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Summary of Cold Crucible Vitrification Tests Results with Savannah River Site High Level Waste Surrogates – 14464

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ABSTRACT

The cold crucible inductive melting (CCIM) technology successfully applied for vitrification of low- and intermediate-level waste (LILW) at SIA Radon, Russia, was tested to be implemented for vitrification of high-level waste (HLW) stored at Savannah River Site, USA. Mixtures of Sludge Batch 2 (SB2) and 4 (SB4) waste surrogates and borosilicate frits as slurries were vitrified in bench- (236 mm inner diameter) and full-scale (418 mm inner diameter) cold crucibles. Various process conditions were tested and major process variables were determined. Melts were poured into 10L canisters and cooled to room temperature in air or in heat-insulated boxes by a regime similar to Canister Centerline Cooling (CCC) used at DWPF. The products with waste loading from ~40 to ~65 wt.% were investigated in details. The products contained 40 to 55 wt.% waste oxides were predominantly amorphous; at higher waste loadings (WL) spinel structure phases and nepheline were present. Normalized release values for Li, B, Na, and Si determined by PCT procedure remain lower than those from EA glass at waste loadings of up to 60 wt.%.

INTRODUCTION

Successful operation of the cold crucible based unit at SIA Radon for vitrification of low- and intermediate-level radioactive wastes facilitated consideration of the Cold Crucible Induction Melting (CCIM) technology for implementation in high level waste vitrification facilities [1]. During the last eight years, SIA Radon researchers investigated the application of CCIM for vitrification of high level wastes (HLW) stored at the US DOE sites [1]. In the framework of collaborations between Savannah River National Laboratory (SRNL) and SIA Radon, high-Fe (Sludge Batch 2 (SB2)) and high-Fe/Al (Sludge Batch 4 (SB4)) Savannah River Site (SRS) HLW surrogates were combined with borosilicate frit in slurries with water contents varying from ~27 wt.% to ~70 wt.%. These feed slurries were successfully vitrified in crucibles up to 418 mm inner diameter. This paper summarizes major results of vitrification tests performed at SIA Radon under contract with SRNL.

WASTES CHARACTERIZATION

According to the Statement of Work SIA Radon performed tests on vitrification of sludges SB2 and SB4 stored in tanks at SRS which have since been processed in the Defense Waste Processing Facility (DWPF) at SRS. The main purpose of waste processing is achieving of maximum waste loading at acceptable chemical durability of waste form. Therefore, we need compromise between these two and determination of maximum waste loading in glass means ultimate value at which glass still remains chemical durability and necessary technological properties.

Chemical compositions of wastes, selected frits used as glass forming additives and glasses at various waste loadings (WL) are given in Table I. Major components in both wastes were sodium, aluminum, iron and uranium. In the SB2 waste Fe prevails over Al whereas in the SB4 waste their weight contents are similar. Al_2O_3 is known to improve chemical durability of silicate glasses but increase electric resistivity [2] that may create problems at electric melting, in that number CCIM, of glass. High Al_2O_3 concentrations in glasses may result in crystallization of nepheline which reduces chemical durability of residual vitreous phase [3]. High concentrations of iron oxides favor formation of spinel structure phase which does not effect on chemical durability of glasses but may effect on rheology of glass melts at high contents (more than ~30 vol.%). High magnetic susceptibility of Fe_2O_3 may also effects strongly on electric melting process.

Table I. Chemical compositions of waste surrogates, frits and SRS waste glasses.

