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SMALL-SCALE, JOULE-HEATED MELTING OF SAVANNAH RIVER PLANT WASTE GLASS

I. FACTORS AFFECTING LARGE-SCALE VITRIFICATION TESTS

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PREPARED FOR THE U. S. DEPARTMENT OF ENERGY UNDER CONTRACT DE-AC09-76SR00001

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Printed in the United States of America

Available from

National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed Copy $4.50; Microfiche $3.00

726239

DP-1535
Distribution Category UC-70

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I. FACTORS AFFECTING LARGE-SCALE VITRIFICATION TESTS

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Publication Date: October 1979

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ABSTRACT

A promising method of immobilizing SRP radioactive waste solids is incorporation in borosilicate glass. In the reference vitrification process, called joule-heated melting (JM), a mixture of glass frit and calcined waste is heated by passage of an electric current. Two problems observed in large-scale tests are foaming and formation of an insoluble slag. A small joule-heated melter was designed and built to study problems such as these. This report describes the melter, identifies factors involved in foaming and slag formation, and proposes ways to overcome these problems.

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SMALL-SCALE, JOULE-HEATED MELTING OF SAVANNAH RIVER PLANT WASTE GLASS

I. FACTORS AFFECTING LARGE-SCALE VITRIFICATION TESTS

INTRODUCTION

Radioactive waste produced from reprocessing nuclear fuel for defense programs at Savannah River Plant (SRP) is stored in large underground tanks on the plant site. This alkaline waste is made up of three parts. The bulk of the waste actinides and fission products are contained in an insoluble sludge of hydroxides and hydrous oxides of iron, aluminum, and manganese.[1-3] The rest of the waste is either in the form of a crystalline salt cake or a nearly-saturated supernatant salt solution. This supernatant solution contains ~95% of the radiocesium and traces of other radionuclides.[4]

Methods to immobilize SRP waste for long-term storage are presently being developed at the Savannah River Laboratory (SRL).[5-9] According to the current reference process, the supernatant liquid is pumped from the tanks. Cesium and the trace amounts of soluble strontium and plutonium are then removed by ion exchange. The sludge and salt cake are washed with water and then separated by centrifugation and filtration. The washed sludge together with the isotopes from the ion exchange step is spray calcined and then incorporated into a borosilicate glass (Figure 1).

Two vitrification methods are currently being studied at SRL. In one method, in-can melting, premelted frit and calcined waste are melted in the final storage container. In the other method, joule-heated melting (JM), the calcine and frit are melted in a ceramic-lined melter by an electric current passing through the molten glass. The glass is continuously poured into the final storage vessel. Currently, JM is the reference process for immobilization of SRP waste.

SUMMARY

The glass chemistry associated with vitrification of Savannah River Plant high level waste sludges was studied using a laboratory-scale melter. Also studied were problems identified in large-scale tests at Battelle-Pacific Northwest Laboratories (PNL). These problems are: formation of a presistent foam, low melting rates, and formation of a slag layer on the bottom of the melter.

