Results of a 50% Waste Loading Vitrification Test Using the Cold Crucible Melter for Savannah River Site Waste

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ABSTRACT

The Cold Crucible Induction Melter (CCIM) is a promising alternative compared to the Joule heated ceramic melter (JHCM) reference technology for vitrification of high level radioactive waste (HLW). Successful tests with 45 wt.% waste loading in the glass facilitated the transition to the third task of the work with waste loading increased to 50 wt.%. The third test was performed using the Radon full-scale vitrification plant equipped with a new cylindrical cold crucible with an inner diameter of 418 mm. Average glass pour rate (average amount of glass poured per 1 hour of run) and specific glass pour rate (average pour rate per melter surface area) reached 16.2 kg/h and ~118.2 kg/(m^2h), respectively. Neither formation of sulfate/chloride salts (“yellow phase”) nor melt foaming were observed. Occurrence of a spinel-type phase in the glass didn’t reduce chemical durability of the glass. Product Consistency Testing (PCT) demonstrated that leaching of lithium, boron, sodium and silicon from glass samples produced in the CCIM were 15 to 30 times lower than the Environmental Assessment (EA) glass used for waste form repository acceptance.

INTRODUCTION

An inductive cold crucible melting (ICCM) technology initially developed for production of single crystals of high-fusible materials and high-temperature glasses [1] was also successfully applied to vitrification of liquid low- and intermediate-level wastes (LILW) at the Scientific & Industrial Association (SIA) “Radon”, Russia [2]. This technology is also being considered as a promising alternative to vitrification of HLW in the JHCM [3-6]. In particular, the CCIM was demonstrated as an alternative route for vitrification of HLW such as high-ferrous waste stored in tanks at the Savannah River Site (SRS) [7,8]. The first two tasks of contract work between Savannah River National Laboratory (SRNL) and SIA “Radon” demonstrated high efficiency of the CCIM with respect to vitrification of surrogate defense waste. In these tests performed in a bench-scale CCIM (216 mm in diameter) waste loading in glass reached 45 wt.% and no problems (yellow phase formation, melt foaming) occurred. This stimulated transfer to the third step of the work – vitrification tests in the industrial-scale (~400 mm diameter) CCIM with increased waste loading (50 wt %) in the glass. The goal of this step of the work was determination of key parameters of the ICCM process in the large-scale CCIM and characterization of the vitrified product with high waste loading.

EQUIPMENT AND FEED PREPARATION

The test was performed using the Radon full-scale vitrification plant [2] energized from a high frequency generator with vibration power of 160 kW operated at a frequency of 1.76 MHz and equipped with a new cylindrical CCIM with inner diameter of 418 mm (Figure 1 *a*,*b*). The CCIM was manufactured from stainless steel pipes 12 mm in outer diameter and 2 mm in thickness. It was equipped with a water-cooled cover having ports for slurry feeding, off-gas removal and visual observation. A pouring unit consisted of a water-cooled tube-in-tube cylinder (Figure 1*c*) and a blocking rod (gate) to stop glass pouring.

a *b* *c*

Fig. 1. View of the 418 mm inner diameter CCIM as manufactured (left), coated with a protection layer (middle), and pouring unit (right).

The chemical composition of the waste surrogate is given in Table I. From the results of previous tests, commercially available (manufactured in the USA) Frit 320 was chosen as a glass forming additive. Its chemical composition is (wt.%): B_2O_3 – 8, Li_2O – 8, Na_2O – 12, SiO_2 – 72. As follows from Table II [9] lab-scale produced glasses from this frit and waste surrogate exhibit appropriate viscosity and leachability parameters and liquidus temperatures providing for their large-scale production.

Two portions of feed were prepared: 1) from waste surrogate and actual Frit 320 (FP-320) and 2) from waste surrogate and chemicals simulating Frit 320 (CP-320). Surrogate waste sludge was thoroughly intermixed with either Frit 320 or mixture of chemicals simulating Frit 320 and formic acid. Formic acid, used for mercury reduction in the current Defense Waste Processing Facility (DWPF) vitrification process, was added in amount of 30 mL per 1 L of the sludge.

Calculated chemical composition of glass (50 wt.% waste loading) is given in Table III. Note that total iron oxides content (recalculated to Fe_2O_3) achieves almost 24 wt.%, therefore, formation of Fe-rich crystalline phase might be expected. In previous tests with 45 wt.% waste loading, a magnetite-type spinel structure phase in the glass was found [7,8].