Oxides	SB2				SB4			
	SB2 HLW surrogate	Frit 320	Glass (50% WL)	Glass (60% WL)	SB4 HLW surrogate	Frit 503-R4	Glass (50% WL)	Glass (60% WL)
Li_2O	-	8.00	4.00	3.20	-	8.00	4.00	3.20
B_2O_3	-	8.00	4.00	3.20	-	16.00	8.00	6.40
F	0.01	-	0.005	0.01	-	-	-	-
Na_2O	12.08	12.00	12.04	12.05	18.71	-	9.35	11.22
MgO	0.24	-	0.12	0.14	2.77	-	1.39	1.66
Al_2O_3	16.83	-	8.415	10.10	25.49	-	12.75	15.29
SiO_2	1.98	72.00	36.99	30.00	2.71	76.00	39.36	32.03
P_2O_5	0.14	-	0.07	0.08	-	-	-	-
SO_3	0.83	-	0.41	0.50	0.87	-	0.43	0.52
Cl	1.51	-	0.75	0.90	-	-	-	-
K_2O	0.09	-	0.045	0.05	0.07	-	0.03	0.04
CaO	3.76	-	1.88	2.25	2.77	-	1.38	1.66
TiO_2	-	-	-	-	0.04	-	0.02	0.02
Cr_2O_3	0.37	-	0.185	0.22	0.20	-	0.10	0.12
MnO	3.89	-	1.945	2.33	5.78	-	2.89	3.47
Fe_2O_3	42.24	-	21.12	25.36	28.99	-	14.49	17.39
NiO	2.17	-	1.085	1.30	1.66	-	0.83	1.00
CuO	0.20	-	0.10	0.12	0.05	-	0.03	0.03
ZnO	0.39	-	0.195	0.23	0.05	-	0.02	0.03
SrO	0.10	-	0.05	0.06	-	-	-	-
ZrO_2	0.79	-	0.395	0.47	0.09	-	0.05	0.05
I	0.04	-	0.02	0.03	-	-	-	-
BaO	0.27	-	0.135	0.16	0.07	-	0.03	0.04
PbO	0.32	-	0.16	0.19	0.38	-	0.19	0.23
U_3O_8	11.75	-	5.875	7.05	9.03	-	4.52	5.42
Ce_2O_3	-	-	-	-	0.21	-	0.11	0.13
La_2O_3	-	-	-	-	0.03	-	0.02	0.02
ThO_2	-	-	-	-	0.02	-	0.02	0.02
Total	100	100	100	100	100	100	100	100

BENCH-SCALE WASTE SURROGATE VITRIFICATION TESTS

Tests were performed at the Radon bench-scale unit equipped with a 236 mm inner diameter cylindrical cold crucible (Figure 1) energized from a 1.76 MHz/60 kW tube generator. Pouring unit (Figure 1) was installed from the bottom of the crucible to pour the glass melt from the level.

Figure 1. View of 236 (left) and 418 mm inner diameter (middle) cold crucibles and pouring unit (right).

The slurries with SB2 waste to be fed into the cold crucible were prepared by two different methods: from mixture of chemicals simulating SB2 waste and Frit 320 (#1 in Table II) and from sludge prepared by procedure recommended by SRNL [4]. Active hydrodynamic regime in the cold crucible is suggested to intensify homogenization processes and accelerate reactions. As a result, Table II demonstrates no significant effect of slurry preparation method on process efficiency. More essential factor is water content in the slurry. Decrease of water content in the slurry with SB2 waste surrogate by 2 times (from 60 to 30 wt.%) increases average and specific glass pour rates by and reduces melting ratio by a factor of approximately 2. At that, volatile losses of B_2O_3, Na_2O and Cs_2O were found to be reduced as well. Even small-sized cold crucible demonstrated high specific productivity (melt pour rate) – more than 2,000 kg/(m^2d), so higher efficiency of large-scale cold crucible would be expected.

LARGE-SCALE WASTE SURROGATE VITRIFICATION TESTS

Large-scale tests were performed at the Radon vitrification facility (RVF) used for treatment of LILW from non-nuclear applications. The RVF was equipped with a 418 mm inner diameter industrial-scale cylindrical cold crucible (Figure 1) energized from a 1.76 MHz/160 kW generator. The crucible was equipped with the pouring unit same type as the bench-scale crucible. Table III summarizes the results of the tests.
The slurries were prepared by the following methods. Slurry SS-320 was produced from sludge prepared by SRNL procedure [5] and Frit 320; slurry CS-320 – from mixture of chemicals and