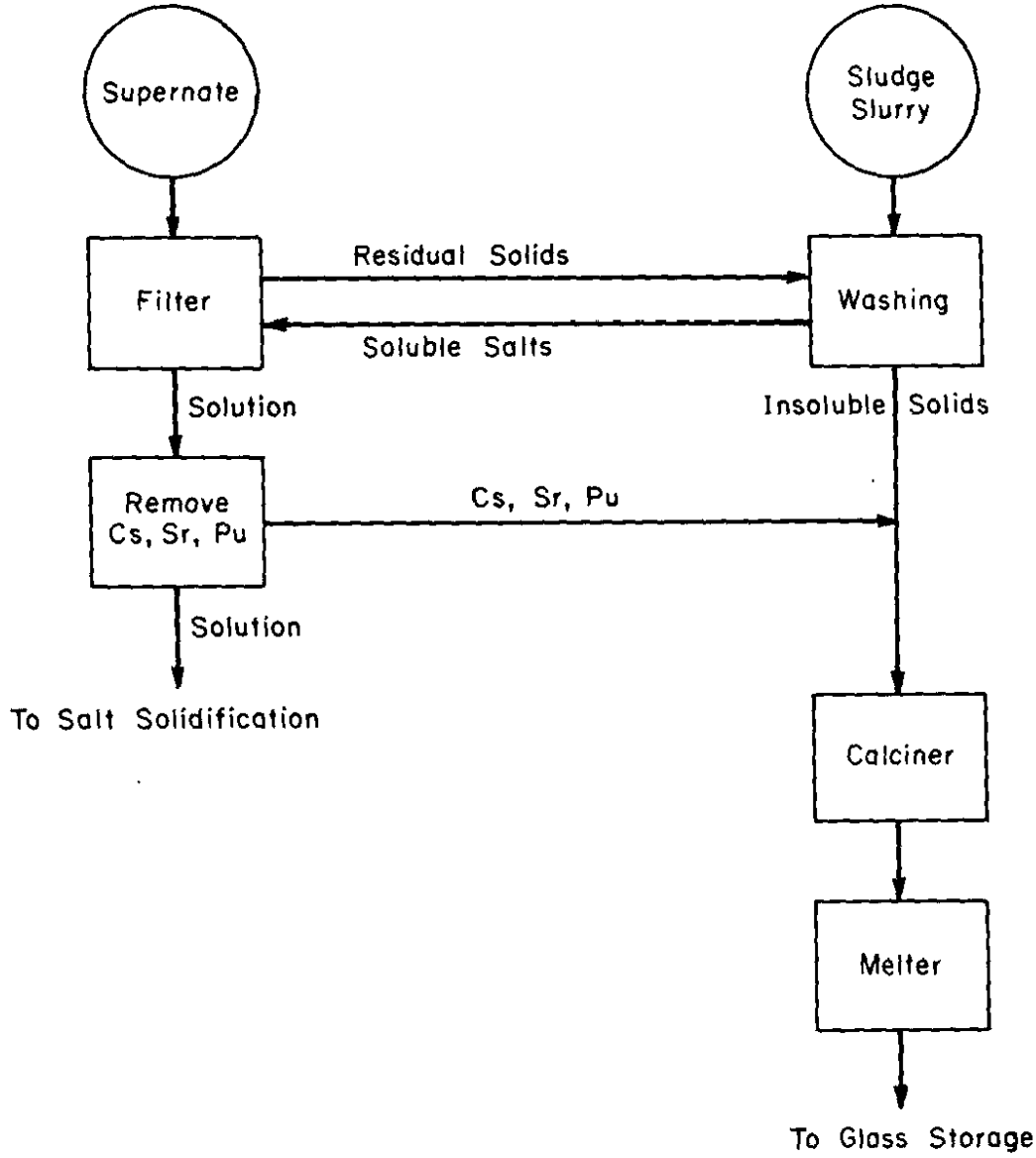


FIGURE 1. Reference Process for Immobilization of SRP Waste

The initial small melter experiments at the Savannah River Laboratory (SRL) demonstrated that when Frit 21 or equivalent glass-former compositions were used, only high-aluminum and

average-sludge glasses produced persistent foams at 1150°C. The foam persistence of average-sludge glasses also increased with the sodium carbonate content of the feed. This foam persistence reduced melting rates. The foam persistence in average sludge-melts was caused by the presence of ferrite-spinel crystals which increased the effective viscosity of the molten liquid in the foam. Therefore, by increasing the melting temperature to reduce the viscosity of the glass, the foam persistence was reduced.

The slag formed in both large (at PNL) and small-scale (at SRL) melters was found to be predominantly the ferrite-spinel phase. Slag formed when the solubility of this crystalline phase in molten glass was exceeded. Slag formation was enhanced by sludges high in iron, by low melter temperatures, long residence times, and by large amounts of sodium carbonate in the feed. In preliminary tests with a frit having increased ferrite-spinel solubility (Frit 411), no slag was observed.

To prepare glass forms containing a maximum amount of waste sludge, it is therefore necessary to eliminate sodium carbonate, control solubility by modifying the glass frit, and maintain a high temperature to increase the solubility of the sludge in the molten glass.

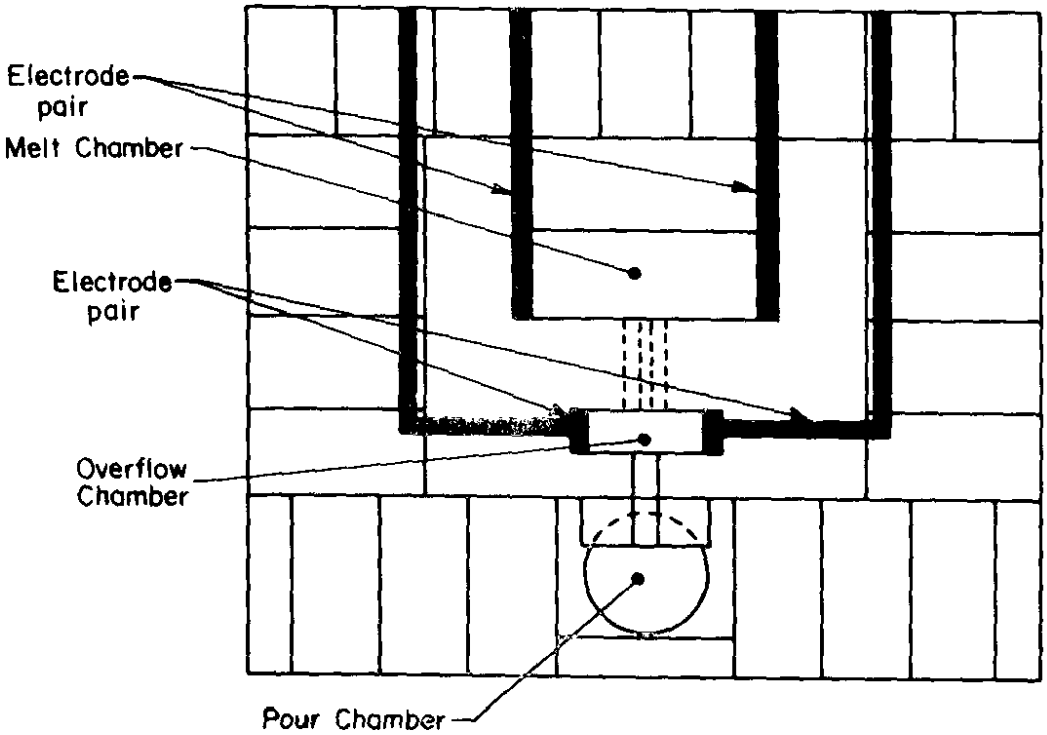
DESIGN AND OPERATION OF THE SMALL-SCALE (SRL) MELTER

Description

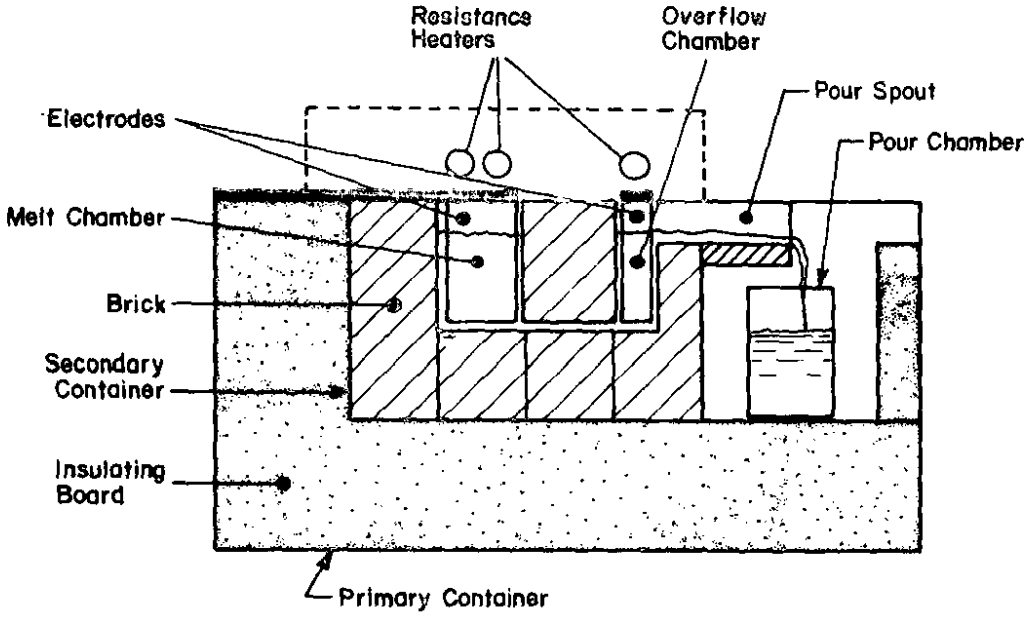
A plan and a section view of the melter are given in Figure 2. The dimensions of the unit are:

