HIGH LEVEL NUCLEAR WASTE FORM DEVELOPMENT:

MINI-MELTER DESIGN AND OPERATION

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ABSTRACT

This research supports the plans of West Valley Nuclear Services, Inc. to stabilize their nuclear waste prior to placemtnt in a repository. The nuclear waste, which is a sludge mixture, will be stabilized by vitrification in a large-scale melter. PNL has developed a process to dissolve the sludge in acid and then vitrify the resulting solution in combination with glass forming additives (or frit) and using various additives to control foaming and non-melting phases in the cold cap. As an alternative, the Vitreous State Laboratory of Catholic University is examining a simpler slurry fed process which eliminates the acid dissolution and foam control additives in order to give improved glass production rates. This paper reports the development of a laboratory-scale slurry-fed mini-melter system used to dynamically model and study alternative process conditions for the full-scale West Valley melter. Specifically, the mini-melter is designed to (1) provide insight into the dynamics of cold-cap formation and digestion in the melter, and (2) demonstrate that simulated West Valley nuclear waste sludge be fed to the melt furnace in the form of the slurry, and be made into a stable, low-leaching glass at a practical rate.

The mini-melter system consists of (1) the feed sub-system to feed the slurry to the melter, (2) the mini-melter, and (3) associated power supplies and controls. The sludge and glass frit are mixed in a feed tank and fed to the mini-melter by a peristaltic pump. The mini-melter accepts the slurry feed on a continuous basis and melts it into glass which is poured continously or batchwise into a stainless steel container for later rheologic, chemical and leaching analyses. The mini-melter consists of two chambers - a melt chamber and a pour chamber. The molten glass in the rectangular melt chamber has a cross-sectional area of 0.0228 m^2 and a depth of approximately 13 cm. The actual melting is accomplished by Joule heating using plane electrodes made of Inconel 690 located on opposite sides of the melt chamber. The temperature within the melt was maintained at 1150 C. Molten glass is poured by tilting the entire mini-melter, using a hydraulic pump, to allow the melt to flow through an Inconel 690 pour tube into the stainless steel container in the pour chamber. Teh particular architecture for the mini-melter was chosed to maximize its flexibility while minimizing engineering complexity.

The feed mixture for the slurry vitrification experiments described in this paper consisted of (1) a commercially prepared sludge, containing approximately 12.2% anhydrous solids, which chemically simulates the West Valley nuclear waste, and (2) SRL-165 borosilicate glass frit at a 400 g/liter glass equivalent loading in the slurry. The mini-melter system was successful in melting this slurry-fed mixture at feed rates up to 35 ml/min, providing a positive basis for further studies on the effects of varying sludge compositions and process conditions on glass production, durability and leachability.

BACKGROUND

This research supports the plans of West Valley Nuclear Services Inc. to stabilize their nuclear waste prior to placement in a repository. The nuclear waste, which is a sludge mixture, will be stabilized by vitrification in a large-scale melter. There are significant differences between West Valley high level waste and those found at the Savannah River Plant. For example, thorium and inorganic ion exchangers, while Savannah River waste has larger concentrations of uranium, aluminum and potassium. Battelle's Pacific Northwest Laboratory (PNL) has developed a process to dissolve the West Valley sludge in acid and then vitrify the resulting solution with glass formers and using various additives to control foaming and non-melting secondary phases in the cold-cap. As an alternative, the Vitreous State Laboratory (VSL) at Catholic University of America (CUA) is developing a simpler slurry fed process which eliminates the acid solution in an attempt to improve glass production rates. A key element of this study is the development of the CUA-VSL laboratory-scale slurry fed mini-melter system to dynamically model and study alternative process conditions for the full-scale West Valley melter.

The objective of the CUA/VSL small-scale continuous melter (mini-melter) system is to demonstrate that simulated West Valley sludge can be mixed with appropriate glass frit or glass formers, be fed to a melt furnace in the form of a slurry, and be made into a stable, leach-resistant glass at a practical rate.

CUA/VSL Mini-Melter Design

The CUA/VSL mini-melter system consists of the feed system to deliver the slurry to the melter, the melter itself, the associated electrical power supplies and controls, and the system for handling the gases evolved during the melting. Figure 1 shows an overall view of the mini-melter system; Fig. 2 is a close-up of the components which penetrate the mini-melter lid.

Fig. 1. The CUA/VSL Mini-Melter Tilted for Glass Pouring.

Fig. 2. Mini-Melter Lid.