Frit 320; slurry CS-503 – from chemicals and Frit 503-R4; slurry SS-503 – from sludge prepared by SRNL procedure and Frit 503-R4. Major conclusions which may be done from Table III are as follows:

- Increase of mass content of water in slurry results in inversely proportional decreasing of glass productivity and direct proportional increasing of specific heat expenses (melting ratio);
- The maximum slurry feeding rate, melt production rate, specific productivity and melting ratio at ~50 wt.% water content in the slurry reached ~40 kg/hr, ~14 kg/hr, ~2400 kg/(m^2d), and ~10 kW h/kg of glass, respectively.
- Decreasing of water content in the slurry to ~30 wt.% increases average melt production rate to ~20 kg/hr;
- Similarly to vitrification in small-scale crucible at vitrification in large-scale crucible no appreciable difference in process variables at feeding of slurries prepared using chemicals and by SRNL procedure.

Table II. Major process variables for vitrification of SB2 and SB4 wastes in the bench-scale unit.

Process Variables		SB2		SB4	
		1	2	3	4
Test duration under steady-state conditions, hr:min		55:25	33:29	4:24	4:52
Average generator's oscillating power, kW		42	54	42.3	45.8
Water content in slurry, wt.%		60	30	31−32	42−43
Mass of slurry processed, kg		436	245	34.8	44.7
Mass of vitrified waste produced, kg		112	148	13.8	14.1
Melt surface temperature, °C		1,210	1,380	1,310	1,300
Average rate, kg/hr:	Slurry feeding	7.9	7.3	7.9	9.2
	Glass production	2.0	4.4	3.1	2.9
Melting ratio, kW·hr/kg		20.6	12.3	13.6	15.8
Specific glass pour rate, kg/(m^2·d)		1,125	2,442	~1,700	~1,590
Volatile losses, wt.%	B_2O_3	25	15	-	-
	Na_2O	12	5	-	-
	Cs_2O	~70	~60		
Heat losses (spent power), kW	Vitrification	22.5/8*	17.5/12*	-	-
	Generator cooling	37.5/39*	22.5/24.5*	-	-
	Cold crucible cooling	36/47*	56.5/60*	-	-
	Off-gas	4/4*	4/4*	-	-

1 – mixture of chemicals and Frit-320, 2 – mixture of sludge prepared by SRNL procedure and Frit-320, 3 and 4 – mixture of chemicals including glass forming additives. * Numerator – power spent at slurry feeding, denominator – power spent at melt homogenization.

PRODUCTS CHARACTERIZATION

The maximum waste loading in the glass not resulting in formation of nepheline reached 55-60 wt.%. Trace of nepheline occasionally occurred in the glasses at 55 wt.% waste loading. At higher waste loadings nepheline content grows quickly. Spinel crystals with a magnetite/trevorite composition and a generalized formula $(Fe,Ni,Mn,Mg)^{2+}(Fe,Cr,Al)^{3+}O_4$ (with trace of Cu^{2+} and Zn^{2+}) were the only crystalline phases observed in all the glassy products at

~10-15 vol.% of the total bulk. The presence of the spinel crystals had no effect on product quality as demonstrated by the high leach resistance of the products (Table IV) determined by PCT procedure [6].
As follows from Table IV, the glassy materials with SB2 waste at 55 wt.% waste loading produced in cold crucibles remain higher chemically durable than those with 40 wt.% waste loading produced in Joule heated ceramic melter. The material produced in cold crucible even at 60 wt.% waste loading has normalized release values comparable with the glass with 40 wt.% SB2 waste loading produced in the ceramic melter.

Table III. Major Process Variables at Vitrification of SRS SB2 (high-Fe) and SB4 (high-Fe/Al) Waste Surrogates in the 418 mm Inner Diameter Cold Crucible.