- Melter chamber: 7.6 cm wide, 22.9-cm long, and 7.6-cm deep. The glass depth is maintained at 6.2 cm.
- Overflow chamber: 3.8-cm wide, 12.7-cm long, and 7.6-cm deep.
- Electrodes in the melt chamber: 1.3-cm thick, 7.6-cm wide, and 7.6-cm high.
- Electrodes in the overflow chamber: 1.3-cm thick, 3.8-cm wide, and 7.6-cm high.

Both sets of electrodes are suspended from the top of the refractories and are powered by separate power supplies. This allows each chamber (melt and overflow) to be regulated at different temperatures.



a. Plan View



b. Cross-Section View

FIGURE 2. Plan and Cross-Section Views of Melter

An *Inconel 690* alloy (Huntington Alloys, Inc., Huntington, West Virginia) pour spout is mounted on the overflow chamber and protrudes into a separately heated pour chamber. This pour chamber is 15.2-cm wide, 10.2-cm deep, and 15.2-cm high. Sample containers are placed in this chamber, and an insulating door is closed to control heat losses. The entire melter is suspended on trunnions and can be pivoted by a motor-driven chain mechanism. A tilt of six degrees is used for continuous pouring. A fifteen-degree tilt empties about 90% of the glass from both chambers.

The refractory in contact with the molten glass is *Monofrax K-3* fused-cast chrome (27%) alumina, a product of the Carborundum Co., Niagara Falls, New York. These glass contact refractories are 7.6-cm thick and are mounted in a stainless-steel secondary container lined with *Monofrax K* laying cement.

The primary stainless-steel container is 76-cm wide, 60-cm deep, and 33-cm high. The secondary container is placed on a 12.7-cm base of ceramic fiber insulation in the primary container. The ceramic fiber insulation between the side walls of the containers varies from 11.5-cm to 15.2-cm in thickness.

A resistance-heater hood with three silicon carbide heaters is mounted on the back edge of the primary container. An insulated operating hood is mounted on the front of the primary container. Both units are hinged so one hood or the other can be positioned above the chambers by a simple pivot motion. An air-cooled feed tube is mounted in the operating hood and receives the simulated calcined waste and frit from a specially designed feeder unit that delivers ~20-g aliquots of feed material at time intervals from one to sixty minutes (Figure 3).

Startup Technique

Overhead silicon carbide resistance heaters are used for startup and for restart. It is necessary to melt the glass charge between the electrodes before the glass can become conductive and self-heating. This initial heating is done with a separate power supply which allows the resistance heaters to heat the ceramic refractory bricks and the glass charge (premelted glass frit) slowly to a temperature at which the melt becomes electrically conducting. When this joule-heating becomes self-sustaining, the resistance heaters are turned off and allowed to cool.

The resistance-heater hood is then removed and the operating hood is placed over the chambers. This insulated hood reduces heat losses from the melter and provides a mounting for the air-cooled feed tube. This is shown in Figure 3.

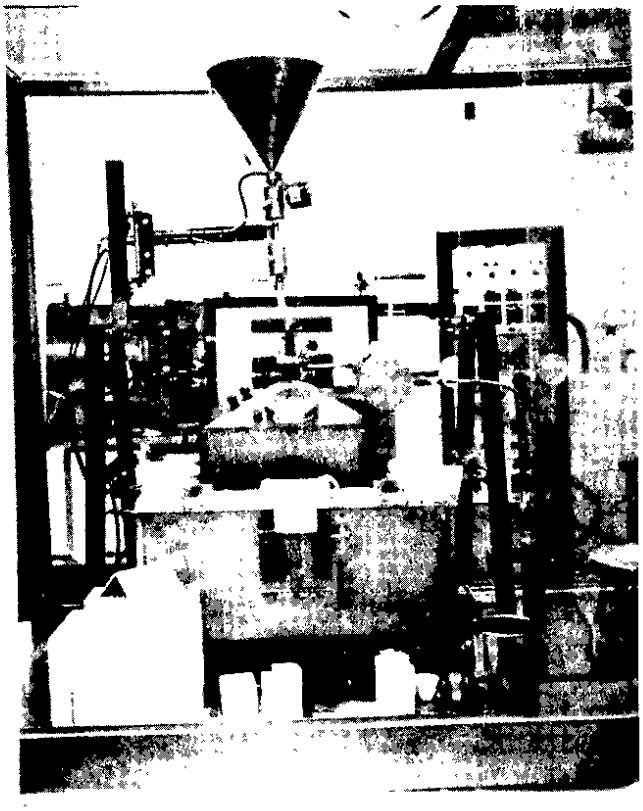


FIGURE 3. Small-Scale Joule-Heated Electric Melter

Both the melt chamber and the pour chamber (Figure 2) are slowly brought up to operating temperatures. The specially designed feeder is positioned over the feed tube, and the melter is ready to operate as a continuous pouring unit.

Melter Control and Operation

Maintaining constant current has proved to be a satisfactory method of control for the system. Constant current is maintained by a phase-angle-firing, silicon-controlled-rectifier (SCR), power unit. This power unit is controlled by a manually-adjusted current control and a manually-adjusted power control. The power control alone is not effective because of the low amount of power drawn by the unit.