Table I. Concentration of Anion/Cation Content of Sludge Feed Simulants (Final Product)

Cations	wt.%	Anions	wt.%
Aluminum, Al	6.27	Carbonate, CO_3^{2-}	3.59
Barium, Ba	0.17	Fluoride, F^-	0.01
Calcium, Ca	1.89	Chloride, Cl^-	1.06
Chromium, Cr	0.18	Iodide, I^-	0.03
Copper, Cu	0.11	Nitrite, NO_2^-	4.10
Iron, Fe	20.81	Nitrate, NO_3^-	1.70
Potassium, K	0.05	Total Hydroxide, OH^-	33.10
Magnesium, Mg	0.10	Oxide, O^{2-}	4.10
Manganese, Mn	2.12	Phosphate, PO_4^{3-}	0.13
Sodium, Na	6.31	Sulfate, SO_4^{2-}	0.70
Nickel, Ni	1.20		
Lead, Pb	0.21	Specific Gravity, g/cm^3	~1.15
Silicon, Si	0.65	Total Solids, wt. %	~20
Strontium, Sr	0.06	Soluble Solids, wt. %	~3
Zinc, Zn	0.22		
Zirconium, Zr	0.41	Total Organic Carbon (TOC) [wet]	<0.05

Table II. Glass Property Data for Frit 320 with Various Sludge Loadings.[9]

Sludge Loading (wt %)	Viscosity (Poise)	PCT B [10] Release (g/L)	Liquidus T (°C)
25	51	1.00	823
30	44	0.80	910
35	36	0.65	990
40	29	0.52	1060
45	23	0.42	1120
50	17	0.34	1180
55	12	0.28	1230
60	8	0.22	1280

Table III. Chemical composition of glass matrices and spinel phase measured by EDS.

Components	Container #1		Container #5			Container #10		F320 (calc.)
	Glass	Spinel	Glass	Spinel	Scan**	Glass	Spinel	
Li_2O	nm	0	nm	0	nm	nm	0	4.00
B_2O_3*	3.30	0	3.72	0	nm	3.93	0	4.00
Na_2O	14.14	0	13.26	0	12.29	14.05	0	12.84
MgO	0.34	0.36	0.14	0.12	0.00	0.16	0	0.14
Al_2O_3	10.60	1.29	12.41	1.66	11.49	11.31	2.11	9.53
SiO_2	49.10	4.4	49.22	1.48	43.48	46.79	1.32	37.12
P_2O_5	0.96	0.22	0.59	0	0.31	0.92	0	0.08
SO_3	0.11	0	0.22	0	0.00	0.25	0	0.47
Cl	0.24	0	0.24	0	0.00	0.09	0	0.85
K_2O	0.14	0	0.16	0	0.20	0.10	0	0.05
CaO	4.29	0.36	2.99	0	2.59	3.07	0	2.13
Cr_2O_3	0.08	0.48	0.10	0.95	0.06	0.12	3.49	0.21
MnO	1.82	3.43	1.79	4.34	2.01	2.06	3.72	2.21
Fe_2O_3	14.82	79.12	14.10	81.76	21.57	18.15	72.45	23.94
NiO	0.20	8.83	0.11	8.88	0.51	0.21	14.74	1.23
CuO	0.29	0	0.28	0	0.08	0.20	0	0.11
ZnO	0.17	0.18	0.10	0	0.38	0.25	0	0.22
SrO	2.30	0.58	1.81	0	1.16	1.77	0	0.06
ZrO_2	0.14	0	0.39	0	0.18	0.24	0	0.44
BaO	0.13	0	0.16	0	0.45	0.10	0.03	0.15
PbO	0.43	0	0.50	0	0.58	0.17	0.06	0.19
I	0.00	0	0.00	0	0.00	0.00	0.08	0.02
Total	100.30	99.25	102.30	99.19	97.35	100.00	98.00	100.00

