at ~ 1050 - 1100 cm^{-1} , two (Q^2) – at ~ 1000 - 1050 cm^{-1} , one (Q^1) – at ~ 950 - 1000 cm^{-1} , and zero (Q^0) – at ~ 900 - 950 cm^{-1} . The wavenumber range of 400 - 550 cm^{-1} corresponded to deformation vibrations in the SiO_4 units [7,8,10].

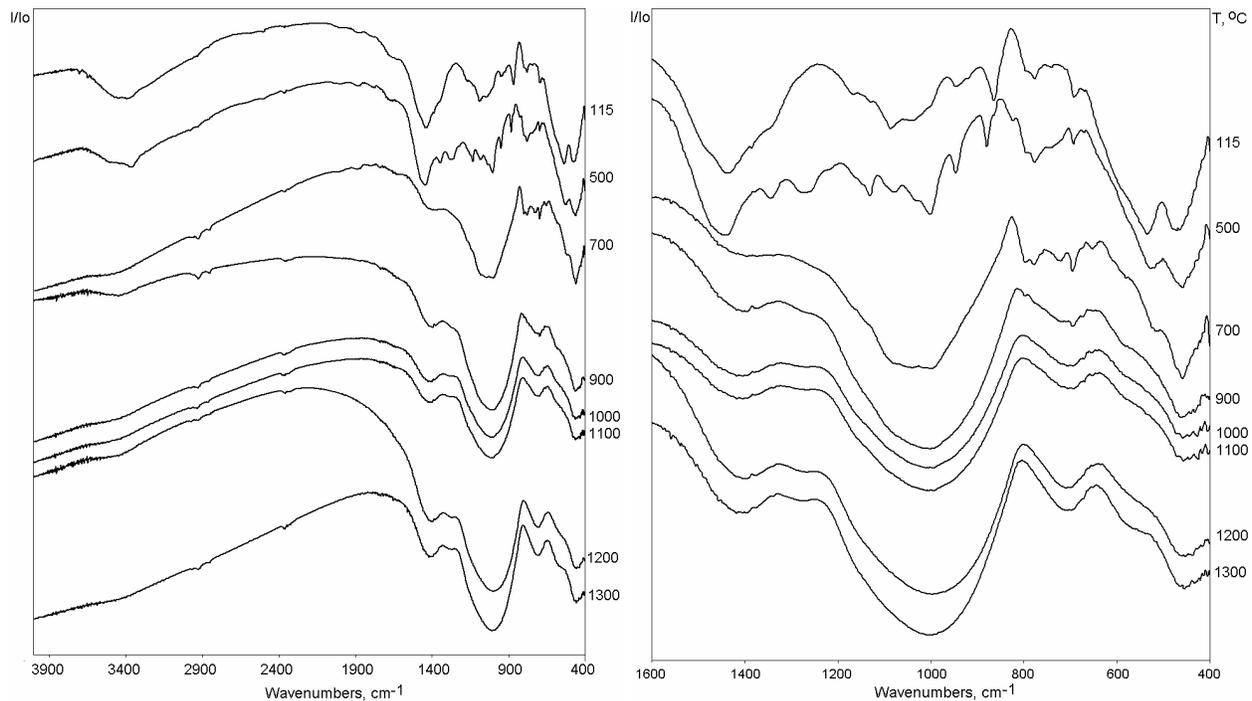


Figure 2. IR spectra within the range of 4000 to 400 cm^{-1} and fragment within the range of 1600 to 400 cm^{-1} of the batch mixtures from SB2 waste surrogate and chemicals simulating Frit 503-R4 heat-treated at various temperatures.

XRD pattern of the dried mixture of waste surrogate and commercially available Frit 320 (GF sample) consisted of strong reflections due to partly altered sodium nitrate NaNO_3 and hematite Fe_2O_3 , weaker peaks due to corundum Al_2O_3 and uranium oxides (UO_2 and U_3O_8) – Figure 1, right. Heat-treatment at 500 $^\circ\text{C}$ resulted in decomposition of major sodium nitrate and formation of $\text{Na}_2\text{U}_2\text{O}_7$ as an interim phase and minor spinel structure phase. Within the range between 500 and 700 $^\circ\text{C}$ hematite reacted yielding the spinel structure phase and two more interim phases similar to $\text{Na}_2\text{U}_{2.5}\text{O}_{8.5}$ and pyroxene-type omphacite ($\text{Fe}_{0.5}\text{Al}_{0.5}\text{Ca}_{0.5}\text{Na}_{0.5}\text{Si}_2\text{O}_6$) as determined by XRD. Increase of temperature to 900 $^\circ\text{C}$ led to reduction in intensity of all the peaks due to initial (quartz) and interim phases and domination by the spinel structure phase. After heat-treatment of the mixture at 1000 $^\circ\text{C}$, spinel was the predominant phase but traces of quartz and interim sodium uranate were still present. The quartz and sodium uranate phases disappeared within the temperature range of 1000 to 1100 $^\circ\text{C}$ (Figure 1, right).