The power requirements of the small melter depend on its heat losses. Compared to a large melter, where heat lost to the glass product is a large factor, virtually all the heat loss of the small melter is to its surroundings. Therefore, additional refractory material was placed around the glass-contact refractory. The insulation helped to prevent thermal shock to the ceramic bricks and also reduced the current density on the electrode.

Power to the small melter is supplied by a 480-volt 3-phase transformer that has a 208-volt 2-phase output. The two output single phases are isolated from each other and from ground. During normal operation, 2.3 kW are required to maintain the 2500 g (5.5 lb) of glass in the main chamber at 1150°C.

Premixed feed is loaded into the hopper above the melter. Aliquots of feed are delivered to the melt surface in the main chamber at pretimed intervals by a pair of air valves. The molten glass passes through a channel (throat) in the brick into the pour chamber. The glass rises and is poured into stainless steel beakers by tilting the melter. Filled beakers can be slow-cooled in the brick fort beside the melter (Figure 3).

For all tests using glass frit, the frit was ground finer than 10 mesh (2 mm), except for the August, 1977, PNL feed which was finer than 100 mesh (150 μm). The amount fed depended on the dryness and particle size of the feed. In general, material larger than 10 mesh (1.7 mm) clogged the hopper outlet and the air valves. Material finer than 10 mesh did not clog the hopper and gave the most reproducible results.

Melter Performance

The melter has been in operation for 18 months. Three shutdowns have occurred during this period; once due to a power failure, and twice for electrode replacement and changing the power transformer unit. Current leakage between the chambers through the channels was inferred by temperature variations of the glass in the chambers and by current readings on the electrode input leads. Serious electrode damage twice caused shutdown of the melter. Erosion in the channels between the chambers was greater than would be expected from normal erosion due to glass flow. The electrode damage and extraordinary erosion were attributed to this current leakage. A new transformer was installed and repairs were made to the melter. Since the unit was restarted, no apparent current leakage has been detected from input current readings, and the glass temperatures have been evenly distributed across the chambers. The constant-current controls maintain a glass temperature within ten degrees of the desired temperature at all times. The temperatures on the air-

cooled outer shell of the melter range from 80 to 120°C. All design changes in this melter have been incorporated in a second melter that was installed in the SRL High-Level Caves to vitrify samples of actual SRP waste.

Feed Delivery

The rate at which feed is delivered to the melt surface (as measured by the average weight of the aliquot) is a good relative indication of the ease of handling solids. The feed delivery rate depends on sludge composition, frit particle size, and feed dryness. Sludges high in iron content, or finely ground frit, or undried material all reduce the feed delivery rate.

Data Handling

Melting rates were determined by measuring the rate of feed addition (g/delivery) and dividing by the time required for disappearance of the batch into the melt and by the surface area utilized for melting. A melting rate less than 0.93 g/(cm^2-hr) implies a residence time greater than the ∿20 hours currently specified in the reference process. Thus, lower melting rates are undesirable.

The foam factor, an empirical measure of foam persistence defined for this work, is a useful measure of foam stability. This parameter characterizes foam behavior in terms of the time required for the melt surface to be free of foam after an aliquot of feed is added to it. This time is usually about twice the time used in determining the melting rate. The foam factor is derived from this by dividing by the weight of the batch, and has units of minutes/gram.

FOAMING OF GLASS MELTS

Large-Scale Glass-Melting Tests (PNL)

In August, 1977, the first full-scale electric melting tests with simulated SRP waste were performed at Battelle-Pacific Northwest Laboratory (PNL). A second series of tests was performed in March, 1978. Several problems were identified in these tests.

- Feed on the melt surface sometimes formed a persistent foam.
- Melting rates were lower than expected from vitrification tests with power reactor wastes.

- After extended maintenance of temperature at 900°C ("idling"), the glass devitrified in the pouring section of the melter, restricting flow.

- A layer of ferrite-spinel crystals formed on the melter bottom.

- After further idling, the glass foamed when reheated.

For the initial test, it was assumed that eluted cesium (obtained from the ion exchange column in the salt decontamination step) would be mixed with the washed sludge as a concentrated sodium carbonate solution. Thus, 85% of the sodium content of the final glass was removed from Frit 21 (the reference glass composition).[10] The resultant frit, Frit 21-A (Table 1), was mixed with sodium carbonate and uncalcined simulated average sludge (Table 2). This material formed a very persistent foam on the melt surface. This foam plugged the pouring section and the line to the canister. The melting rate was very low: 250 to 500 kg (500 to 1000 lb) per day.

The second test substituted the batch chemicals that comprise Frit 21-A for the premelted frit. Although some foaming was noted, the melting rate increased to at least 1500 kg (3000 lb) per day. After the test, the melter was allowed to cool to ~900°C. After being held at this temperature for approximately 6 weeks ("idling"), the pouring section was found to be plugged by needle-like crystals (later identified as sphene, $CaSiTiO_5$), probably from devitrification of the glass. Subsequently, a 5-cm (2-in.) thick layer of ferrite-spinel crystals was found at the bottom of the melter after about 8 weeks of idling. When the melter was reheated to operating temperature, a foam formed which plugged the off-gas line.

A second series of tests at PNL, designed to investigate the foaming problem further, was completed in April, 1978. For these tests, the added amount of sodium carbonate from salt decontamination was assumed to be 70% of the sodium content of the final glass. The resultant glass-former composition, Frit 21-B (Table 1), was added as a premelt frit in one test, and as batch chemicals in two other tests. In two subsequent tests with Frit 21-B, TiO_2 was deleted to determine its influence on the foaming behavior. A test was performed with unmodified Frit 21 for comparison. For these tests, simulated composite sludge (Table 2) was used. The final test in this series used simulated composite sludge precipitated at SRL, calcined at PNL, and melted with Frit 21-B. This sludge was later found to be ~30% deficient in sodium. Only the last batch foamed excessively.