* - potentiometric titration

** - scanning over area 100 × 100 μm.

nm - not measured

ICCM RUN

A starting melt using glass breakage from previous test was prepared and run for 1 h 44 min. The slurry feed to initiate the testing was fed using a peristaltic pump. When ~90 kg of the start-up slurry was fed into the CCIM, feeding was interrupted and the melt was kept for several minutes until complete homogenization occurred. The molten start-up glass was then poured into containers. Slurry feeding was restarted using the batch feed with actual Frit 320 (FP-320). Slurry feeding and melt pouring was controlled by temperature measured using a Pt/Pt-Rh thermocouple. Melt surface temperature was measured using an optical pyrometer “Promin”. Major process variables are given in Table IV. As seen from this Table, no significant differences between feeding of slurry with actual and surrogate frits were observed. Higher glass productivity and lower heat expenses were observed when feeding with the actual frit slurry. These increases, however, can be attributed to the increase in solids loading offered by feeding with the actual frit. Comparing the results of this test with previous tests [7,8] indicated that enlargement of the cold crucible diameter by approximately 2 times increased slurry capacity (feeding rate) by about 5 times and glass productivity by about 3 times at similar specific glass productivity. Moreover, application of the larger cold crucible reduced the melting ratio (kW×h/kg of glass) by a factor of approximately two.

During the test campaign, 1215.7 kg of slurry was processed and 417.8 kg of glass was produced. Very high specific glass pour rate [~99.3 kg/(m^2×h)] was achieved. This exceeds the specific glass pour rate of the JHCM (19.8 kg/(m^2×h)) [11] by about 5 times.

Weight loss values for Na_2O and B_2O_3 measured by the difference between the amounts fed to the CCIM and found in the vitrified product are shown in (Table IV). The calculated differences are approximate values because it was impossible to determine the exact amount of glass produced from specific portions of the slurry and some amount of glass remains in "dead volume" of the CCIM. Nevertheless, weight losses for both Na_2O and B_2O_3 were found to be significantly lower when actual Frit 320 was used as glass forming additives as compared to feeding of slurry containing mixture of glass forming chemicals rather than frit. This is consistent with LILW vitrification experience at SIA "Radon" where natural datolite containing chemically bound boron is used as a source of boron for borosilicate glass production and has been shown to reduce boron volatility.[2]

Table IV. ICCM Process Variables in the Test #5/6

Process variables	FP-320[1]	CP-320[2]	Total
Duration, hours:minutes	13:08	18:44	31:52
Water content in the slurry, wt.%	~45	~60	~55
Average vibrating power, kW	154	154	154
Weight of vitrified slurry, kg	464.8	750.9	1215.7
Weight of produced glass, kg	213.2	204.6	417.8
Melt surface temperature, ^{0}C	700 - 1150	700 - 1150	700 - 1150
Melt temperature at 50 mm depth, ^{0}C	Up to 1350	Up to 1350	Up to 1350
Off-gas temperature, ^{0}C	100 - 200	100 - 200	100 - 200
Slurry feed rate, kg/h	35.4	40.1	37.8
Glass pour rate, kg/h	16.2	11.0	13.6
Specific glass pour rate, kg/(m^2×h)	118.2	80.3	99.3
Heat expenses on slurry vitrification, kW×h/kg	4.4	3.8	4.1
Melting ratio, kW*h/kg of glass	9.5	14.1	11.8
Na_2O weight loss, %	~3	~7	~5
B_2O_3 weight loss, %	~9	~17	~13

[1] Actual Frit 320,

[2] Mixture of chemicals simulating Frits 320.

Visual observations indicated neither melt foaming due to reduction of Fe(III) to Fe(II) nor formation of a secondary sulfate-chloride "yellow" phase on the melt surface occurred during the test campaign.

The CCIM was operated for a total of 37 hours and more than 31 hours under steady-state conditions. Visual inspection showed very weak traces of corrosion (darkening and caverns of up to 0.1 mm in depth) on the internal surface of the crucible pipes in area in contact with the melt and in locations on the pouring unit. Following the inspection, it was determined that the CCIM vessel and pour unit were suitable for further use.

PRODUCT CHARACTERIZATION

Chemical compositions of the products were determined by X-ray fluorescent (XRF) spectroscopy using a PW-2400 Philips Analytical BV unit equipped with quantitative analytical Philips SuperQuantitative & IQ-2001 Software, atomic absorption spectroscopy (AAS) using a Perkin-Elmer 403 spectrometer, and emission flame photometry (EFP) to determine Na and K using a PFM-U 4.2 flame photometer (Russian design).