The slurry feed system consists of a feed tank, a feed pump, and associated feed lines, connections, and sampling ports. The simulated West Valley sludge and glass frit/glass formers are mixed as a batch in the feed tank, where it is mixed by a propeller mixer. The peristaltic feed pump, with fine speed control, feeds the slurry at a controlled rate to the melter. Silicone tubing is used in this part of the feed system because of its abrasion resistance. The inside diameter of all feed lines is ¼ inch or larger; this is more than six times the maximum particle size expected in the slurry, a design parameter intended to minimize clogging. The feed enters the melter through a water-cooled feed tube in the melter's lid, seen in Fig. 2. A sample port consisting of a polyethylene tee, silicone tubing, and a pinch clamp is provided in the line between the feed pump and the feed tube. A short length of ¼ inch i.d. tygon tubing connects the sample tee to the feed tube. All tubing lines are kept as short and as straight as possible to discourage clogging in the lines.

The mini-melter accepts the slurry feed on a continuous basis and melts it into glass which is poured into a stainless steel container for further testing. The melter can be operated with continuous feeding and pouring if it is tilted 10^o to 15^o or more during feeding.

The melter consists of two chambers - a melt chamber and a pour chamber. The melt chamber is made of Monofrax K-3 refractory bricks supplied by Sohio Carborundum. The bricks are 4-½ inches thick and are cemented together with type K cement, also supplied by Carborundum. The bricks were arranged to form a 7-7/16 x 5-5/8 x 9 inch high melt chamber.

The principal source of heat to the glass melt in this chamber is Joule heating using a pair of Inconel 690 electrodes (6 x 9 x ¼ inch thick) located at opposite sides of the chamber. The electrodes are designed for a maximum current density of 7 A/in^2 although a current density no larger than 5 A/in^2 is preferable to extend the life of the electrodes. The electrodes were placed directly opposite one another across the 5-5/8 inch width of the chamber. In constructing the mini-melter, small spaces were left between the electrodes and the bricks, resulting in the spacing between the electrode faces being 4-3/4 inches. Thus, the cross-sectional area of the melt surface between the electrodes is 35.3 in^2 (0.0228 m^2). The electrodes were welded to 2 inch wide x ¼ inch thick straps of Inconel 690 which served to provide physical strength and integrity to the connection to the electrical bus.

Additional heat, primarily used for start-up and study purposes is supplied by two bayonet style silicon carbide radiant heaters manufactured by I^{2}R Element Co. The heaters are 0.75 inch in diameter with a 12 inch active heating length. They are enclosed in mullite sleeves and are located in the lid just above the melt chamber.

The bricks forming the melt chamber are backed up with ½ inch thick M-board insulation obtained from Babcock & Wilcox. Around this is a stainless steel inner shell. The inner shell is insulated with 4 inches of M-board around the sides and 2 inches at the bottom. The outer shell of the mini-melter is mild steel.

An Inconel 690 pour tube (½ inch inside diameter) is located in a hole drilled diagonally through the brick separating the melt and pour chambers. The pour tube extends from the bottom of the melt chamber to a point 5-½ inches above the botton of the pour chamber. The pour tube extends 3-½ inches into the pour chamber at an angle of 15^o above horizontal. This allows the molten glass to pour into the center of the stainless steel catch container during a pour while any glass remaining in the pour tube after a pour will drain back into the melt chamber. The pour chamber is lined with 4 inches of M-board insulation and has an insulated door to allow for insertion and removal of the catch container. Heat is provided in the pour chamber by 2 bayonet style silicon carbide radiant heaters (I^{2}R Element Co.), 5/8 inch in diameter with a 6 inch heating length. These pour chamber heaters are located directly above the pour tube. A cylindrical resistance wire heater, placed over the end of the pour spout, was added later providing 200 watts of additional heating. Prior to pouring, the temperature in the pour chamber is raised to the 1000^{o}C range using these heaters. The cylindrical pour spout heater can raise the temperature of the spout by more than 100^{o}C if required for good pouring.

To pour molten glass from the melt chamber, the entire mini-melter assembly is tilted by a hydraulic jack located at the end opposite the pour chamber door, as seen in Fig. 1. The axle is attached to a steel stand which serves as the support for the melter. For continuous operation a tilt of 16^{o} was found convenient.

The stainless steel feed tube, seen in Fig. 2, is made of three concentric pipes. The ¼ inch i.d. inner pipe feeds the slurry into the center of the melt chamber. The two pipes surrounding the feed pipe, connected at the bottom, are for water cooling. Cool water is fed into the middle pipe through which it flows downward before being forced into the outer pipe through which it flows upward, ultimately into a drain. This cooling is necessary to prevent the rapid evaporation of the slurry water in the feed tube which would result in clogging.