TABLE 1

Composition of Frits

Component	Frit Designation				
	21	*21-A*	*21-B*	*21-BX*	*411*
SiO_2	52.5 wt %	62.3 wt %	60.4 wt %	68.3 wt %	58.3 wt %
Na_2O	18.5	3.3	6.3	7.1	12.5
B_2O_3	10.0	11.9	11.5	13.0	11.1
TiO_2	10.0	11.9	11.5	-	-
CaO	5.0	5.9	5.7	6.4	5.6
Li_2O	4.0	4.7	4.6	5.2	12.5

TABLE 2

Composition of Simulated Sludges

Component	Sludge Designation			
	High-Iron	*Average*	*Composite*	*High-Aluminum*
Fe_2O_3	71.6 wt %	48.9 wt %	33.7 wt %	6.1 wt %
Al_2O_3	6.5	29.0	49.4	87.6
MnO_2	4.8	13.1	11.0	5.0
CaO	4.9	3.4	3.5	0.4
NiO	12.2	5.6	2.4	0.9

After the first test in the series, probing of the melter showed that the ferrite-spinel slag on the melter bottom had virtually disappeared. However, after the last test, a slag layer was again observed. The PNL tests with compositions equivalent to Frit 21 are summarized in Table 3.

TABLE 3

Tests in Large-Scale Equipment at PNL

Test	*Glassformers Added As:*	*Sludge Form*[a]
August, 1977	Frit 21-A + Na_2CO_3; chemicals-high carbonate	Uncalcined chemicals
March, 1978-1	SiO_2, Na_2CO_3, H_3BO_3, TiO_2, $CaCO_3$, Li_2CO_3; chemicals-high carbonate	Uncalcined chemicals (hydroxides, carbonates)
2	Same	Calcine
3	SiO_2, Na_2CO_3, $Na_2B_4O_7$, TiO_2, $CaSiO_3$, LiOH; chemicals-low carbonate	Calcine
4	Frit 21-B + Na_2CO_3	Calcine
5	Frit 21	Calcine
6	Frit 21-B + TiO_2 + Na_2CO_3	Calcine
7	Frit 21-BX + Na_2CO_3	Calcine
8	Frit 21-B + Na_2CO_3	Calcine

[a]The August, 1977, Test used simulated average sludge. The March, 1978, Tests 1 through 7 used simulated composite sludge. Test 8 used a mixture of composite and average sludge prepared at SRL.

Small-Scale Simulation of PNL Tests (SRL)

To study problems such as those found in large-scale tests, a small continuous melter was designed and fabricated at SRL. Samples of the feed used at PNL [Frit 21-A (~100 mesh) + Na_2CO_3 + 27.5 wt % average sludge] were fed to the SRL melter (Table 4). Excessive foaming severely limited the melting rate of this composition. The foam layer above the melt was ~5-cm (2-in.) thick. The observed melting rate was 1.55 g/(cm^2-hr) which was equivalent to 390 kg (860 lb) per day in the PNL melter. The rate observed at PNL was ~250 to 500 kg per day. A slag layer also formed on the bottom of the SRL melter.

The SRL melter was usually fed with 10 mesh (1.7 mm) frit rather than the 100 mesh (150 μm) frit from PNL. For comparison of test results, a test was also made in the SRL melter with PNL calcine and 10 mesh frit (Table 4). The melting rate decreased by a factor of 3.7 (compared to the -100 mesh PNL feed), and the foam above the melt persisted over twice as long. A similar test was done with simulated average sludge made at SRL. This composition also foamed excessively (Table 4).

TABLE 4

Simulations of August, 1977, PNL Test

Feed[a]	*Melt Temp., °C*	*Foam Factor*[b]	*Melting Rate, g/(cm²-hr)*
PNL feed (100 mesh frit)	1150	3.0	0.57
	1180	0.5	1.61
PNL sludge + 10 mesh frit[c]	1150	6.8	0.14
	1180	2.3	0.53
SRL sludge + 10 mesh frit[c]	1150	2.0	0.51
	1180	1.0	0.76

[a]All feeds were 27.5 wt % average sludge, and the equivalent of 72.5 wt % Frit 21, made from Frit 21-A and sodium carbonate.

[b]*An empirical measure of foam persistence (see text).*

[c]See text.

Several of the tests done in March, 1978, at PNL were also simulated at SRL. The results are listed in Table 5. In all cases, the foam factor* was less than 1, indicating that foaming would not be a problem. As already mentioned, foaming was observed in only one test with these melts at PNL. The initial batch (Test PNL-2) foamed copiously at startup. However, the slag layer present at the bottom of the melter when this test began probably contributed to this.

Tests with Average Sludge

Melts containing average sludge were made at 1150°C. As the data in Table 6 show, the foam factor and melting rate clearly depend on the amount of sodium carbonate fed to the melter. However, reduction of the sludge loading from 27.5 wt % to 25 wt % did not greatly affect the melting rate. Increase of the temperature from 1150 to 1180°C increased the melting rate and decreased the foam factor for all melts. This points out the importance of melting at a temperature where no crystalline phase will exist in the melt. The batches containing sodium carbonate were much more sensitive to temperature than the batch that contained Frit 21 (no sodium carbonate).

*An empirical measure of foam persistence. For definition, see section below entitled "Data Handling."

TABLE 5

Simulations of March, 1978, PNL Tests

Test[a]	*Melt Temp., °C*	*Foam Factor*[b]	*Melting Rate, g/(cm²-hr)*
PNL-2	1150	0.9	0.50[c]
PNL-3	1150	0.9	1.29[c]
	1180	0.4	1.61[c]
PNL-4	1150	0.4	1.2
	1180	0.3	1.3
PNL-5	1150	0.2	14.3
	1180	0.2	17.4
PNL-6	1150	0.7	1.63
PNL-7	1150	0.3	2.60
PNL-7[d]	1150	0.4	3.22
Frit 21 alone	1150	0.1	33.2

[a]All tests contain 25 wt % simulated composite sludge, except the last one.

[b]An empirical measure of foam persistence (see text).

[c]Feed rate very low, which probably limited the melting rate.

[d]Feed contained Frit 21-BX + sodium carbonate, adjusted to maintain same frit-to-sludge ratio as other tests.