Parameters		SB2			SB4	
Glass forming additive (frit)		SS-320	CS-320	Average (total)	CS-503	SS-503
Test duration, hr:min		13:08	18:44	(31:52)	29:40	32:50
Average generator's vibration power, kW		143	150	147	121.6	134.1
Water content in slurry, wt.%		~45	~60	~55	27−28	50−52
Mass of slurry vitrified, kg		465	751	(1,216)	745.8	1307.9
Mass of glassy product produced, kg		213	205	(418)	414.3	458.6
Average melt surface temperature, °C		1,160	1,160	1,160	1,300	1,300
Average slurry feeding rate, kg/hr		36	40	38	25.1	39.8
Average melt production rate, kg/hr		16	11	13.5	14	14
Melting ratio, kW·hr/kg	Slurry processing	4.0	3.8	3,9	4,8	3,4
	Melt production	8.8	13.8	11.3	8.7	9.6
Heat losses (spent power), kW	Vitrification	27	25	26	36	34
	Generator's cooling	27	24	25.5	38	37
	Cold crucible cooling	43	48	45.5	22	25
	Off-gas	3	3	3	4	4
Specific glass productivity, kg/(m^2·d)		2,830	1,910	2,370	~2,450	~2,450
Volatile losses, wt.%	Li_2O	-	-	-	~8	
	Na_2O	3	7	5	3.5-8	
	Cs_2O	-	-	-	48-60	
	B_2O_3	9	17	13	4,5-12	
	SiO_2	-	-	-	0.1	
	CaO	-	-	-	0.5-2	
	MnO	-	-	-	3-7	
	Fe_2O_3	-	-	-	2-5	

For the glasses and glassy materials with SB4 waste the following conclusions may be reached:

- No direct effect of thermal history of the lab samples on its chemical durability;
- Normalized release values for B, Li and Na, with few exceptions, produced under the same conditions increase with the increase of waste loading in the glassy materials;
- There is minor effect of waste loading on normalized release values for Si that is due probably to formation of high-silica layer on the surface of glass grains;
- The materials produced in cold crucible have chemical durability similar to that of lab-scale samples;

- All the samples containing up to 60 wt.% waste loading have normalized release values for B, Li, Na and Si by at least one order of magnitude lower than those from EA glass;
- All the samples with SB4 waste, even at 66 wt.% waste loading have normalized release values for all the elements lower than those of EA glass.

COMPARISON OF RESULTS OBTAINED IN SMALL- AND LARGE-SCALE COLD CRUCIBLES

As follows from comparison of the data presented in Tables II and III, increase of crucible inner diameter from 236 to 418 mm, i.e. by about 1.8 times, results in increasing specific glass productivity and decreasing melting ratio by 1.5-2 times depending on water content in the slurry. At vitrification of slurries in the cold crucible with 236 mm inner diameter the vitrification process itself (water evaporation, calcining, calcine melting and melt homogenization) takes on average about 15% of total power, loss with off-gas does not exceed 4%, the rest is spent for cooling of cold crucible and generator's tube whereas in the crucible with 418 mm inner diameter an effective power spent for vitrification ranges between 25% and 36% of total power. Therefore, as expected the use of large diameter cold crucibles is preferable since the efficiency achieves 25-36%.

CONCLUSIONS

Feasibility of vitrification of high-Fe and high-Fe/Al SRS wastes by CCIM has been successfully demonstrated. The maximum slurry feeding rate, melt production rate, specific productivity and melting ratio at ~50 wt.% water content in the slurry reached ~40 kg/hr, ~14 kg/hr, ~2400 kg/(m^2d), and ~10 kW h/kg of glass, respectively. Further improvement of the CCIM parameters may be achieves by reduction of water content to ~30 wt.%. The CCIM process for high-Fe/Al waste is some more power efficient than that for high-Fe waste: thermal power spent for vitrification is 34-36% and 25-27%, respectively. Vitrified high-Fe waste are composed of major vitreous phase and minor spinel. Vitrified high-Fe/Al waste has similar phase composition but may contain nepheline at more than 60 wt.% waste loading. Maximum waste loading not resulting in nepheline formation should be limited by 55-60 w.%. Normalized release values for B, Li, Na and Si from such glassy materials at lower than those from EA glass by at least one order of magnitude.

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