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DESIGN AND OPERATION OF SMALL-SCALE GLASS MELTERS FOR IMMOBILIZING RADIOACTIVE WASTE

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Abstract - A small-scale (3-kg), joule-heated, continuous melter has been designed to study vitrification of Savannah River Plant radioactive waste. The first melter built has been in non-radioactive service for nearly three years. This melter has **Inconel®** 690 electrodes and uses **Monofrax®** K-3 for the contact refractory. Several problems seem in this melter have had an impact on the design of a full-scale system. Problems include uncontrolled electric currents passing through the throat, and formation of a slag layer at the bottom of the melter. The performance of a similar melter in a low-maintenance, radioactive environment is also described. Problems such as halide refluxing, and hot streaking, first observed in this melter, are also discussed.

INTRODUCTION

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

Processes for immobilizing 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 salt cake is redissolved and the salt solution is pumped from the tanks. Cesium and the trace amounts of soluble strontium and plutonium are then removed from this solution by ion exchange. The sludge phase is 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 fed to a joule-heated melter. In the melter sludge is mixed with glass formers (in the form of premelted frit) and converted to a borosilicate glass (Figure 1). The expected calcined waste composition and the possible variations in each component are shown in Table I.

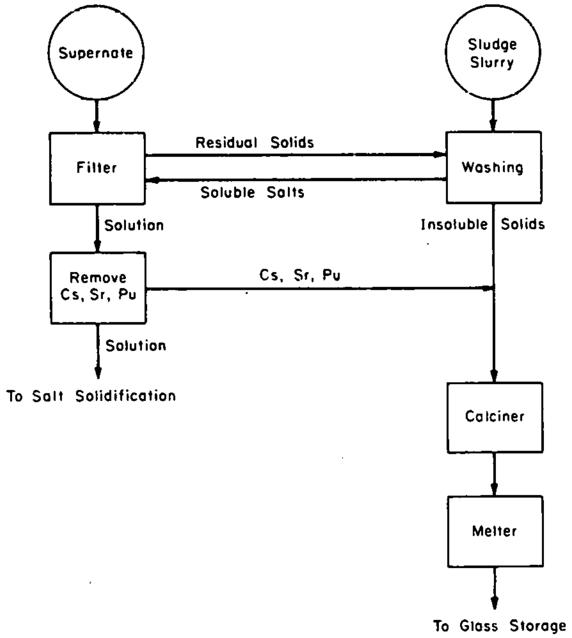


FIGURE 1. Reference Process for Immobilization of SRP Waste

TABLE I

Composition of Calcined SRP Waste*

Component	Amount wt % Average	Possible Range
Fe_2O_3	47	15-56
Al_2O_3	9	1-51
MnO_2	13	4-13
U_3O_8	4	0-13
CaO	4	1-6
NiO	6	2-10
SiO_2	1	0.4-2
Na_2O	7	4-7
Na_2SO_4	1	0.5-1.5
Zeolite**	8	8-9

* Major components only - waste will also contain small amounts of halides, fission products, and soluble salts.

** Used to remove cesium from supernate.

DESIGN OBJECTIVES

Small-scale melters are intended to evaluate basic design concepts for application to large-scale equipment and to study the glass-making process. Tests involve (1) varying glassformer and waste compositions, and (2) studying the durability of materials of construction that are subjected to various temperatures. Because of the inherent corrosiveness of waste glasses, the melter must be able to withstand rather harsh conditions. Since component failure must be expected, replacement of electrodes and other parts must be simple and rapid.