Thermocouples are located in the melt in an Inconel 690 sheath, adjacent to the feed tube and in the pour chamber adjacent to the pour tube outlet. The Type S thermocouple in the melt is connected to a current proportional temperature controller which in turn regulates a silicon control rectifier (SCR) power controller which adjusts the power to the electrodes to maintain the melt temperature. The other two thermocouples (Type S) are used for temperature measurement, and are connected to a read-out.

The temperature controller is a Love Controls model 74 controller. The power to the elctrodes is controlled by a SCR manufactured by Eurotherm, Inc. The current between the electrodes is thus determined by the output voltage of teh SCR and the effective resistance of the glass melt. The output of the SCR is fed to 2 step-down low-voltage high-current transformers manufactured by General Electric Co. The transformer primaries are connected in parallel and the secondaries in series.

The resistance of the molten glass is a rather strong function of the temperature, falling with temperature roughly as an exponential function of -k/T in the temperature range of interest. The constant k is approximately 9000 K and depends somewhat upon the depth of the melt. The order of magnitude of the resistance at the typical operating temperature of 1150 C is 0.15 ohms.

Power for the radiant dilicon carbide heaters in the melt and pour chamber headspaces is adjusted manually by means of 50 A variable autotransformers manufactured by General Radio Co.

Steam and other gases generated during the melt process are exhausted through a duct system. The hot gases are cooled by dilution with room air which is also exhausted through the venting system. A damper is used to regulate the flow of the gases from the mini-melter to minimize heat losses while maintaining adequate exhaust ventilation.

Feed Slurry Preparation

A specially mixed sludge, supplied by AFF, Inc., was prepared to simulate the West Valley sludge. The composition of this simulated sludge, containing 12.2% anhydrous solids, is given in Table I. The slurry feed used in the experiments reported in this paper consisted of 15 gallons simulated sludge, 22.76 kg SRL-165 glass frit (obtained from the Savannah River Laboratory), and sufficient deionized water to bring the final volume to 20 gallons. This recipe results in the production of a glass in the melter that is quite near the reference composition for the West Valley vitrification process. The glass resembles rather closely the Savannah River Laboratory TDS-165 glass with certain important differences. Specifically, the glass produced in the CUA/VSL mini-melter contains significantly higher concentrations of phosphorus, lower concentrations of aluminum, a larger concentration of ZRO_2 (simulating U and Th), a lower concentration of iron, but essentially the same concentrations of alkalis, boron and silica. In general, the feed mix could be suspended with modest agitation. Delivering the feed as a slurry to the mini-melter presented no major difficulty, although it was noticed that toward the end of a batch, feeding became more difficult as the tendency for plugging increased. It was also noticed that if themix was allowed to stand for 24 hours, substantial settling occurred resulting in the appearance of approximately 10% of the volume being occupied by a clear liquid atop a murky solid. Little additional settling results from allowing the mix to stand for another 48 to 72 hours. The mix can be resuspended with very gentle stirring. There seems to be little tendency for the sludge/frit mix to form large solid aggregates.

Melting Simulated West Valley Sludge With SRL-165 Frit

The CUA/VSL melt campaign was intended to demonstrate the West Valley waste could be vitrified in combination with Savannah River TDS-165 frit. Properties of the resulting glass are discussed in another paper being presented at this meeting.

The set point temperature in the melt was held at 1150^{o}C; generally, the temperature was maintained quite close to this value although at times during the feeding it dropped to as low as 1100^{o}C. The power to the melt chamber lid heater, when it was in use, was about 1 kw and the power to the pour chamber lid heater was about 2.5 kw.

Runs were made both with and without melt chamber lid heaters in use. With the lid heaters on, a feed rate of 35 ml/min was maintained. During feeding, the cold-cap atop the melt grew until it covered essentially the entire melt chamber; when this happened the feed rate was reduced slightly to allow the cold-cap to be digested in the melter. The slurry feed showed some tendency to dry in the region between the feed tube outlet and the cold-cap, forming columns that sometimes extended to the tip of the feed tube. These columns would become unstable, fall onto the cold-cap and subsequently be digested into the melt. At times, the columns caused a partial clogging of the feed tube, but this condition never lasted more than a few seconds before the normal flow would resume.

With the lid heaters off, a maximum feed rate of 20 ml/min was maintained. The cold-cap was quite stable during this run. During the run without lid heating, the mini-melter electrodes typically drew 170 A at 22 volts. This was sufficient to maintain a melt temperature of 1150^{o}C without additional heat from the lid heaters. In this operating configuration, the temperature in the melt chamber headspace varied from 600 to 750^{o}C, depending on the condition of the cold-cap.