It was observed that major phase formation reactions in the batches with both chemicals and actual Frit 320 were completed within the temperature range of 700 to 900 $^\circ\text{C}$ and residual

unreacted quartz and intermediate products were dissolved in the glassmelt between 900 and 1000 °C although the last grains of quartz disappeared within the range of 1000 to 1100 °C.

Application of commercially available Frit 320 rather than a mixture of chemicals increased the temperature range of phase formation reactions in the batch mixture because no low temperature eutectics were formed and shifted completion of the reactions to some higher temperature range – 900 to 1000 °C (Figure 1, right). Nevertheless, residual quartz and intermediate phases were completely dissolved within the same range as in the case of chemicals (1000 to 1100 °C).

At low temperatures (115 and 500 °C), IR spectra of the mixtures containing actual Frit 320 (Figure 3) demonstrated moderate absorption at 3300-3700 cm^{-1} (multiple lines due to vibration of O—H groups in various compounds), strong narrow peak due to valence (stretching) vibrations of N—O bonds in NO_3^- ions at 1384 cm^{-1} , some broader bands with maximum at 1025 cm^{-1} (ν_{as} valence vibrations of Si—O bonds in the Frit 320) and 400-600 cm^{-1} (superposition of deformation vibrations in SiO_4 tetrahedra and valence vibrations in iron- and aluminum-oxygen groups), and numerous weak bands within the range between 600 and 900 cm^{-1} due to straining (deformation) vibrations in NO_3^- ions, ν_{s} vibrations in deformed SiO_4 tetrahedra and other Me—O bonds. After heat-treatment of the mixture at 500 °C, a significant amount of sodium nitrate was still present that was consistent with XRD data but total number of the absorption bands decreased. Reactions in the mixture were mainly completed between 900 and 1000 °C, when the spectrum becomes typical of silicate glass (Figure 3). The spectra of the specimens heat-treated at higher temperatures (1100, 1200 and 1300 °C) show that the structure of glass remained the same.

The primary feature of the reactions in the system with actual frit was formation of the spinel structure phase at relatively low temperature (lower than 500 °C). Traces of the spinel-type phases were found even after drying of slurry at 115 °C (Figure 1, right). Hematite co-existed with spinel within the range of 500 to 700 °C but relationship of hematite to magnetite-type spinel was strongly changed in favor of the latter within the range of 700 to 900 °C. The mechanism of the phase formation in the batch mixture with actual frit was more complicated as compared to the mixture with chemicals (formation of higher number of intermediate compounds) but complete melt homogenization was achieved at lower temperature range (1000-1100 °C) as compared to the mixture of chemicals (1100-1200 °C) and the melt was more homogeneous (Figures 2-4).

Microscopic analyses provided additional insight into glass formation. Comparison of the samples obtained from mixtures of SB2 waste surrogate and either chemicals or actual Frit 320 at the same temperatures (1100, 1200 and 1300 °C) showed that the glasses prepared using frit were more homogeneous as compared to the glasses prepared using chemicals (Figure 4, 1-7). The sample prepared from waste surrogate and chemicals at 1100 °C consisted of areas of pure light-yellow glass and areas composed of light-yellow glass containing inhomogeneously distributed inclusions of spinel grains (Figure 4, 1). The glass prepared at 1200 °C was also inhomogeneous. Transparent glass was predominant but spinel inclusions were also present. Major part of the matrix glass contained fine cubic crystals or aggregates of fine spinel grains (Figure 4, 2). Dark glass contained both fine spinel grains and larger (up to 0.5 mm in size) skeleton-like spinel crystals. The areas up to 2 mm in size in which the spinel dominated over

glass were also observed. The specimen melted at 1300 °C was fully composed of aggregate consisting of skeleton-like spinel crystals and colorless glass (Figure 4, 3). The skeleton-like crystals from various areas of the thin section were markedly different on quantitative ferrous oxides to glass ratio due to inhomogeneous partitioning of ferrous oxides in the specimen.