MELTER DESCRIPTION

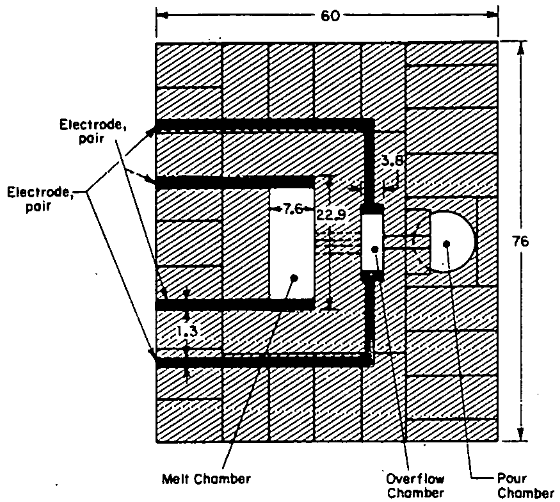
Plan and section views of the melter are given in Figure 2. Prominent features include the following:

- Both sets of electrodes are suspended from the top of the refractories and are power supplies; this allows operation of each chamber (melt and overflow) at different temperatures.

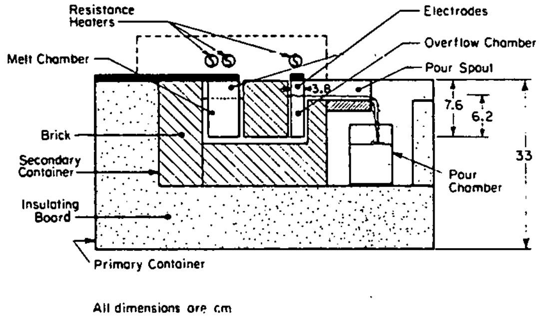
- An Inconel® 690 alloy (Huntington Alloys, Inc., Huntington, West Virginia) pour spout is mounted on the overflow chamber and protrudes into a separately heated pouor chamber. This pour chamber is 15.2 cm wide, 10.2 cm deep, and 15.2 cm high. Sample containers are placed in this chamber, and an insulating 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 provides 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 (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-heated 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 received the simulated calcined waste and frit from a specially designed feeder unit that delivers 20-g aliquots of feed material at time intervals of one to sixty minutes (Figure 3).



a. Plan View



b. Cross-Section View

FIGURE 2. Plan and Cross-Section Views of Melter

STARTUP TECHNIQUE

Overhead silicon carbide resistance heaters are used to start and restart the melter. The glass charge between the electrodes must be melted before it can become conductive and self heating. Power for initial heating comes from separate power supplies, 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 jouleheating 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. 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.

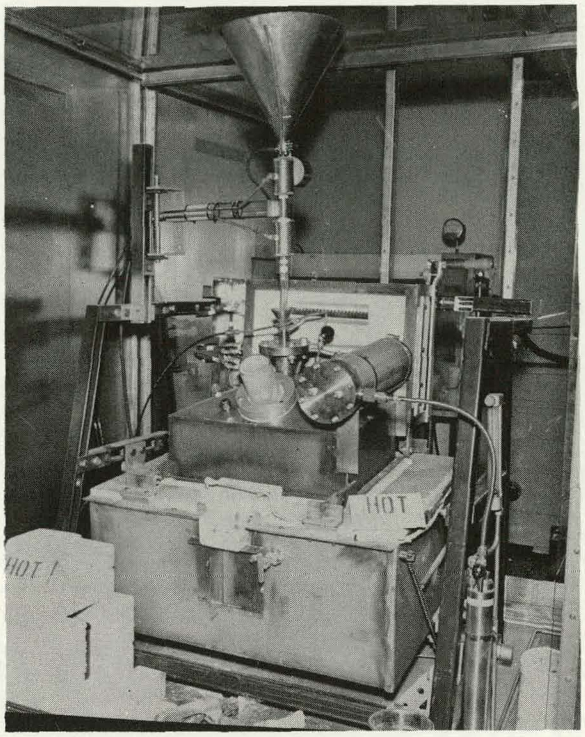


FIGURE 3. Small-Scale, Joule-Heated Electric Melter

MELTER CONTROL AND OPERATION

Maintaining constant current has proved to be a sastifactory 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. Power control alone is not effective because of the low amount of power drawn by the unit. The constant current control maintains a glass temperature that is within 10°C of the desired temperature at all times.

Power requirements of the small melter depend on heat losses. Compared to a large melter, where heat input 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. Temperatures on the outer shell of the melter range from 50 to 90°C.