TABLE 6

Tests with Melts Containing "Average" Sludge

Frit Form	*Sludge Amount*	*Melt Temp., °C*	*Foam Factor*[a]	*Melting Rate, g/(cm²-hr)*
Frit 21-A + sodium carbonate (85% Na_2O from Na_2CO_3)	27.5	1150	2.0	0.51
		1180	1.0	0.76
Frit 21-B + sodium carbonate (70% Na_2O from Na_2CO_3)	27.5	1150	2.2	0.81
		1180	0.7	1.38
Frit 21 (no sodium carbonate)	27.5	1150	0.8	6.70
		1180	0.6	8.06
Frit 21-B + sodium carbonate	25	1150	2.2	0.81
		1180	0.7	1.29

[a]An empirical measure of foam persistence (see text).

The compositions of the frits and simulated sludges are listed in Tables 1 and 2. Frits 21-A and 21-B are modifications of the reference frit, Frit 21, to which sodium carbonate would be added to form Frit 21 melts. Frit 21-BX is a further modification of Frit 21 in which TiO_2 is omitted.

Feeds containing sodium carbonate quickly spread across the entire melt surface with a great deal of frothing. Feeds without sodium carbonate stayed in a conical pile (angle of repose ~30° from the horizontal, ~5 cm (2 in.) across at the base). Because uniform coverage of this area is assumed, the calculated melting rates are biased toward low (conservative) values.

The feed delivery rate decreased as the ferric oxide content of the sludge increased (Table 7). This was probably due to moisture sorption, because drying the feed increased the feed delivery rate significantly (Table 8). Using a small frit particle size reduced the feed delivery rate by up to 35%.

TABLE 7

Effect of Sludge Composition on Feed Delivery

Sludge[a]	*Iron Oxide, wt %*	*Feed Delivery Rate, g/aliquot*	
		Frit 21	*Frit 21-B + Na_2CO_3*[b]
High-Iron	71.6	17.6	17.6
Average	48.9	21.9	19.8
Composite	33.7	23.5	21.2
High-Aluminum	6.1	24.3	26.3

[a]All glass feed compositions were 75 wt % glassformer and 25 wt % sludge; frit was 10 mesh (1.7 mm). See Table 2 also.

[b]Equivalent glass composition to Frit 21 + sludge.

TABLE 8

Effect of Frit Dryness and Particle Size on Feed Delivery

Sludge	*Frit Particle Size*	*Dried?*	*Feed Delivery Rate, g/aliquot*
High-Iron	-10 mesh	No	17.6
		Yes	20.2
Average	-10 mesh	No	21.9
		Yes	23.1
Composite	-10 mesh	No	23.5
	-50 mesh	No	20.5
	-100 mesh	No	15.3

[a]All feeds contained 75 wt % Frit 21 and 25 wt % of the indicated sludge.

Foam Persistence

In general, foam persistence depends on three factors:[11]

(1) The temperature. Foam persistence decreases with increasing temperature.

(2) The composition of the gas and the glass. These will determine the surface tension of bubbles; however, they have not yet been fully investigated for SRL waste glasses.

(3) The viscosity of the liquid. As the viscosity increases, so does the foam persistence. Thus, high-aluminum-sludge glass produced the most persistent foam (Table 9).

TABLE 9

Effect of Sludge Composition on Foam Persistence

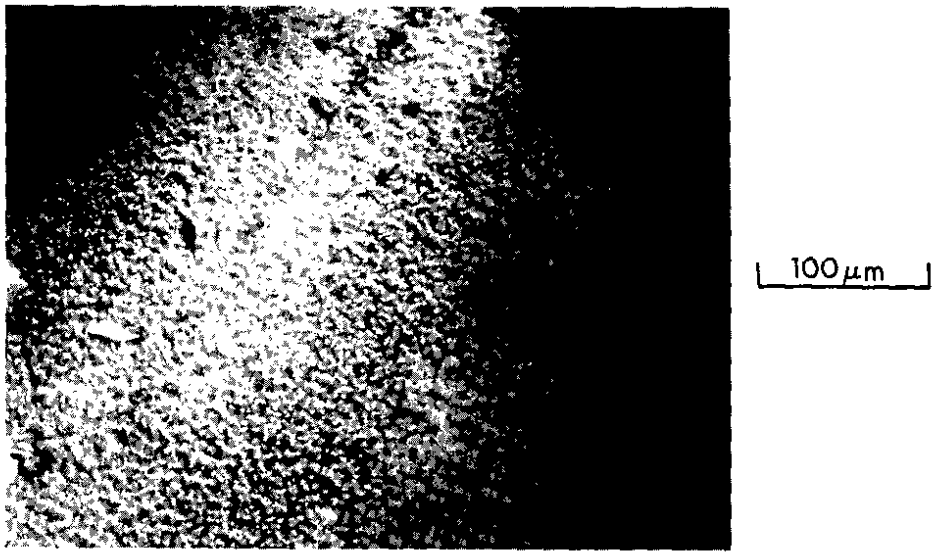
Sludge[a]	*Melt Temp., °C*	*Foam Factor*[b]	*Melting Rate, g/(cm²-hr)*
Composite	1150	0.4	1.22
	1180	0.3	1.24
High-Iron	1150	0.8	1.55
	1180	0.5	1.61
High-Aluminum	1150	2.6	0.67
	1180	1.1	0.90
Average	1150	2.2	0.81
	1180	0.6	1.29

[a]All melts contained 25 wt % of the indicated sludge, and the equivalent of 75 wt % Frit 21, made from Frit 21-B and sodium carbonate.

[b]An empirical measure of foam persistence (see text).

Only high aluminum or average sludge-glasses with Frit 21 (or equivalent compositions) produce persistent foams at 1150°C. Persistent foams reduce the melting rate. Foam persistence is primarily a viscosity/temperature effect. The foam persistence of average-sludge melts increases with increasing sodium carbonate content of the feed. The foam persistence in average-sludge melts is caused by the presence of ferrite-spinel crystals which increase the effective viscosity of the molten liquid in the foam.