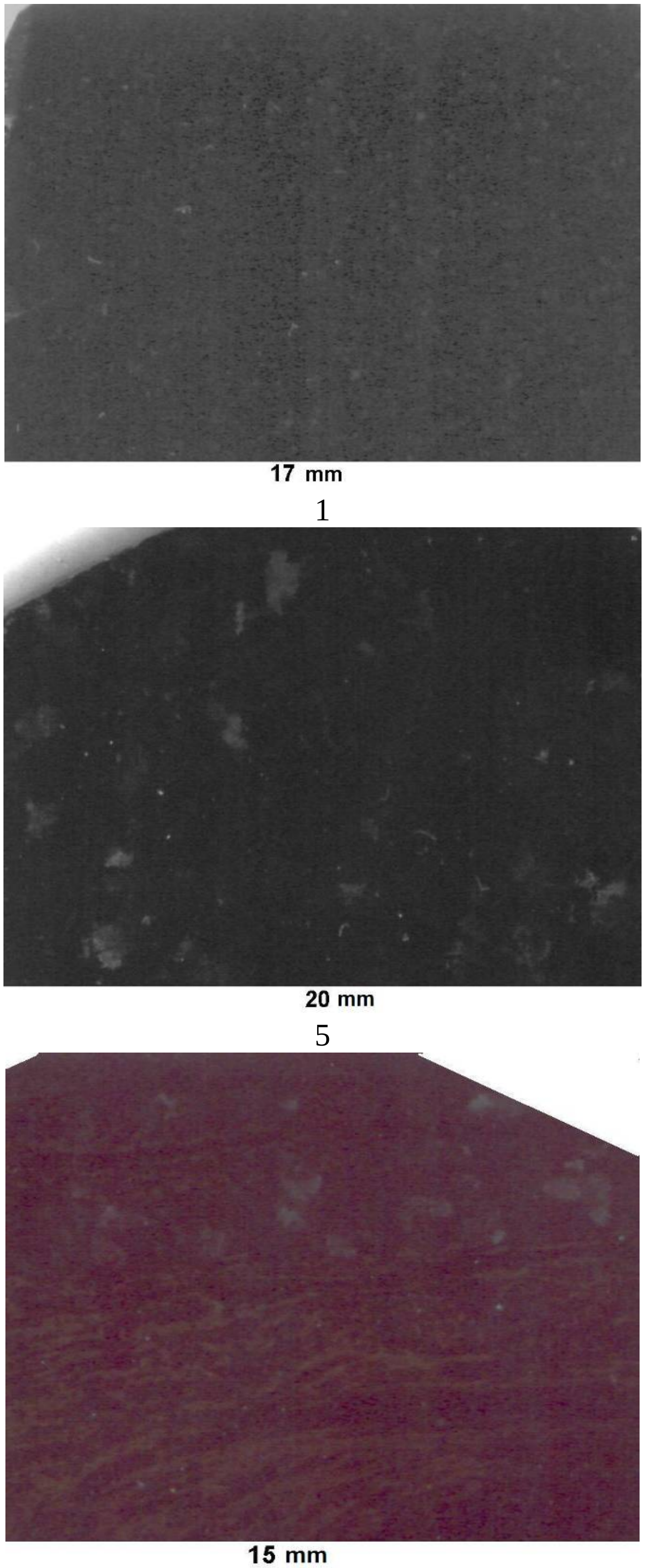
Products were characterized with X-ray diffraction (XRD) using a DRON-4 diffractometer, optical microscopy using a Polam L-213 microscope, and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) using a JSM-5300 + Link ISIS analytical unit. Leach resistance of products was determined using the PCT-A procedure (7-day crushed glass leach test at 90 ^{0}C).[10]

As follows from optical microscopy (Fig. 2), the products sampled from containers ## 1, 5, and 10 are not fully homogeneous and contain areas with variable color due to crystalline inclusions, cords, and matrix glass. Grain size gradually grows from container #1 to #10.

Similar to previous tests with 45 wt.% waste loading, the glass with 50 wt.% waste loading contained a magnetite-type crystalline phase with the spinel structure (Fig. 3). XRD patterns also demonstrated very weak reflections which may be assigned to sodium sulfate (“yellow phase”). Investigation of the vitrified samples in more details using SEM/EDS showed no yellow phase inclusions in the bulk of the samples. The spinel structure magnetite was found to be the only phase in the glass. Traces of yellow phase may have occurred on the surface of the glass blocks in the containers.

