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Defense Waste-Vitrification Studies During FY 1980

W. J. Bjorklund

August 1981

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DEFENSE WASTE-VITRIFICATION
STUDIES DURING FY-1980

W. J. Bjorklund

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Pacific Northwest Laboratory
Richland, Washington 99352

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I. SUMMARY AND CONCLUSIONS

During FY-1980, Pacific Northwest Laboratory (PNL) tested three vitrification processes on simulated high-level radioactive waste typical of that stored or being produced at U.S. defense facilities. Processes tested included a spray calciner/in-can melter, spray calciner/ceramic melter and direct liquid feeding of a ceramic melter. Tests were made on pilot-scale as well as full-scale equipment. Over 16,000 kg of glass product were produced from 68,000 L of simulated waste. Several compositions were tested, and the glass products were evaluated. Emphasis was placed on determining the processing rates and the ability of the waste to be processed. Off-gas data were collected on several runs. Major conclusions drawn from this test program are divided into processing results, glass-product results, and general information.

The processing results center around conclusions concerning glass foaming, corrosion, glass-melting rates, slurry-feeding rates, and the operation of the spray calciner. Foaming of the waste-frit mixture occurred in all melting tests, but it was not as serious a problem in the in-can melter as it was in the ceramic melter. Glass foaming was caused by several factors including glass reboil (release of dissolved gasses), oxidation-state changes of the waste elements (primarily iron, nickel and manganese) and the quality of mixing of the calcine and frit. The addition of organic reducing agents to the waste feed reduced the foaming, but excess quantities of these agents will lead to metal precipitation in the glass. This precipitation is potentially more harmful in the ceramic melter; however, high concentrations of organics were handled satisfactorily.

Severe corrosion of the metallic and refractory materials of construction occurred when the ceramic melter was operated at temperatures greater than 1200°C, and the processing temperatures were subsequently limited to 1150°C.

Glass-melting rates of 85 kg/h to 100 kg/h ($>290 \text{ kg/h-m}^2$) were demonstrated with the spray calciner/in-can melter process while using 24-in.-dia cans and feeding wastes containing coal and EDTA. Rates of $>40 \text{ kg/h-m}^2$ were

achieved with the direct liquid-feed process using the ceramic melter. Slurry-feeding rates with the ceramic melter were boosted when using radiant heat from above the glass surface.

The spray calciner was operated at feed concentrations equivalent to 144 g of oxide/L.

The liquid-fed process produced the best quality glass product. Large canisters of glass showed more signs of surface cracking when the glass was poured into stainless steel canisters than when it was poured into carbon steel canisters.

Finally, we found that representative sampling of liquid-waste streams to the vitrification equipment was very difficult because of the quantity of large undissolved particles in the feed stream. Major emphasis will be placed next year on the development of direct liquid feeding with special emphasis on feed systems, off-gas systems as well as the performance of the melter.

II. INTRODUCTION

The immobilization of radioactive waste by forming it into a glass or vitreous form has been under study at PNL for several years. Many generic studies have been performed to investigate the wastes that would be generated from a fuel cycle needed for power reactors. The waste produced from defense-related activities has also been studied by PNL.

Since 1977 PNL has been working directly with the Savannah River Laboratory in their efforts to provide technology for a proposed Defense Waste Processing Facility at the Savannah River Plant in South Carolina. Pacific Northwest Laboratory has also been providing generic vitrification technology that is applicable to defense waste through programs sponsored at the Lead Site^(a) by the U.S. Department of Energy (DOE). During FY-1980 testing of vitrification processes using spray calcination/in-can melting, spray calcination/ceramic melting and direct slurry feeding to a ceramic melter was completed. Of primary concern at the start of the year was the effect of the mixing of components, either before or during vitrification, on the process and product. The spray calciner-ceramic melter was considered the "reference process" at the start of the year and the spray calciner/in-can melter was the backup. While direct liquid feeding was first considered only a promising alternative, it later became the reference process with the spray calciner/in-can melter as the backup. This report describes the results of those process tests using simulated defense-type wastes. The equipment and processes are also described, and brief summaries of the tests are included.