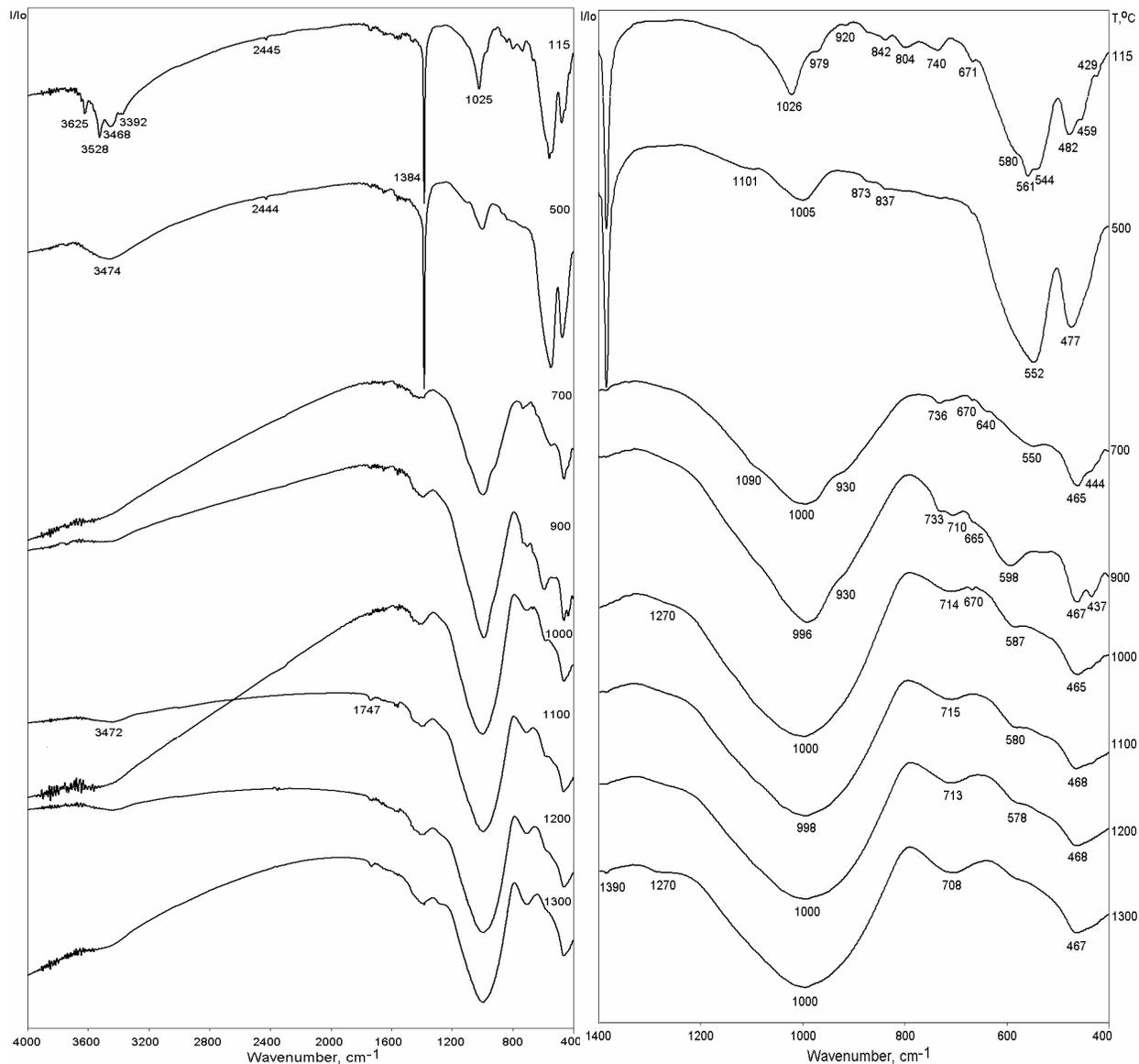


Figure 3. IR spectra within the range of 4000 to 400 cm^{-1} and fragment within the range of 1600 to 400 cm^{-1} of the specimens produced from SB2 waste surrogate and actual Frit 320 (left) and heat-treated at various temperatures.