During the early melting stages of feeds containing Frits 21-A or 21-B, the main liquid phase in contact with the sludge is molten sodium carbonate. Photomicrographs of actual foam samples (Figure 4) from PNL show a fine crystalline material dispersed in a (gray) glassy matrix. At bubble interfaces (Figure 4b), these small crystals have ripened into ferrite-spinel crystals containing Fe, Ni, Ca, Ti, Mn, and Na. Christie, Darnell, and Dustin,[12] and Yosim[13] observed extremely rapid reactions between sodium carbonate and ferric oxide to form a ferrite spinel ($Na_2Fe_2O_4$). At 840°C, they found the reaction to be complete in two seconds; at 1050°C, to be complete in 25 ms. These authors have further shown that the solid reaction product is only very slightly soluble in sodium carbonate (~20 ppm).



a. Bubble surface.

b. Intersection of bubble and surface.

FIGURE 4. Foam Samples from August, 1977, Test at PNL

Previous studies of the rheological behavior of SRP waste glasses showed that the ferrite-spinel crystals can cause glass melts to become non-Newtonian, pseudoplastic fluids.[14] For the very low shear rates in the glass melter, these crystals would greatly increase the effective viscosity. Although high-iron sludge melts are more likely to form such crystalline phases, the apparent viscosity of a high-iron sludge melt should be, at most, half that of an average sludge melt at the same shear rate and sludge loading.[14]

Effect of Sludge on Foam Persistence

Melting rates and foam factors of melts containing 25 wt % of each sludge and 75 wt % Frit 21-B + sodium carbonate were measured. In all cases, as the temperature increased, the foam factor decreased.

Qualitatively, the foam from Frit 21-A batches was incorporated into the melt by a different mechanism than the foam from Frit 21 batches. Gas collected beneath Frit 21-A foam layers, then gradually escaped by finding breaks in the layer. Thus, Frit 21-A foams were almost exclusively incorporated into the melt by collapse of foam onto the melt surface and gradual dissolution. Frit 21 foams tended to form larger bubbles, which then drained into the molten liquid and ruptured. Thus, Frit 21-A foams were more stable because of the high apparent viscosity of the material around the bubbles.

For the batches with composite or high-iron sludge, the foam produced was incorporated into the melt primarily by bubble drainage and rupture. The foam from the average sludge melt at 1180°C also disappeared in this way. This is similar to the behavior of a soap film in water.

As Table 9 shows, however, the melting rate depended strongly on the foam factor only for average and high-aluminum sludge-melts. For both, the foams produced were observed to be very refractory, and were incorporated into the melt by bubble collapse onto the hot surface, rather than by drainage of bubbles and their eventual rupture. This indicates that the foam material was not fluid enough to flow back into the melt.

Possible Solutions to Foaming

This study indicates that there are several ways to reduce foaming.

Because the liquidus (temperature at which no crystals will occur) for the ferrite-spinel phase is ~1150°C, operation above this temperature should speed incorporation of this phase into the melt. As previously noted, increasing the temperature dramatically improved the rate of incorporation of the foam layer into the melt.

Use of another low-melting liquid with sodium carbonate might also speed the incorporation of the foam into the melt. It may dissolve the sludge oxides and/or reduce the viscosity of the melt. Scouting experiments showed that ferric oxide is rather soluble in molten sodium borate or boric acid (10 to 20 wt %). Both of these compounds melt at least 100°C below sodium carbonate.

Reducing the TiO_2 content of the glass does not reduce the amount of foam, but does increase the melting rate. The chemical interactions are complex, but TiO_2 stabilizes ferrite crystals in waste glasses. Elimination of TiO_2 from the melt and increasing the other frit components proportionately increases the melting rate. This increase is probably caused by the increase in the molar ratio of frit to sludge (i.e., there is more glass to dissolve the sludge, on a mole basis).

SLAG FORMATION

The tendency of a given batch to form a slag was determined by observing the precipitation of crystalline material at the pour spout. This is reported as a time, in arbitrary units. Longer times imply a reduced tendency to form slag.

The slag formed in both the small-scale and the PNL melters has been identified as primarily ferrite-spinel crystals in a glass matrix. The data indicated that slag forms as a result of exceeding the solubility of this crystalline phase in molten glass. Slag formation is increased by sludges high in iron, low temperatures in the melter, long residence times, and large amounts of sodium carbonate. In preliminary tests with a frit with increased solubility for ferrite spinel (Frit 411), no slag was observed.

Simulation of the August, 1977, PNL Test

When samples of the feed used at PNL (Frit 21-A + sodium carbonate + 27.5 wt % average sludge) were melted in the small-scale melter, a slag formed on the melter bottom after a volume of about one-third of the melter capacity had been added. This slag plugged the throat and pour spout, and restricted flow.

When the temperature in the melter was increased, bubbles were observed on the melt surface. Pure Frit 21 was then fed to the melter, which dissolved the crystalline material, permitting material flow again.

During the test, two effects were observed that indicated that a phase more conductive than the glass was being formed. As shown in Figure 5, the temperature profile of the melt had changed drastically. In the hottest regions of the small-scale melter, the temperature had dropped significantly while in the cooler regions, the temperature was almost unchanged. Also, the power input had decreased by 5 to 10%.

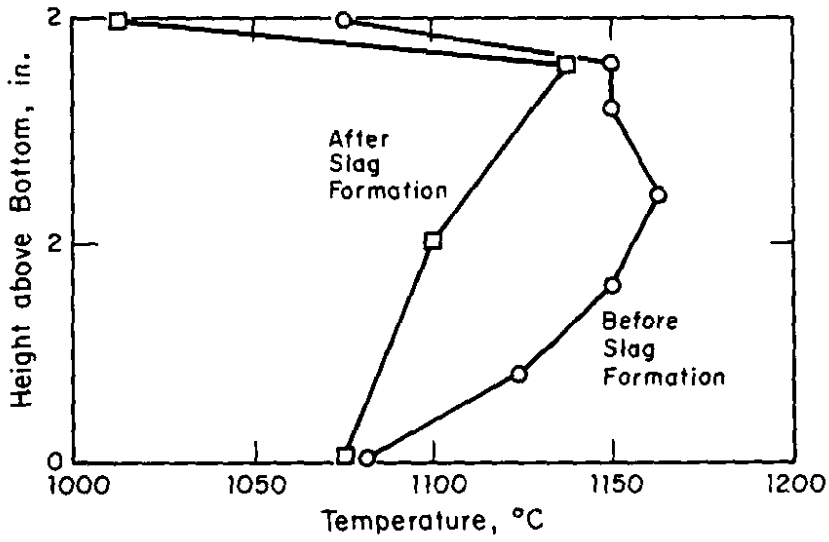


FIGURE 5. Effect of Slag on the Temperature Profile of the Small-Scale Melter

Samples of the slag were examined microscopically and by x-ray diffraction. The major phases present were ferrite spinels, of general formula MFe_2O_4, where M is any bivalent cation. Elemental analyses showed large amounts of Ca, Ni, and Ti, as well as iron. This same ferrite-spinel phase has been identified as the major component in slags produced during full-scale tests at PNL with simulated SRP sludges.