Power to the small melter is supplied by a 480-V, 3-phase transformer that has a 208-V, 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).

MELTER PERFORMANCE

The melter described above has been in operation for 30 months. Four forced shutdowns have occurred during this period, three for replacing electrodes and one for replacing the power transformer unit. All electrode replacements occurred in the small pour chamber. The first shutdown occurred 10 weeks after startup, and was the most serious. One of the pour chamber electrodes was severed completely at the melt line and lost contact with the glass. The busbar arc discharged to the K-3 brick, and dug a trench 15 cm long and 18 cm deep. When the melter was emptied, severe wear was discovered at the throat, mainly toward the destroyed electrode. Before shutdown, large variations in the temperature across the melt chamber had been noticed. Current readings on the electrode input leads had indicated that current was leaking through the throat. After a transformer was installed and repairs were made to the melter, the melter was restarted. Since then, no apparent current leakage has been detected from input current readings, and glass temperatures have been evenly distributed across the chambers.

Since the restart that followed the transformer replacement, two more electrode failures have occurred. In both cases, gas evolution was observed at the electrode that ultimately failed. Each electrode was severed at the melt line, but discharge to the K-3 refractory was prevented by laying K grout on top of the brick.

Electrode failures resulted from electrolysis, which was caused by a DC potential from the SCR current controller. The potential necessary to cause gas (O_2) evolution was found to be a constant for a given glassformer composition and temperature. As Table II shows, the potential necessary for gas evolution increases as the alkali content of the glassformer decreases. Titania in the glassformer decreases this potential. However, an argon blanket above the melt greatly increases this potential, and might extend electrode life. In this case, the SCR current controller was modified to eliminate DC. For a large-scale application, this problem is best avoided by having the SCR on the primary side of the transformer.

During tests with waste compositions high in Fe_2O_3, a crystalline precipitate of $NiFe_2O_4$ formed a slag on the floor of the melter. This slag formation had two effects on melter operation. Power input at constant current dropped by as much as 20%. Also, the temperature profile of the melt changed drastically (Figure 4).

TABLE II

DC Potential Necessary for Electrolysis at 1150°C

Glassformer	Potential, V
Low alkali (Frit 21)	0.16
Same - TiO_2 (211)	0.22
High alkali (22)	0.12
Same - TiO_2 (221)	0.18
Very high alkali (411)	0.12
Low alkali with argon blanket	0.60

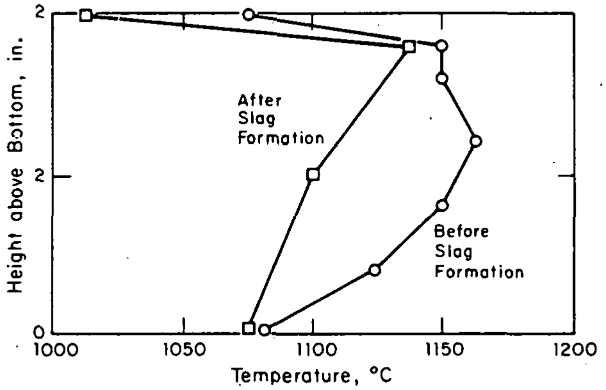


FIGURE 4. **Effect of Slag on the Temperature Profile of the Small-Scale Melter**

MELTER PERFORMANCE IN RADIOACTIVE SERVICE

A similar melter was designed and installed in the SRL shielded cells. All design flaws that were identified during the work described above were corrected in this melter. This melter has been used to vitrify actual waste, and to perform studies with waste components which cannot be conveniently investigated elsewhere.