Since several processes were being tested simultaneously with each having an impact on the other's development, it was necessary to change the direction of the testing program many times to incorporate current development findings. The results of these tests were difficult to present in strictly a developmental or chronological order that would be easily understood. We attempted to present the data in such a manner so as to explain the development findings and their implications.

(a) Savannah River has been selected by DOE as the lead-site coordinator for all HLW programs.

III. PROCESS AND EQUIPMENT DESCRIPTION

The principle process equipment tested during FY-80 is described in this section. This equipment includes a spray calciner, an in-can melter and various joule-heated (electric) ceramic melters.

The spray calciner is used in conjunction with the melting systems as part of a two-step process for vitrification; however, it will be discussed as a separate operation for convenience. If glass is being made, the spray calciner has always been operated with an in-can melter or joule-heated ceramic melter. One objective during the year was to eliminate the need for the spray calciner in the vitrification process by using direct, liquid feeding of ceramic melters (see Section III.D).

The reader should be aware of the versatility of the equipment operated at PNL; melters primarily designed for one mode of operation are often used in other modes. For example the liquid-fed ceramic melter (LFCM) is often used to melt dry, feed mixtures when capacity data is needed. The description that follows depicts the equipment in the normal mode of operation.

A. SPRAY CALCINER

The spray calciner (Larson 1980) (Figure 1) consists of a spray chamber, cone section, furnace, vibrators, and off-gas filter assembly. Atomized waste feed is sprayed into the top center of the spray chamber, which is a vertical cylinder externally heated by a concentric, cylindrical furnace. The high velocity at which the atomizing air and waste-feed droplets enter the spray chamber, in addition to the temperature difference between the chamber wall and the evaporating water droplets, creates a high degree of turbulence in the calciner. The combination of this violent convective-heat transfer, along with the radiant-heat transfer, allows drying and calcination of the liquid waste at a high rate.

After passing through the spray chamber, water vapor and atomizing air entrain a large percentage of the calcine particles. More than 99.9% of the entrained particulates are removed from the off gas by sintered-metal filters.

FIGURE 1. Full-Scale Spray Calciner

A periodic pulse of blowback air removes a layer of calcine that collects on the filters. This calcine then falls to the cone section and is discharged to a melter (either in-can or ceramic) along with the calcine that falls directly from the calcination chamber. All surfaces are sloped at least 60° from horizontal to avoid calcine accumulation by allowing the calcine to slide off the surfaces.

Although glass-forming chemicals called frit can be added with the waste-feed slurry, frit particles are normally added to the calciner cone section through an airlock valve. The airlock valve can be timed simultaneously with the filter blowbacks to obtain as much frit and calcine mixing as possible as the frit and calcine fall through the calciner cone into the melter below.

Two vibrators are mounted 180° apart at mid-height of the chamber. These vibrators are supported independently of the furnace to minimize vibration to the furnace elements and to the fire brick insulation. To assure that the calciner is kept free of calciner-powder buildup, each vibrator is usually actuated for 2-s pulses several times an hour.

Design features of the full-scale spray calciner are shown in Table 1 and Table 2. A spray calciner flowsheet for a typical vitrification process for defense waste is shown in Figure 2. This schematic shows the calciner coupled to a ceramic melter (see B below). The calciner can also be coupled to the in-can melter (see Section C). Two sizes of spray calciners were tested at PNL-- the full-scale unit described above and a smaller pilot-scale unit with similar features. A third laboratory-size unit is also available.

B. CALCINE-FED CERAMIC MELTER (CFCM)

The CFCM is an electric-heated glass melter designed to be coupled with PNL's full-scale spray calciner. In this mode, the bottom of the spray calciner is connected to the lid of the glass melter. The spray-dried and partially calcined, metal salts formed in the calciner and the glass-forming frit that is added to the calciner cone drop directly onto the surface of the molten glass in the melter below. This connection also enables the gases that accompany the melting process to vent back through the calciner to the off-gas system.