Fine (up to few a microns in size) individual spinel crystals and their aggregates were evident in the SEM-images of the samples from containers but some grains may have reached ~100 μm (Fig. 4).

Chemical compositions of matrix glass and spinel phase are given in Table III. Taking into account that Li_2O in glasses was not determined (due to the available analytical techniques) analytical sums may exceed 100 wt.%. Note: Li_2O concentrations are given as theoretical values in Table III. It should also be noted that some fraction of iron exists



1

5

10

Fig. 2. Optical microscopic images of the samples from containers ## 1, 5, and 10.

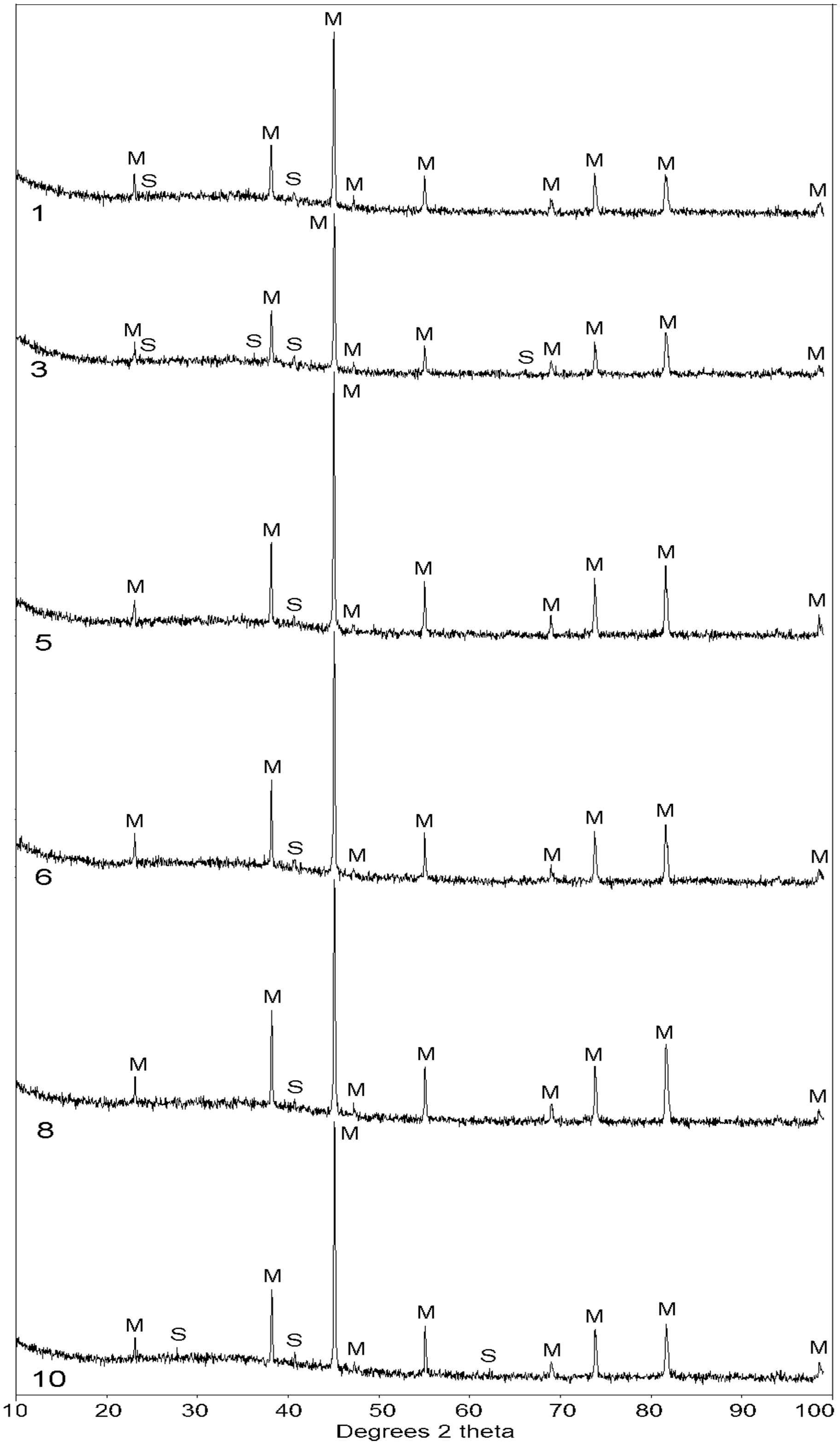
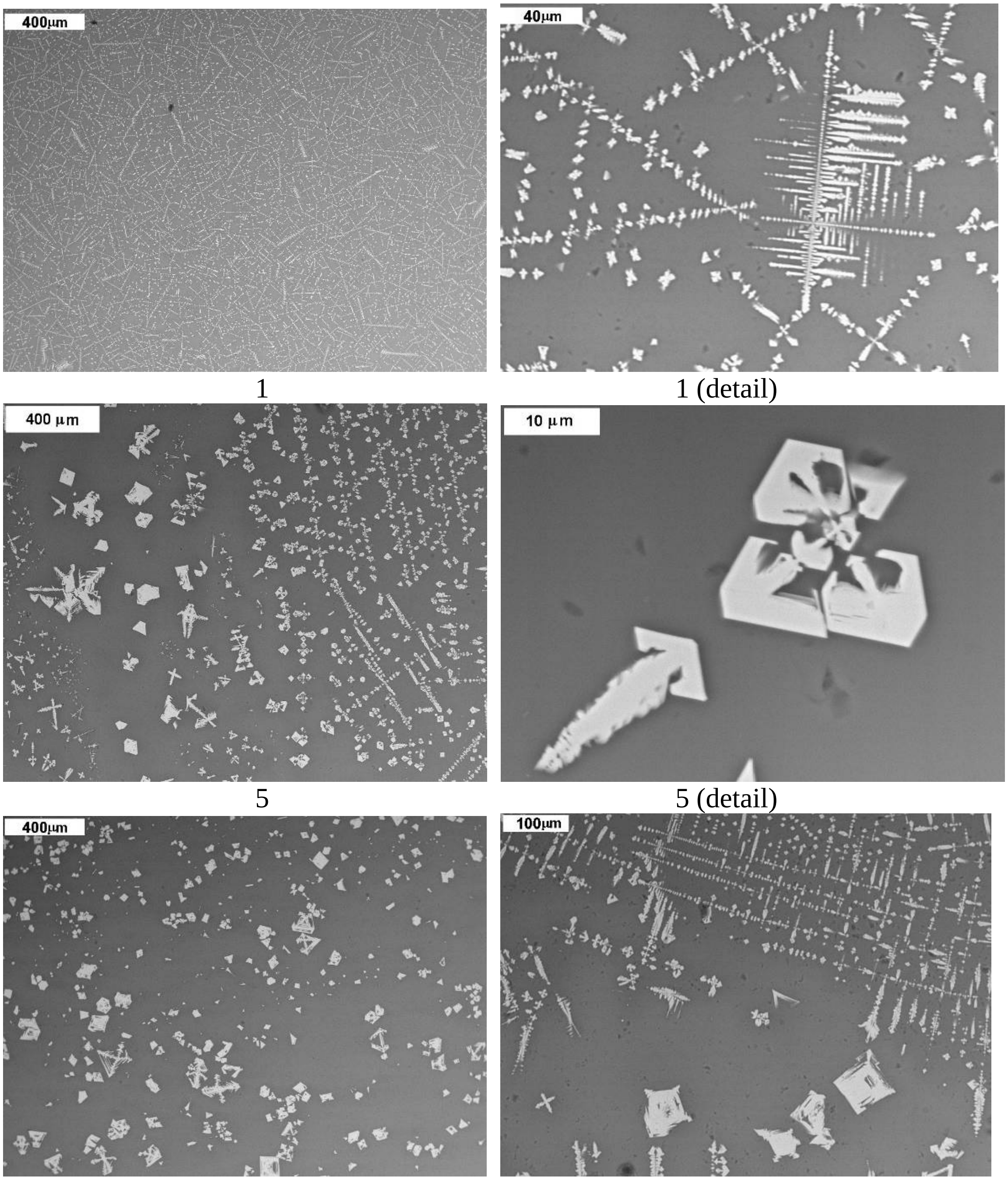


Fig. 3. XRD patterns of vitrified materials produced in the test with 50 wt.% waste loading in glass. The container # is indicated below pattern. M – magnetite-type spinel, S – sodium sulfate?