Effect of Sludge Composition

The time to form a slag from a batch containing 25 wt % of each sludge in Frit 21 is listed in Table 10. In each case, the

TABLE 10

Effect of Sludge Composition on Slag Formation

Sludge[a]	*Relative Time to Form Slag*
Average	1.0
High-Iron	1.2
Composite	5.0
High-Aluminum	>0.5

[a]All melts were made at ~1150°C with Frit 21 and a feed rate of ~2 g/min.

small-scale melter contained molten Frit 21 alone before starting the test. As the results show, average-sludge melts will form slags slightly faster than will high-iron sludge melts, even though high-iron sludge could form more ferrite spinel. Examination of the slag indicated that the particle size of the ferrite crystals from high-iron sludge was ~2/3 that of crystals from average sludge. Because settling velocities are proportional to the square of the radius of the particle,[15] this could explain the accelerated slag formation of average sludge.

Composite sludge formed a slag very slowly. However, when maintained at 900°C for 2 days, melts which had previously been slag-free formed a slag. Tests with high-aluminum sludge were terminated after ~1/2 melter capacity had been added, because of the slow melting rate of this material. No slag was observed.

Further tests were performed with average sludge because it produced slag most readily. The effects of sodium carbonate, temperature, and throughput were investigated.

Table 11 shows that removing Na_2O from the frit and adding it to the melt as sodium carbonate increased the rate of slag formation. The reaction between sodium carbonate and ferric oxide was shown previously to be involved in stabilizing foams produced above the melt. This reaction produces the ferrite spinel, $Na_2Fe_2O_4$.

TABLE 11

Effect of Sodium Carbonate on Slag Formation

Frit[a]	*Relative Amount of Sodium Carbonate Added*	*Relative Time to Form Slag*
21	0	1.0
21-B	70	0.75
21-A	84	0.6
21, 21-B, 21-A[b]	0 to 84	~2.0

[a]All melts contain 25 wt % average sludge and were melted at 1150°C unless otherwise noted.

[b]Melting temperature = 1180°C.

All the above tests were performed at 1150°C. When the batch was melted at 1180°C, slag formation decreased. Generally, average sludge melts formed slags at greater than one melter capacity, independent of the presence of sodium carbonate.

For all of these tests, the instantaneous throughput was 2 g/min. As the throughput decreased, slag formation accelerated for all Frit 21-sludge melts that formed a slag. Lower throughputs allowed the ferrite spinel more time to settle to the bottom of the melter.

Tests with Frit 411

A modified frit, Frit 411 (Table 1), which has greater solubility for ferrite spinel than Frit 21 was also tested. In preliminary tests of Frit 411 containing 25 wt % simulated sludge, no slag formation was observed even at processing temperatures as low as 1000 to 1050°C. In fact, slag deposits left from previous Frit 21 tests were partially dissolved by the Frit 411-sludge melts.

Mechanism for Slag Formation

All tests reported here indicate that slag formation is the result of exceeding the solubility of the ferrite-spinel phase in the molten glass. Generally, sludge-Frit 21 melts formed slags

more readily as the iron content of the sludge increased, and as the temperature decreased. The effect of throughput and the rapid slag formation shown by average sludge melts is probably due to sedimentation velocity differences. As the throughput is decreased, the residence time of the glass in the melter is increased, and more material can settle to the melter bottom.

The effect of sodium carbonate is probably also kinetic. Sodium carbonate reacts very rapidly with ferric oxide to form ferrite spinel ($Na_2Fe_2O_4$). This sequence should form more ferrite spinel than is formed in the absence of sodium carbonate, thus increasing the amount of undissolved material. An additional indication that this is occurring is provided by changes in power level during feeding. When no feed is being added, all Frit 21 melts consume the same power at constant current. When feeds containing little or no ferric oxide are added, the power level increases by 10 to 20%. However, when feeds containing average or high-iron sludge are added to the melt, an instantaneous drop in power is observed. Wiley[16] found that Frit 21 melts containing ferrite spinel had significantly lower resistivities than melts without this phase. Because power is proportional to resistivity, the power drop is probably indicative of ferrite spinel formation. The power drop is larger for Frit 21-B + sodium carbonate feeds when compared to Frit 21 feeds (12% compared to 6% decrease in power level).

In addition to the problem of pluggage of orifices by slag, the tests show another consequence of slag formation. The solubilities in borosilicate glass of most gases (particularly oxygen and carbon dioxide) decrease with increasing temperature. Thus, when glass is heated, it releases gas, or "reboils." A slag can act as a nucleating agent for bubble formation, leading to formation of a foam. In fact, in a common procedure for measuring gas evolution from glass, a refractory material is introduced into the melt and the subsequent bubble formation observed.[17]

Possible Solutions to Slag Formation

In general, decreasing the amount of undissolved material should reduce slag formation. There are several methods to do this:

(1) Reduce the amount of sludge to be incorporated in glass. Although probably not viable for routine use, both PNL and SRL have found that operation with Frit 21 alone (no sludge added) can eliminate previously formed slags.

(2) Increase the melting temperature. This increases the solubility of the slag "phase" in the glass.

(3) Eliminate sodium carbonate. This reduces the amount of material which must be dissolved, by eliminating the reaction between sodium carbonate and ferric oxide.

(4) Increase the solubility of the glass for slag by changing the frit composition. This probably explains the lack of slag formation with Frit 411.

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