TABLE 1. Design Features of the Full-Scale Spray Calciner

<u>Design Features</u>	<u>Parameters</u>
<u>Calcination Chamber</u>	
Inside diameter, m	0.91 (36 in.)
Height, m	3.20 (10.5 ft)
Heat transfer area, m ²	9.15 (99.0 ft ²)
Material	310 SS
Wall thickness, cm	0.64 (0.25 in.)
<u>Furnace</u>	
Type	Electric Resistance
Number of zones	4
Length of zones, m	0.76
Zone power, kW	150
Heating elements	Kanthal 1-A
Maximum temperature	1000°C
Voltage	480
Phase	3
<u>Vibrators</u>	
Number	2
Type	Pneumatic, dry lubricant
Location	180° apart at midplane of chamber side
Model	Vibramight 1300 AC
Motive air pressure	40 psig
Manufacturer	Cleveland Vibrator Company

TABLE 2. Filter Design Features of the Full-Scale Spray Calciner

Filters	Pore Size (μm)	Filter Size	Filter Material Thickness, cm	Filter Material	Internal Support	Number of Filters	Surface Area	
Before 1/80(c)	10	5.1 cm in dia x 91.4 cm	0.32	316 SS	(a)	51	80.0 ft ²	7.44 m ²
	65	7.0 cm in dia x 91.4 cm	0.16	316 SS	(b)	34	73.4 ft ²	6.82 m ²
							153.4 ft ²	14.26 m ²
After 1/80(c)	10	7.0 cm in dia x 91.4 cm	0.16	316 SS	(b)	28	60.5 ft ²	5.62 m ²
	10	5.1 cm in dia x 91.4 cm	0.32	Inconel	(a)	3	4.7 ft ²	0.44 m ²
	40	7.0 cm in dia x 91.4 cm	0.16	316 SS	(b)	33	71.3 ft ²	6.62 m ²
							136.5 ft ²	12.68 m ²

(a) Internally supported by a solid 316 SS center rod.

(b) Internally supported by a perforated 316 SS cylinder.

(c) Due to corrosion (Dierks et al. 1980), the spray calciner filters were replaced 1/80. Since funding was not available to purchase filters of a more corrosion resistant material, stainless steel filters on hand were used as replacements. Three Inconel filters were installed to obtain future corrosion data on this material.

SPRAY CALCINER	
NORMAL OPERATING PARAMETERS	
@ FLOW CONDITIONS	
FILTER PRESSURE DROP	8-10 IN H ₂ O
CALCINER FURNACE POWER CONSUMPTION	(kW)
ZONE 1	90
ZONE 2	92
ZONE 3	55
ZONE 4	53
TOTAL	290
CALCINER BARREL TEMPERATURE	(°C)
ZONE 1	750
ZONE 2	755
ZONE 3	755
ZONE 4	800
CALCINER FURNACE TEMPERATURE	(°C)
ZONE 1	875
ZONE 2	875
ZONE 3	840
ZONE 4	840
CALCINER FILTER HOUSING TEMPERATURE	(°C)
UPSTREAM OF FILTERS	250
DOWNSTREAM OF FILTERS	240
CALCINER CONE TEMPERATURE	(°C)
DIRECTLY UNDER BARREL	230

		<div> <div>ATOMIZING AIR (A)</div> <div>SLURRY FEED</div> <div>FRIT</div> <div>AIR IN LEAKAGE (A)</div> <div>AIR BLOWBACK (A)</div> <div>CALCINE</div> <div>TOTAL OFF-GAS</div> <div>GLASS</div> </div>							
PARAMETERS	STREAM #	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
MASS FLOW kg/hr		174.8	323.7	50.4	21.9	1.97	19.6	502.8	70
VOLUMETRIC FLOW	SCFM	80			10	0.90		310	
	STANDARD liters/hr	1.36×10^5	300		1.70×10^4	1.53×10^3		5.28×10^5	
TEMPERATURE °C		AMBIENT	< 50	AMB	AMB	AMB	250	250	1150
PRESSURE	psig	30	12		0	40			
	inches H ₂ O VACUUM						5	5	5
SPECIFIC GRAVITY			1.08						2.6
VOLUMETRIC FLOW AT LISTED CONDITIONS	CFM	28.7			10.9	0.26		606	
	liters/hr	4.88×10^4	300		1.86×10^4	448		1.03×10^6	25
POWER INPUT	kW								55
COOLING LOSSES	kW								25