1 1 (detail)

5 5 (detail)

10 10 (detail)

Fig. 4. SEM-images of the samples from containers ## 1, 5, and 10.

as Fe(II) especially in spinels. Chemical composition of spinel phases may be recalculated to formulae (at assumption that silicon, calcium, strontium, and probably some aluminum oxides found in spinel were captured from surrounding glass at EDS-measurements):
$(Mg_{0.03}Mn_{0.11}Fe_{0.46}Ni_{0.40})(Fe_{1.93}Cr_{0.02}Al_{0.03})O_4$ (container #1),
$(Mg_{0.02}Mn_{0.14}Fe_{0.52}Ni_{0.31}Zn_{0.01})(Fe_{1.89}Cr_{0.03}Al_{0.08})O_4$ (container #5), and
$(Mg_{0.01}Mn_{0.13}Fe_{0.38}Ni_{0.47}Zn_{0.01})(Fe_{1.79}Cr_{0.11}Al_{0.10})O_4$ (container #10).
The spinel phases concentrate the iron group elements (Fe, Cr, Ni), and Al, Zn, and Mg.

The degree of crystallinity determined from SEM images using Corel Photo-Paint 12 software was estimated to be ~10-15 %.Results of leach testing of the products (Table V) showed that normalized release of glass constituents at 50 wt.% waste loading in the glass were comparable to release values at 45 wt.% waste loading in the glass. The normalized elemental release rates were noticeably lower than those measured for a glass with 40 wt.% waste loading that was formulated for possible production in the JHCM. Moreover, the normalized elemental release rates were greater than an order of magnitude lower than the EA glass. The PCT-A response of the EA glass is used for waste form repository acceptance. These positive results stimulate further study on the increasing of waste loading in the glass.

Table V. PCT results for glass products with SRS waste surrogate.

Glass ID	Normalized Release (g/L)			
	B	Li	Na	Si
Test #2 Container 10 (45 wt.% waste loading)	0.53	0.75	0.82	0.45
Test #3 Container 1 (50 wt.% waste loading)	0.50	0.68	0.92	0.33
Test #3 Container 5 (50 wt.% waste loading)	0.46	0.65	0.74	0.30
Test #3 Container 10 (50 wt.% waste loading)	0.64	0.74	0.82	0.35
JHCM [11] (40 wt.% waste loading)	1.47	1.31	1.60	0.79
Environmental Assessment (EA) glass [12]	16.70	9.56	13.35	3.92

CONCLUSION

Vitrification tests on a SRS defense waste surrogate using the 418 mm inner diameter CCIM have demonstrated high efficiency of the ICCM technology (glass pour rate and specific glass productivity reached 16.2 kg/h and ~118.2 kg/(m^{2}h), respectively) and high quality of the final product. At 50 wt.% waste loading the final product was composed of ~86-88% vitreous and ~12-14% crystalline phase. The latter was found to be magnetite-type spinel with general formula $(Mg^{2+}_{0.01\ldots0.03}Mn^{2+}_{0.11\ldots0.14}Fe^{2+}_{0.38\ldots0.52}Ni^{2+}_{0.31\ldots0.47}Zn^{2+}_{0.00\ldots0.01})(Fe^{3+}_{1.79\ldots1.93}Cr^{3+}_{0.02\ldots0.11}Al^{3+}_{0.03\ldots0.10})O_4$. No melt foaming due to reduction of Fe(III) to Fe(II) nor sulfate-chloride “yellow phase” formation on melt surface in the CCIM during the melting run were observed. Traces of “yellow phase” formation may have occurred on the surface of the solidified product in the containers but no evidence of “yellow phase” was found in the bulk of the vitrified blocks. Normalized releases of B, Li, Na, and Si from vitrified products with 50 wt.% waste loading were determined using the PCT-A procedure. The normalized releases were found to be 15 to 30 times lower than those from the EA glass used for waste form repository acceptance.

ACKNOWLEDGEMENTS

The work was performed under Contract "Advanced Melter Technology Application to the Defense Waste Processing Facility (DWPF) – Cold Crucible Induction Heated Melter (CCIM)" funded by US DOE. Authors thank Mr. B.S. Nikonov for SEM/EDS examination of the products

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