Sample prepared from waste surrogate and actual Frit 320 at 1100 °C consisted of light-yellow nearly clear glass containing non-uniformly distributed spinel crystals of 5 to 10 μm in size. Major crystals had square cross-sections and minor ones had regular hexangular and octangular cross-sections. Small spots of glass containing a minor amount of individual spinel

grains alternated with black irregular shaped spots composed of dense aggregates of fine spinel grains (Figure 4, 4). Some of the densest spinel aggregates were fully opaque. The dense spinel aggregates were typically composed of the finest grains. It is known that the smaller the grain size the higher the degree of oversaturation of the melt with respect to the mineral crystallized. The variability in the spinel distribution in the glass matrix pointed to inhomogeneous distribution of ferrous oxides in the melt.

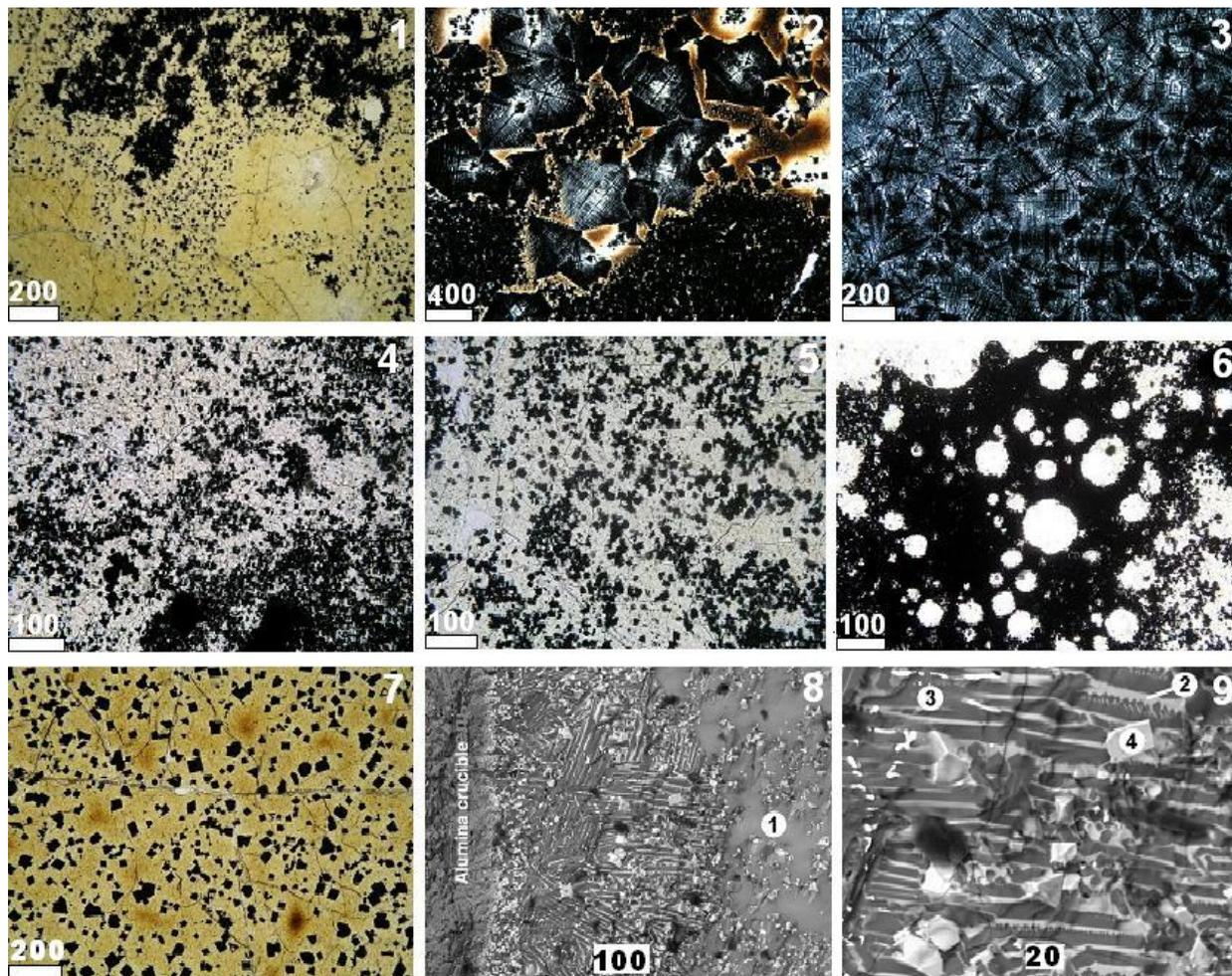


Figure 4. Optical Microscopy (1-7) and SEM (8,9) Images of the Glasses Produced from SB2 Waste Surrogate and Chemicals (1-3) or Actual Frit 320 (4-9) at 1100 °C (1,4), 1200 °C (2,5,8,9) and 1300 °C (7).

1 – Glass-1, 2 – Glass-2, 3 – Nepheline, 4 – Spinel. Scale bars are in μm.

Sample from waste surrogate and actual frit melted at 1200 °C contained spinel grains non-uniformly distributed within the glass matrix (Figure 4, 5). A specific feature of this sample was occurrence of numerous regular round shape voids of several microns to 1 mm in diameter (Figure 4, 6). Their distribution in the glass bulk is also non-uniform. It should be noted that areas containing minor spinel grains are normally free of voids. These voids can be suggested to be gas bubbles due to incomplete degassing. As follows from their distribution, formation of gas

bubbles occurred preferably in glass matrix zones with elevated concentration of ferrous oxides, therefore, this may supposedly be oxygen.

The GF specimen melted at 1300 °C contained two different areas. One area was composed of light-brown colored glass containing minor randomly distributed fine spinel crystals (Figure 4, 7). The other one was composed of nearly clear glass with high amount of both fine individual spinel crystals and dense opaque nearly black spinel aggregates. A general observation was as follows: if spinel content in glass was higher then the brown color of the glass was darker.