(A) AIR ASSUMED TO BE 79% N₂ AND 21% O₂ (BY MOLE OR VOLUME)

FIGURE 2. Spray Calciner/Ceramic Melter Flowsheet

Some of the salient features of the melter (Dierks 1980) can be seen in Figure 3. The melter is totally contained within a rectangularly-shaped Inconel-601[®] box about 205.7 cm x 155 cm x 114 cm (81 in. x 61 in. x 45 in.) in size. The melting tank directly under the calciner is about 117 cm x 71 cm x 89 cm (46 in. x 28 in. x 35 in.) and lies across one end of the containment vessel. Normally, the glass is about 30.5 cm (12 in.) deep in the tank with 18 cm (7 in.) of insulation under the melting-tank lid. The vapor space above the glass is limited to 40.6 cm (16 in.).

A massive Inconel-690[®] electrode is positioned at each end of the melting tank. These two electrodes are pressed tightly against the end walls and set on the melter tank floor. While glasses are effective insulators at room temperature, their electrical resistance decreases as the glass temperature increases until, in the range of 900^{°C} to 1200^{°C}, they become good electrical conductors. Thus, if the glass is first brought up to this temperature range by a startup technique, an electrical current will flow through the glass by applying an electrical voltage to the two, immersed, slab electrodes, and energy will be dissipated through the glass (as it is in any electrical conductor) by virtue of the joule-heating effect. By controlling the voltage applied to the electrodes, the current flow through the glass and the resultant glass temperature can be controlled.

Molten waste glass is very corrosive and tends to dissolve most metals and other materials of construction. Fuse-case refractories (ceramic-type materials) have excellent resistance to glass corrosion and are used to line melting tanks and molten-glass conduits. However, these linings have relatively poor thermal insulating properties and must be backed with other refractories. These other refractories do not need to be as corrosion-resistant as the lining refractories, but they should have better insulating properties.

As the mixture of spray-dried material and glass formers (frit) falls on the surface of the molten glass in the melter, the metal salts calcine completely to oxides and fuse with the glass formers into fluid-glass. As the

[®]Inconel-601 and Inconel-690 are registered trademarks of Huntington Alloys Division of the International Nickel Company, Inc., Huntington, West Virginia.

FIGURE 3. Calcine-Fed Ceramic Melter

glass level rises in the melter tank, molten glass from the floor of the melter flows through the underflow throat in the base of the wall and rises in a channel behind the melter wall. At the top of the riser section, the glass flows down the discharge trough and free-falls from the discharge lip to a receiving canister below. The receiving canister is coupled securely to the containment vessel of the melter with a short section of flexible, metal pipe to prevent air from leaking into the melter, which is normally operated at 12.7 cm (5 in.) of water vacuum.

C. IN-CAN MELTER

In addition to the ceramic melter, the spray calciner can be coupled to the in-can melter forming the spray calciner/in-can melter process (Larson 1980). This process shown in Figure 4 uses the heated-wall spray calciner to convert high-level liquid waste to a calcine. The calciner is coupled directly to the in-can melter, which is simply a sophisticated, pot furnace containing a waste canister as the melting crucible. The in-can melter is used to incorporate the waste oxides from the calciner with the glass-forming frit to produce a borosilicate-type glass. The glass-forming frit is added to the calcined HLLW through an airlock just above a diverter. The diverter or connecting section (Petkus 1981) is used to allow two in-can melting furnaces to be used; however, only one furnace was used at PNL. A gravimetric feeder is used to meter the frit at a rate proportional to the rate that calcine is being generated. No special calcine and frit-blending step is used. The off gas from the melter is vented back to the calciner filters through the same lines that convey the batch to the melter. Therefore, the diverter valve is designed to direct solids down one leg of the connector without shutting off the flow of gases coming up through the other leg. Load cells are used to monitor the canister filling.