No insoluble secondary phases (killer scums) were observed during either run. After cessation of feeding, the cold-cap would completely dissolve into the melt within a few minutes.

TABLE I

West Valley (WV) Sludge and Simulated Sludge Compositions

Oxide	WV Sludge g/kg	Hydroxide	WV Sludge g/kg	Simulated Sludge g/kg
AgO	0.01	Ag	0.01	0.00
Al_2O_3	50.34	$Al(OH)_3$	77.03	77.03
AmO_2	0.31	AmO_2	0.31	0.00
B_2O_3	2.58	H_3BO_3	4.58	4.58
BaO	1.86	$Ba(OH)_2 \cdot 8H_2O$	2.08	0.00
CaO	20.30	$Ca(OH)_2$	15.23	22.13
CdO	0.01	$Cd(OH)_2$	0.01	0.00
CeO_2	2.80	CeO_2	2.80	5.43
CoO	0.01	$Co(OH)_2$	0.01	0.00
Cr_2O_3	8.25	$Cr(OH)_3$	11.18	11.18
Cs_2O	0.17	$CsNO_3$	0.24	0.00
Eu_2O_3	0.06	$EuO_{3/2}$	0.06	0.00
Fe_2O_3	474.78	$Fe(OH)_3$	478.02	478.02
Gd_2O_3	0.01	$GdO_{3/2}$	0.01	0.45
HgO	0.19	$Hg(OH)_2$	0.02	0.00
K_2O	2.46	KNO_3	5.28	5.43
La_2O_3	0.06	$LaO_{3/2}$	0.06	2.60
MgO	3.37	$Mg(OH)_2$	4.88	0.00
MnO_2	54.12	$MnOOH$	54.74	54.74
MoO_3	0.37	H_2MoO_4	0.41	0.00
Na_2O	38.86	$NaNO_3$	106.58	106.58
Nd_2O_3	4.86	$NdO_{3/2}$	4.86	1.81
NiO	11.84	$Ni(OH)_2$	14.70	14.70
NpO_2	0.94	NpO_2	0.94	0.00
P_2O_5	104.58	$FePO_4 \cdot 2H_2O$	275.36	275.36
PdO_2	0.29	Pd	0.22	0.00
Pm_2O_3	0.01	$PmO_{3/2}$	0.01	0.00
Pr_6O_{11}	1.34	PrO_2	1.36	0.57
PuO_2	0.31	PuO_2	0.31	0.00
Rb_2O	0.02	$RbOH$	0.02	0.00
RhO_2	0.57	Rh	0.43	0.74
RuO_2	3.17	RuO_2	3.17	3.17
SO_3	12.52	$CaSO_4 \cdot 2H_2O$	26.93	27.63
Sb_2O_3	0.01	Sb_2O_3	0.01	0.00
SeO_2	0.02	SeO_2	0.02	0.00
SiO_2	11.33	SiO_2	11.33	11.33
Sm_2O_3	1.11	$SmO_{3/2}$	1.11	0.45
SnO_2	0.02	SnO_2	0.02	0.00
SrO	0.08	$Sr(OH)_2$	0.10	0.00
TeO_2	0.12	TeO_3	0.13	0.00
Tc_2O_7	0.08	$TcO_{7/2}$	0.08	0.00
ThO_2	149.45	ThO_2	149.45	0.00
UO_2	23.37	UO_2	23.37	0.00
Y_2O_3	0.73	$Y(OH)_3$	0.91	0.00
ZnO	0.04	$Zn(OH)_2$	0.05	0.00
ZrO_2	12.27	ZrO_2	12.27	93.39

A major limitation to the processing rate during both runs was the glass viscosity at the pour spout. The glass was quite viscous as it drained from the pour spout into the catch container in the pour chamber. This limited the overall rate at which the glass could be produced. Increasing the heat into the pour chamber, or adding a heater directly on the pour spout as was done later, results in a higher temperature in the pour spout, and improves the pour rate significantly by lowering the viscosity of the molten glass in the pour tube.

CONCLUSIONS

This experiment clearly demonstrated that simulated West Valley sludge could be mixed with appropriate glass frit, fed to a melter as a slurry and made into glass. The feed rate was found to be very dependent on the heat supplied to the melt, with additional heat resulting in higher processing rates being achieved. While the cold-cap was observed to cover the entire melt during these runs, a stable cold-cap was achieved. In neither of the runs was a non-melting secondary phase (killer scum) observed. A major limitation on the overall processing rate is the glass viscosity at the pour spout, although this did not prove to be a serious problem to overcome.