ESTIMATING MELT RATE FOR SAVANNAH RIVER SITE HLW SIMULANTS

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ABSTRACT

Compositions of three frits with various content of boron, calcium, sodium and lithium were developed for vitrification of SB5 and SB6 slurries to be processed at the Defense Waste Processing Facility (DWPF).

A series of melter runs were performed at Khlopin Radium Institute (KRI) to determine the melt rate for the SB5 and SB6 simulants with different compositions of the frits. These runs were performed in a laboratory scale melter with liquid feeding referred to at KRI as the SMK melter. During these melter runs, the optimal frit composition #550 was selected for processing with both slurries at a larger-scale Joule heated melter referred to at KRI as the EP-5 melter.

INTRODUCTION

The V. G. Khlopin Radium Institute (KRI) performed a series of successful experiments to measure rate of melting for Savannah River Site high-level waste (HLW) feeds in 2007 and early 2008. Using the current Joule heated melter technology employed at the Savannah River Site (SRS) DWPF the potential exists for improving waste throughput by tailoring the frit composition to speed the rate at which the feed material is incorporated into the melt pool.

The study is intended to expand upon the earlier work in support of frit development for Sludge Batch 5 and Sludge Batch 6 (SB5 and SB6), the next sludge batches to be processed at the DWPF. Experiments were designed to provide the data necessary to better understand the impact of frit components such as boron, calcium and sodium (and others) on melt rate for sludges with both high concentrations of aluminum (sludges from the HM process) and low concentrations of aluminum (sludges where the aluminum dissolution process has been applied). In addition, KRI has the capability of operating lab-scale melters both with and without agitation in the form of bubblers. Because it may be feasible to add bubblers to the DWPF melter, it is of interest to determine the impact of agitation on melt rate for SRS-type feeds.

EXPERIMENT

Fabrication of Frits and Sludge Simulants for Vitrification

The frits were produced from batches containing chemicals, such as boric acid, lithium and sodium carbonates, calcium oxide, and silica. The silica particle size did not exceed 120 µm. The batches for the frit preparation contained chemicals in the required proportions and were thoroughly mixed. The mixtures were placed into platinum boats to be heated and held at 1250ºC for 1.5 hours.

The glass frit melting showed that all glass frits looked like clear glass. We analyzed the glass frits using XDA, EPMA, and SEM methods. According to the XRD, the frits are X-ray amorphous. Calculated of Na, Ca, Si oxides content as well as analytical data according to the EPMA are shown in the Table I.

Table I. Compositions of Glass Frits

Component			B_2O_3	Li_2O	Na_2O		CaO		SiO_2	
Frit			cal	cal	cal	anal	cal	anal	cal	anal
	418	Content, wt	8	8	8	7,5	–	–	76	76,5
	550		12	8	7	7,1	–	–	73	72,9
	551		8	7	8	8,1	5	4,8	72	72,1

Table I shows that the Na, Ca, and Si oxides content in all frits match the target values. According to the SRS Simulant Sludge Compositions and Preparation Instructions batches SB5 and SB6 were imitated by sludges SMR-2 and SMR-4, correspondently.

After an intense agitation of the content of the bottles with a 3 L batch in each bottle ~ 25 mL of representative samples were taken to measure the following:

- specific gravity;
- total solids %;
- calcine %;
- calcine factor.

The total solids % and calcine % were determined according to the procedure entitled: drying/calcining (total solids % and calcine % determination). The values, as well as the calcine factor as an average of 3 measurements, are given in Tables II.

Table II. Characteristics of the Final SMR-2 and SMR-4 Sludge

Bottle #	Waste mass, g	Specific gravity, g/mL	Total solids, wt %	Calcine,wt %	Calcine factor
SMR-2	3427,83	1,11	17,35	12,28	0,71
SMR-4	3661,17	1,11	16,42	11,79	0,72

Table III shows the SMR sludge simulant compositions based on the quantities of the chemicals listed in the Procedure.