Gradual changes of the glass texture from edge of alumina crucible to glass bulk could be observed by both optical and electron microscopy (Figure 4, 8,9). The border zone was composed of thin black layer of fine spinel crystals. The next layer, about 200 to 500 µm from the edge of the crucible, had essentially the nepheline composition. Nepheline formed regularly oriented layers alternating with glass (Figure 4, 9). As follows from SEM/EDS analyses (Table II), nepheline contained (in wt.%) 23-24 Na₂O, ~34 Al₂O₃, ~39 SiO₂, 2-3 Fe₂O₃ as well as <1 CaO and K₂O. Randomly distributed spinel grains were also present.

Nepheline was present only in the contact zone between the alumina crucible and the melt, where the high-temperature glass melt interacted with the alumina crucible. As a result, the contact zone was enriched with alumina creating the conditions for producing nepheline. No nepheline was found in the major bulk of the glass melt and solidified glass. Spinel was also present as individual regular crystals. Semi-quantitative chemical compositions of nepheline, spinel and contact glass are given in Table 2. The vitreous phase in the contact zone, as compared to the target glass composition, was strongly depleted with ferrous oxides due to their incorporation in the spinel phase and enriched with uranium oxides (Table 2). To achieve more homogeneous distribution of uranium oxides, additional agitation, similar to what occurs in the cold crucible where the products obtained are highly homogeneous [4,11], may be required.

CONCLUSIONS

Application of commercially available frit as a glass forming additive rather than mixture of chemicals (LiOH·H₂O, H₃BO₃, NaNO₃, SiO₂) in the vitrification of SB2 high-ferrous HLW surrogate reduces the temperature range for the completion of chemical reactions in the batch and melt homogenization from 1100-1200 °C to 1000-1100 °C. The glasses prepared using frit were found to be more uniform as compared to those prepared using chemicals. Minor nepheline was present only in the contact zone between the glass melt and the alumina crucible and its formation was caused by transfer of Al₂O₃ in the glass melt/crucible contact zone. No nepheline was found in the glass bulk. The glass in the contact zone was enriched with uranium oxides. To avoid this segregation an agitation is required. Such melt agitation is achieved during melting in the cold crucible.

ACKNOWLEDGEMENT

Author thank Dr. B.I. Omelianenko and Mr. B.S. Nikonov (IGEM RAS) for optical and SEM/EDS study of the samples.

Table II. Chemical Compositions (wt.%) of Co-Existing Phases in the Contact Zone between Glassmelt and Alumina Crucible.