D. LIQUID-FED CERAMIC MELTER

The liquid-fed process (see Figure 5) offers an attractive, (Brouns et al. 1980) simplified alternative in comparison to the other vitrification process for converting the high-level waste to glass. In the liquid-fed processes,

FIGURE 4. Spray Calciner In-Can Melter System

FIGURE 5. Liquid-Fed Ceramic Melter Process

frit is mixed with the liquid waste and the combined waste-frit slurry is fed to the melter. The slurry is then dried, calcined and melted continuously as it floats on the surface of molten glass. The need for a precalcination process is eliminated.

The LFCM (Figure 6) was specifically designed for liquid feeding. It is a joule-heated melter with two sets of Inconel-690 electrodes and a melting-surface area of 1.05 m^2 . Both sets of electrodes enter from the side of the melter and are completely submerged in the molten glass. The upper set of electrodes has twice the surface area of the lower set. This design allows for a large amount of the power to be dissipated near the melting-surface. The lower set of electrodes is used for power dissipation near the floor to raise the floor temperature. This location for the electrodes results in better convective mixing and reduction in the precipitation of insoluble crystals near the floor. This design of the electrodes also allows the use of only the lower set of electrodes to keep the melter in an idling state. By doing so, the exposed glass-surface temperature is lowered, which reduces heat losses and, more importantly, reduces off-gas volatility during idling.

During operation, the glass is continually pouring into a canister by way of an overflow system. Effluents are removed under vacuum through an off-gas treatment system that consists of an ejector-venturi scrubber, a condenser and a packed scrubber. The liquid-fed ceramic melter is fundamentally similar in design to the calcine-fed ceramic melter, and, in fact, the calcine-fed ceramic melter could be used for liquid feeding with minor modifications.

E. EXPERIMENTAL CERAMIC MELTER (ECM)

The experimental ceramic melter (see Figure 7) is a joule-heated ceramic-lined melter designed as a low budget, expendable melter useful in development and testing. This melter was also used to study the processability of different glass formulations before testing them in the larger equipment.

The ECM uses two pairs of cylindrical Inconel-690 rod electrodes at opposing ends of the melter cavity. The melter can, however, operate with any suitable electrode material obtainable in 2-in. rods. Pouring of the melt is

FIGURE 6. Liquid-Fed Ceramic Melter (LFCM)

FIGURE 7. Experimental Ceramic Melter

controlled either by a tilting mechanism or by inserting a platinum tube in the riser section that will airlift the melt from the cavity.

F. ADVANCED GLASS-FORMS MELTER (AGFM)

The advanced glass-forms melter (see Figure 8) is a joule-heated ceramic-lined melter originally designed as a hot-cell prototype. It has been used recently as a melter that is equipped to study advanced waste forms such as marbles. There are two electrodes in the main melter cavity, which are placed opposite each other at the ends of the cavity. The electrode design incorporates a cooling-matrix plane. Air is circulated through the planes horizontally to cool the electrode surface that is in contact with the molten glass. This feature should make it possible to operate the melt cavity at 1200°C and still maintain the electrode surface at 1050°C to avoid rapid, electrode oxidation. The design also incorporates "feet" similar to those in the calcine-fed ceramic melter that extend toward each other at the bottom of the electrodes. The feet reduce the distance between the electrodes and make it possible to get a higher current flow and a higher melt temperature on the cavity floor. This higher temperature should cause convection currents on the floor. There are also two sumps in the melter. One of the sumps has an electrode plate for joule-heating, which will maintain a higher temperature in this region. If sludge moves into the sump, the sludge can be airlifted into the receiving canister.