The concentration of macrocations such as Mn, Fe, Na, Al and K in these sludge stimulants was measured by AE-ICP method. It was well established that the targeted and calculated on the AE-

ICP data concentrations of the analyzed cations for both types of the sludge stimulant in all bottles are in agreement.

Table III. Estimated Compositions of SMR Sludge Simulants

SMR-2			SMR-4		
Cation	g/1 L of the sludge	wt.% in calcined solids	Cation	g/L of the sludge	wt.% in calcined solids
Mn	3,84	2,73	Mn	5,15	3,464
Fe	32,80	23,30	Fe	38,8	26,113
Ni	1,38	0,98	Ni	1,58	1,070
Ca	2,86	2,03	Ca	3,67	2,468
Na	23,31	16,56	Na	26,80	18,037
Al	18,62	13,23	Al	12,2	8,211
Ba	0,30	0,21	Ba	0,35	0,236
Ce	1,80	1,28	Ce	1,98	1,333
Cr	0,28	0,20	Cr	0,37	0,247
Cu	0,10	0,07	Cu	0,13	0,094
K	0,23	0,16	K	0,30	0,200
Mg	0,38	0,27	Mg	0,44	0,294
Pb	0,33	0,23	Pb	0,37	0,247
Si	2,39	1,70	Si	3,75	2,526
Ti	3,00	2,13	Ti	2,62	1,763
Zn	0,16	0,11	Zn	0,21	0,141
Zr	0,57	0,41	Zr	0,72	0,482
	Σ 92,35 g/L	Σ 65,60 %		Σ 99,44	Σ 66,926

SMK melter system

The laboratory scale melter (SMK) was used to perform tests on melt rate optimization and frit selection.

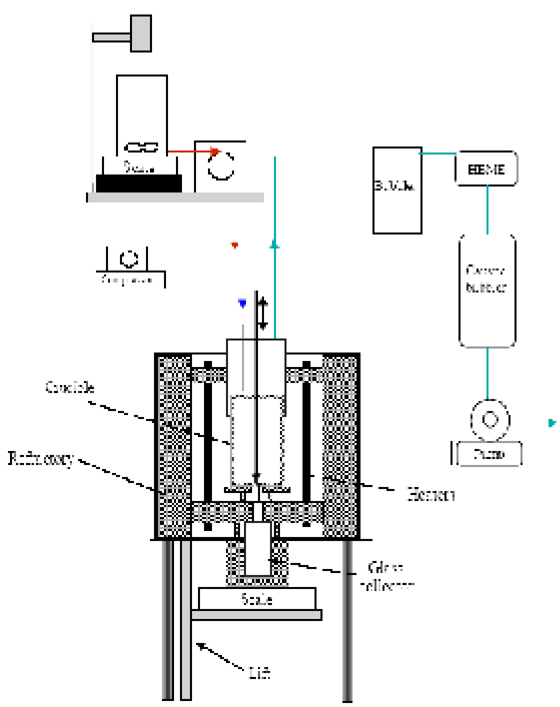

Fig.1 General layout of the SMK melter system

The SMK melter is intended for experiments on evaluation of frit compositions on waste loading, cold cap consumption, as well as physical and chemical characteristics of produced glasses. The SMK melter is equipped with systems and mechanisms that provide for dry or liquid feeding, off-gas purification, air bubbling, glass pouring, and visual observation of the vitrification process. Fig. 1 shows an overall schematic of the SMK melter and Table IV provides information on its major parameters.

Table IV. Parameters of SMK Melter

Parameter	Value
Maximum Operating Temperature	1200ºC
Inner Diameter	89 mm
Crucible Cavity Height	280 mm
Total Volume	1800 cm^3
Glass Pool Surface Area	62 cm^2
Average Glass Volume	1200 cm^3
Average Glass Depth	180 mm
Average Glass Mass	1,1-1,2 kg
Crucible Material	Inconel-90
Heating rods	SiC

RESULTS

Frit selection

The melt rate was measured by tracking the feed rate required to maintain sufficient cold cap coverage (90-95% of surface) and the time required to consume the cold cap at the completion of feeding. During the experimental runs, KRI also performed visual observations of the cold cap behavior on the melt surface, sludge boiling on the cold cap surface and morphology of the cold cap during its consumption. After the melts were poured from the crucible melter, the glass was sampled for analysis.