One of the waste components which could potentially have great impact on waste vitrification is chloride. At any given time, the waste could contain up to 2 wt% chloride. Experiments with a waste-glass feed doped with NaCl showed that NaCl refluxes in the vapor space above the melter. After 7 days' exposure to chloride, an air-cooled feed pipe failed. However, the most startling effect was observed after these tests. The power to the melter at constant current dropped from 2000 to 1600 watts. The melt temperature had decreased from 1150°C to 1000°C. When a batch of feed was added to the melt surface, the power suddenly surged to 2000 watts. The melt surface appeared to be covered by a film which was disrupted by feeding. Although this surface layer could not be analyzed, presumably NaCl, and possibly Na_2SO_4, formed this insoluble layer on the melt surface. Because molten salts such as these have very low resistivities, even thin layers would preferentially carry current and consequently drop the melt temperature. This is analogous to hot-streaking with more conventional glass compositions. However, chlorides present in actual waste will not be as volatile as the NaCl and the phenomena noted here should not be as pronounced.

This melter operated in a radioactive environment for 12 months without requiring any major maintenance. The melter was subsequently removed from service and replaced by a similar melter.

IMPACT ON FULL-SCALE MELTER DESIGN

Studies using the small melters have significantly aided in defining the chemistry of waste vitrification. Phenomena such as foaming, reboil, slag formation, and product devitrification have all been clarified through use of this melter. Most of these studies have been reported elsewhere[10], and will not be discussed here. However, the small melters have also affected full-scale equipment design or process development.

One area where the small melters have had an obvious impact is that of material performance. The contact refractory, Monofrax® K-3, has performed well when not in the electrical firing path. Inconel® 690 electrodes have also performed well, when DC has been eliminated from the circuit. It must be noted here that direct current electrolysis apparently causes greater corrosion than does high AC current density.

Another area of impact is that of defining possible problems in the highly sensitive throat area. As shown earlier electrical firing through the throat can cause severe throat wear, and so is not being considered in current melter designs. Since slag formation could potentially plug the throat opening, the throat opening in present designs is several inches above the melter floor.

Finally, small melter studies (up to 0.25 m^2 melt surface area) can be used to size future full-scale equipment. We have found good correlation between area-specific glass production rates in the small melters and those in large-scale equipment[11]. Minimum residence times necessary for acceptable durability (as determined on small melters) are much shorter than expected. Continued study in this area appears to have great potential for development of optimal full-scale equipment.

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REFERENCES

1. R. M. Wallace, H. L. Hull, and R. F. Bradley. **Solid Forms for Savannah River Plant High-Level Waste.** USAEC Report DP-1335, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, S.C. (1973).

2. J. A. Stone, J. A. Kelley, and S. McMillan. **Sampling and Analyses of SRP High-Level Waste Sludges.** USERDA Report DP-1399, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, S.C. (1976).

3. J. A. Stone. **Separation of SRP Waste Sludge and Supernate.** USERDA Report DP-1414, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, S.C. (1976).

4. R. S. Ondrejcin. **Chemical Compositions of Supernates Stored in SRP High-Level Waste Tanks.** USAEC Report DP-1347, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, S.C. (1974).

5. R. F. Bradley, et al. "Solid Forms for Savannah River Plant Radioactive Waste." In **High-Level Radioactive Waste Management,** American Chemical Society, Washington, D.C. (1976). p9.

6. J. A. Stone. **Evaluation of Concrete as a Matrix for Solidification of Savannah River Plant Waste.** USERDA Report DP-1448, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, S.C. (1977).

7. J. A. Kelley. **Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste - Nonradioactive and Tracer Studies.** USERDA Report DP-1382, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, S.C. (1975).

8. J. A. Kelley. **Radioactive Studies: Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste.** USERDA Report DP-1397, E. I. du Pont de Nemours & Company, Savannah River Laboratory, Aiken, S.C. (1975).

9. G. H. Thompson. **Evaluation of Mineralization Processes for SRP Wastes.** USERDA Report DP-1389, E. I. du Pont de Nemours and Company, Savannah River Laboratory, Aiken, S.C. (1975).

10. M. J. Plodinec, **Vitrification of Savannah River Plant Radioactive Waste-Process Development Studies,** presented at American Ceramic Society Glass Division Fall Meeting. Bedford, Pennsylvania, October 11, 1979.

11. M. J. Plodinec, **Improved Glass Compositions for Immobilization of SRP Waste,** presented at Materials Research Society Annual Meeting, Boston, Massachusetts, November 26, 1979.