FIGURE 8. Advanced Glass-Forms Melter

IV. RUN SUMMARIES

Twenty major tests were performed in FY-1980 producing 16,658 kg of waste glass from over 68,000 L of simulated high-level defense-waste slurry. In addition 1843 kg of calcine were produced separately. These runs are listed in Table 3. Each run is further described later in this section. The reader will find it useful to refer to Table 3 when reading individual run discussions.

The first 16 experiments were operations in which the waste was calcined or calcined then vitrified. The last four experiments describe tests in which the liquid waste was vitrified directly. Runs 4, 7, 14, 18, and 20 were major tests where considerable data was taken and attempted demonstration of process reliability was made. Other runs were more scoping in nature and generally of much shorter duration.

The waste compositions for these tests are summarized in Table 4. The waste composition changed during the year as components were added once their behavior was better understood or for specific studies of compositions. The waste is representative of that presently stored at the Savannah River Plant located in South Carolina and is referred to as TDS waste in this report. The waste is somewhat different for calciner operations as opposed to direct liquid-fed melter operations, as it normally would not have glass formers added before calcination (see Table 3, column 5). When tests for direct liquid-feeding to a ceramic melter were made, the glass formers were slurried with the waste (see Table 3, column 6).

The glass-forming chemicals (frit) were designed as a processing frit only. Glass development is being refined by the sponsor of many of these tests.^(a) The frit used (called Frit-211) is a processing frit known to make a representative glass product that could be processed by all equipment units. However, the chemical durability of the frit, such as leach resistance, should not be viewed quantitatively but rather the leach rate of the processes should be compared. Further discussion of the leach rate is in Section V.

(a) Savannah River Laboratory, Aiken, South Carolina.

TABLE 3. Summary of Runs During FY-80

Run	Date	Equipment	Operating Time	Product Quantity kg of glass	Canisters	Liters of Feed	Rate	Purpose of Test	Comments
1	10/79	LFCM (powder fed)	27.5 h of feeding 37 h of foam recovery 8 h downtime	2480	two 24-in. cans		90 kg/h, 86 kg/ h-m ²	Determine rate with well-mixed powder feed (Calcine+frit)+ Cornstarch	Well-mixed Dry Batch TDS + Frit- 211
2	10/79	Full-Scale Spray Calciner	7 h		NA	1730 L	255 L/h	Demonstrate TDS + sodium metasilicate and cornstarch	Successful test at 17.25 g/L Na ₂ O·SiO ₂ ·5H ₂ O scaling at 35.51 g/L
3	10/79	ECM	5 h	30	NA	NA	5-7.5 kg/h 138 kg/h-m ²	Run composition from 2 above in melter	50% greater capac- ity than previous tests--no foaming or spinel
4	11/79	Full-Scale SC/CM	5 days 110 h	4220	3.5 @ 24 in. dia	19,180 L	257 L/h, 60 kg/h 214 L/h, 50 kg/h	Demonstrate improved mixing of frit and calcine	Run plagued by foaming-mixing, inconclusive, Na- metasilicate scaled up calciner
5	11/79	Pilot-Scale SC/ICM	6 h	81	One 8 in. dia	280 L	10 kg/h	Test coal and EDTA added to feed	Made excellent looking glass
6	3/80	Full-Scale Spray Calciner	3 h		NA	1000 L	~300 L/h	Determine maximum concentration to run in calciner	Demonstrated 144 g oxide/L, >2 times previous maximum
7	3/80	Full-Scale SC/ICM	3 days 33 h of feeding	2160	Two 24 in. dia no fins 7 ft tall	8000 L @ 100 g of oxide/L	242 L/h 75-100 kg/h	Melt @ 1050°C and 1150°C without fins and high organic con- tent	
8	3/80	ECM	6 h	59	NA		9.8 kg/h 181 kg/h-m ²	First test of high organic material in CM (from Run 7 above)	
9	6/80	AGFM	10 h	289	NA	NA	28-35 kg/h, 116-145 kg/h- m ²	Test of high organic feed in large ceramic melter (from 11 below)	No metal detected
10	7/80	AGFM	7 h	185	NA	NA	109-123 kg/h- m ²	Retest of 9 above	