Table V shows target glass compositions for the SMR-2 and SMR-4 sludge simulants and the EPMA data.

The EPMA and SEM data show that the all glasses had a homogeneous distribution of the major components in the volume, and their content was close to the target values. Spinel was detected in the SMR-2 glasses with Frits 551 and 418.

Table V. Glass Compositions (wt%) according to EPMA Data

oxide	SMR-2						SMR-4					
	Frit											
	418		550		551		418		550		551	
	target	anal.	target	anal.	target	anal.	target	anal.	target	anal.	target	anal.
MnO_2	1,63	1,73	1,63	1,65	1,63	1,59	2,07	1,89	2,07	1,94	2,07	2,05
Fe_2O_3	12,62	13,09	12,62	12,42	12,62	12,20	14,14	14,17	14,14	13,72	14,14	14,22
NiO	0,47	0,34	0,47	0,44	0,47	0,59	0,52	0,50	0,52	0,54	0,52	0,55
CaO	1,08	0,99	1,08	1,49	4,18	3,57	1,31	1,43	1,31	1,24	4,40	3,84
Na_2O	13,41	12,80	12,79	11,47	13,41	14,41	14,17	14,75	13,55	14,22	14,17	13,86
Al_2O_3	9,47	9,93	9,47	9,80	9,47	9,89	5,87	6,11	5,87	6,03	5,87	6,19
BaO	0,09	n/d*	0,09	n/d	0,09	n/d	0,10	n/d	0,10	n/d	0,10	n/d
CeO_2	0,60	0,39	0,60	0,40	0,60	0,47	0,62	0,58	0,62	0,58	0,62	0,58
Cr_2O_3	0,11	0,10	0,11	0,15	0,11	0,10	0,14	0,24	0,14	0,24	0,14	0,29
CuO	0,04	n/d	0,04	n/d	0,04	n/d	0,05	n/d	0,05	n/d	0,05	n/d
K_2O	0,07	0,93	0,07	1,28	0,07	n/d	0,09	n/d	0,09	n/d	0,09	n/d
MgO	0,17	n/d	0,17	n/d	0,17	n/d	0,19	n/d	0,19	n/d	0,19	n/d
PbO	0,10	n/d	0,10	n/d	0,10	n/d	0,10	n/d	0,10	n/d	0,10	n/d
SiO_2	48,50	48,17	46,65	47,15	46,02	46,30	49,16	49,19	47,30	47,88	46,69	47,86
TiO_2	1,35	1,24	1,35	1,20	1,35	1,22	1,11	1,10	1,11	1,10	1,11	1,16
ZnO	0,05	n/d	0,05	n/d	0,05	n/d	0,06	n/d	0,06	n/d	0,06	n/d
ZrO_2	0,21	0,14	0,21	n/d	0,21	0,13	0,25	n/d	0,25	n/d	0,25	n/d
SO_3	0,08	0,25	0,08	0,17	0,08	0,25	0,10	n/d	0,10	n/d	0,10	n/d
P_2O_5	0,05	n/d	0,05	n/d	0,05	n/d	0,04	n/d	0,04	n/d	0,04	n/d
B_2O_3	4,96	4,96	7,44	7,44	4,96	4,96	4,96	4,96	4,96	4,96	4,34	4,34
Li_2O	4,96	4,96	4,96	4,96	4,34	4,34	4,96	4,96	7,44	7,44	4,96	4,96
Total	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0

*) – non detected

Table VI provides major parameters for the SMK experimental runs with SMR-2 and SMR-4 simulants.