Oxides	Nepheline		Spinel	Glass-2	Target glass**
Li ₂ O	-	-	-	-	4.00
B ₂ O ₃	-	-	-	-	4.00
Na ₂ O	23.10	23.56	-	12.27	12.04
Al ₂ O ₃	33.92	34.14	11.70	9.39	8.41
SiO ₂	38.89	38.64	-	32.88	37.01
SO ₃	-	-	-	1.44	0.41
Cl	-	-	-	1.21	0.75
K ₂ O	0.39	0.44	-	-	0.04
CaO	0.80	0.95	-	5.60	1.88
Cr ₂ O ₃	-	-	2.88	-	0.19
MnO	-	-	5.38	2.18	1.94
Fe ₂ O ₃	2.90	2.27	69.59	8.26	21.14
NiO	-	-	9.66	-	1.08
CuO	-	-	-	0.52	0.10
ZnO	-	-	0.78	-	0.19
UO ₂	-	-	-	14.55	5.87
Total	100.00	100.00	100.00	88.00*	100.00

* Li₂O and B₂O₃ are not determined by EDS; ** also contains 0.12 MgO, 0.13 BaO, 0.16 PbO, 0.05 SrO, 0.39 ZrO₂, 0.07 P₂O₅, 0.01 F, 0.02 I. Dashes mean that the component either was not determined or its content is <0.01 wt.%.

REFERENCES

1. K.D. GERDES, J.R. HARBOUR, J.C. MARRA, D.K. PEELER, J.A. ROACH, J.D. VIENNA, T.B. CALLOWAY, A.S. ALOY, S.V. STEFANOVSKY and M.D. BONDARKOV, "The U.S. Department of Energy – Office of Environmental Management's International Program," Waste Management '07, Tucson AZ, February 25 – March 1, 2007. ID 7514, 2007. CD-ROM.
2. K.D. GERDES, J.C. MARRA, D.K. PEELER, J.R. HARBOUR, K.M. FOX, J.D. VIENNA, A.S. ALOY, S.V. STEFANOVSKY and M.D. BONDARKOV, "Current Progress and Future Plans for the DOE Office of Environmental Management International Program," Waste Management '08, Phoenix, AZ, February 24-28, 2008. ID 8192, 2008. CD-ROM.
3. C.C. HERMAN, "Summary of Results for Expanded Macrobatches 3 Variability Study," WSRC-TR-2001-00511 (2001).
4. A.P. KOBELEV, S.V. STEFANOVSKY, O.A. KNYAZEV, T.N. LASHCHENOVA, A.G. PTASHKIN, M.A. POLKANOV, E.W. HOLTZSCHEITER, J.C. MARRA, "Results of a 50% Waste Loading Vitrification Test Using the Cold Crucible Melter for Savannah River Site," Waste Management '06, Tucson, AZ, February 26 – March 2, ID 6127, 2006. CD-ROM.

5. S.V. STEFANOVSKY, J.C. MARRA, "The Effect of Waste Loading on the Structure and Leach Resistance of Borosilicate Glass for Savannah River Site SB2 Waste Immobilization," Waste Management '07. Proc. Int. Conf. Tucson, AZ, ID 7132, 2007. CD-ROM.
6. J.C. MARRA, E.W. HOLTZSCHEITER, "Sludge and Glass Compositions for Cold Crucible Induction Melter (CCIM) Testing," SRT-ITB-2004-00027, Rev. 0, Savannah River National Laboratory (2004).
7. K. NAKAMOTO. "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc. New York, London (1964).
8. I.I. PLUSNINA, "Infrared Spectra of Minerals," MGU, Moscow (1977).
9. V.A. KOLESOVA, "Vibrational Spectra and the Structure of Alkali Borate Glasses," *Glass Physics and Chemistry* (Russ.) **12** [1] (1986) 4-13.
10. J. WONG, C.A. ANGELL, "Glass Structure by Spectroscopy," Marcel Dekker, Inc. New York – Basel (1976).
11. S. STEFANOVSKY, J.C. MARRA, A. AKATOV, O. STEFANOVSKY, "Characterization of Vitrified Savannah River Site SB4 Waste Surrogate Produced in Cold Crucible," Materials Science & Technology 2008 Conference & Exhibition, October 5-9, 2008, Pittsburgh, PA. Abstract Book, 2008. P. 6.