TABLE 3. (contd)

Run	Date	Equipment	Operating Time	Product Quantity, kg	Canisters	Liters of Feed	Rate	Purpose of Test	Comments
11	5/80	Full-Scale Spray Calciner	100 h	1800 kg of calcine	NA	19,000 L	190 L/h ave.	Produce calcine/test rates at various temperatures	Demonstrated calcine rates from 400-700°C barrel temperature. Material contained Na ₄ EDTA, coal and cornstarch. 50 L/h shown to be the maximum rate at 400°C
12	3/80	Pilot/Scale Spray Calciner	8 h	33.6 kg of calcine/frit	NA	126L	10-20 L/h	First test of -200 mesh frit in feed to calciner	Successfully tested 100% frit in feed for short duration run
13	6/80	Pilot-Scale SC/ICM	6 h	26.7 kg of glass	One 8 in. dia w/fins	100 L	5 kg/h	First melter run with -200 mesh frit in feed. Did not indicate mixing was helpful in the SC/ICM	
14 A,B	8/80	Full-Scale SC/ICM		2085 kg of glass	Two 24 in. dia no fins	6660 L		Mixing experiments--first can sparged. 2nd frit in feed	
15	4/80	Pilot-Scale Spray Calciner	5 h		NA	100 L		Produce special calcines for process chemistry studies	
16	6/80	Pilot-Scale Spray Calciner	8 h	10 kg calcine	NA	200 L	25-30 L/h	Test N ₂ atomization and urea feed additive	
17	11/79	ECM (Liquid Fed)	12 h	20.4 kg of glass	NA	60 L	31 kg/h-m ² 5.5 L/h	Liquid feeding test with cornstarch additive	
18	1/80	LFCM	65 h total	1050 kg of glass	One 24 in. dia	2800 L slurry	38.1 kg/h-m ² 62 L/h ave.	First large-scale liquid feeding experiment. Over-feeding rate established as 105 L/h	
19	6/80-8/80	ECM					14-42 kg/h-m ²	Series of six short tests	
20	9/80	LFCM	5 days	3962 kg of glass	Two 24 in.	9400 L	38.8 kg/h-m ² to 57 kg/h-m ²	First test on rebuilt melter using lid heaters for boosting	
TOTALS				16,648 kg of glass, 1,832 kg of calcine		68,636L			

TABLE 4. Simulated Defense Waste Feed Compositions Used in FY-80

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Waste Constituent	kg's Required per 1000 kg's of Glass	Assumed Oxide Equivalent	kg's Oxide per 1000 kg's of Glass	Concentration Ranges for Calciner, g/L of Col (1)	Concentration Ranges for Direct Liquid Feeding ^(b) g/L of Col (1)	Equivalent Carbon, g/L	Normal Con- centration from Col (6), g/L
FeOH ₃	195.4	Fe ₂ O ₃	146.6	45.6 to 69.7	70 to 100.3		74.93
Al(OH) ₃ /Al ₂ O ₃ 3H ₂ O	49.0	Al ₂ O ₃	32.0	11.43 to 17.5	17.5 to 25.15		16.35
MnO ₂	39.0	MnO ₂	39.2	9.10 to 13.92	14.0 to 20.02		20.02
Ni(OH) ₂ /NiO 2H ₂ O	21.1/25.2	NiO	17.16	5.88 to 8.99	7.5 to 10.83		8.77
Ca(CO ₃) (12/wt% C)	17.8	CaO	10.02	4.15 to 6.35	6.4 to 9.14	1.10	5.12
Na(NO ₃) Na(NO ₂)	8.2	Na ₂ O Na ₂ O	2.97	1.91 to 2.93	2.9 to 4.21		1.55
-20+50 Mesh Anthracite Coal (65.4 wt% C)	8.1	CO ₂	---	2.17 to 2.89	4.16	2.72	---
Na ₂ SO ₄	4.0	Na ₂ SO ₄	4.01	0.93 to 1.43	1.4 to 2.05		2.05
C ₆ H ₁₀ O ₅ (cornstarch) (38.9 wt% C)	1.6	CO ₂ + H ₂ O	---	0.43 to 6.99	0.82 to 3.6	0.32	---
CsNO ₃	0.2	Cs ₂ O	0.40	0.071	0.283		0.204
RuNO(NO ₃) ₃		RuO ₂	0.17		0.204		0.086
Sr(NO ₃) ₂	0.2	SrO	0.16	0.071	0.166		0.081
Sb ₂ O ₃ (10 ² x Normal) ^(a)		Sb ₂ O ₃	0.15		0.079		0.079
SeO ₂ (10 x Normal)		SeO ₂	0.08		0.040		0.040
Cd(NO ₃) ₂ (10 ⁴ x Normal)		CdO	0.04		0.036		0.019
TeO ₂		TeO ₂	0.05		0.024		0.024
Zeolite ^(c)	29	SiO ₂	14.11	23.65 7.77 to 10.35	10.4 to 14.89		12.09
		Al ₂ O ₃	5.69				
		CaO	3.13				
		Na ₂ O	0.72				