Table VI, Major Parameters of SMK Runs with SMR-2 and SMR-4 Sludge

Frit #,	Sludgevolume; cm^3	Σoxides in the waste sludge, g	Frit, g	Feeding rate, L/hr	Cold cap consumption,
	SMR-2				
«551»	3300	420,37	658,8	1,31	11min
«550»	3700	420,36	685,8	1,50	8min 42 s
«418»	3687	417,16	681,0	1,47	10min
	SMR-4				
«551»	3522,5	443,7	730,0	1,72	11 min 24s
«550»	3326	443,2	730,0	1,60	8min 18s
«418»	3418	442,2	730,0	1,21	9 min

Based on the results, shown in Table VI data and of the glass analysis the following conclusions can be made:

SMR-2 Sludge Simulant

1. When the cold cap covered 90% of the melt surface, the sludge simulant feeding rates were the same for Frits 418 and 551 and 11% higher for the sludge simulant with Frit 550.
2. The time required for consumption of the cold cap when it covered 90% of the melt surface was approximately the same for the runs with Frits 551 and 418, and 1 – 1,5 minutes less for the run with Frit 550.
3. The glass-pouring rate for all frit compositions was approximately the same, specifically: 34,6 g/min for Frit 550; 35,1 g/min for Frit 418, and 37,5 g/min for Frit 551.
4. The Frit 550 containing glass did not have spinel inclusions.

SMR-4 Sludge Simulant:

1. When the cold cap covered 90% of the melt surface, the sludge simulant feeding rates were the same for Frits 551 and 550, and 27% lower for the sludge simulant with Frit 418.
2. The time required for consumption of the cold cap when it covered 90% of the melt surface was approximately the same for the runs with Frits 551 and 418, and 1 – 1,5 minutes shorter for the runs with Frit 550.
3. The glass-pouring rate upon completion of feeding (Pour 2) was the same for Frits 551 and 418, and by 30% higher for Frit 550, i,e. the melt with Frit 550 had a lower viscosity.

Comparison of whole experimental results and visual observations allowed concluding that optimal frit composition is Frit 550 for the both sludges SMR-2 and SMR-4.

Experimental runs with and without bubbling

Based on the preliminary made choice of Frit 550 the evaluation of bubbling on the melt rate was performed only with this frit.
Table VII summarizes the experimental results on the melt rate with and without of bubbling for both SMR-2 and SMR-4 sludge simulants.

Table VII, Influence of bubbling on the feeding rates and cold cap consumption

Sludge	Sludge, cm^3	Σoxides in the waste sludge, g	Frit, g	Feeding rate, L/hr	Cold cap consumption	Conditions of melting
SMR-2	3351	423,74	691	1,60	9 min 20s	without bubbling
SMR-2	3301	423,74	691	1,70	5min 58s	bubbling, 0,5 L/min
SMR-4	3684	447,37	730	1,61	8 min 37s	without bubbling
SMR-4	3905	447,37	730	1,76	7min 57s	bubbling, 0,5 L/min

Bubbling rate equal to 0,5 L/min was used due to normalized amount of 83 $L/m^2 \cdot min$ quoted to the melt surface area in SMK.
From Table VII it could be seen that in case of SMR-2 cold cap consumption time was significantly reduced (~35% less) with addition of bubbling, while feeding rate was enhanced only slightly.
In case of SMR-4 effect of bubbling was not so noticeable in cold cap behavior, but feeding rate was increased.

It was assumed that difference in behavior of these two sludges could specify in terms of viscosity melts. SMR-2 based melt is more viscous because of that additional stirring enhanced it processing capability more significantly.

CONCLUSION

Vitrification testes have been performed at lab-scale melter system SMK using two type sludge simulants SMR-2 and SMR-4 batched with three different frits. Frit composition #550 was selected as an optimal for both sludges and it was recommended to use for testing in larger scale melter EP-5.
Addition of bubbling enhanced the vitrification process for both sludges, but in case of SMR-2 it was more significant.

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