TABLE 4. (contd)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Waste Constituent	kg's Required per 1000 kg's Glass	Assumed Oxide Equivalent	kg's Oxide per 1000 kg Glass	Concentration Ranges for Calciner, g/L of Col (1)	Concentration Ranges for Direct Liquid Feeding g/L of Col (1)	Equivalent Carbon, g/L	Normal Con- centration from Col (6), g/L
$\text{Na}_4\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2$ (d) (31.6 wt % C)	22.7	---		8.10	0 to 11.65	3.68	
Al_2O_3 4SiO ₂ H ₂ O (e) (Bentonite)		$\text{Al}_2\text{O}_3/\text{SiO}_2$			0 to 7.8		
NaCl	4.6	Na_2O		0 to 2.37(f)			
NaF	0.5	Na_2O		0.12 to 0.18			
Na_2O SiO ₂ 5H ₂ O		---		0 to 35.51			
SiO ₂		SiO ₂		1.45			
NaOH		Na_2O		0.61			
Na_2CO_3		Na_2O		0.05			
Glass Formers (Frit)	(720 total)				258 to 369.6		369.6
SiO ₂ - 58.3 wt%	419.76	SiO ₂	421.68	Glass Formers			215.47
Na_2O - 20.6 wt%	148.32	Na_2O	149.01	generally fed			76.14
B_2O_3 - 11.1 wt%	79.92	B_2O_3	80.30	as separate			41.03
CaO - 5.6 wt%	40.32	CaO	40.51	stream 193 to			20.70
Li_2O - 4.4 wt%	31.68	Li_2O	31.81	257 g/L			16.26
				equivalent			
TOTALS			999.98		(562 Ave.)	7.82 (1.5 wt%)	510.98

(a) Amounts increased for analytical detection purposes.

(b) Normally 1948 L of slurry = 1000 kg of glass.

(c) Linde IonSiv IE-95 defined composition: 80%
 $\text{CaAl}_2\text{Si}_4\text{O}_{12}$ 6H₂O, 20% $\text{Na}_4\text{Ca}_{1.5}\text{Al}_3\text{Si}_8\text{O}_{24} \cdot 8\text{H}_2\text{O}$

Actual Chemical Analysis:

CMPD	wt%
Al_2O_3	17.2
CaO	3.9
Fe_2O_3	4.0
MnO_2	0.1
Na_2O	4.4
SiO ₂	68.9
Other	1.9

(d) $\text{C}_2\text{H}_4\text{N}_2(\text{CH}_3\text{COO})_4\text{Na}_4$ = ethylene diamine tetrasodium acetate (Na_4EDTA).

(e) Optional additive used as suspending agent @ 2 wt% of product.

(f) Flowsheet value = 1.12 g/L.

A. CALCINATION-VITRIFICATION TESTS

Run #1--Calcine-Fed LFCM Run

This was a unique run in which previously produced calcine oxides^(a) were blended with frit and fed to the liquid-fed ceramic melter.

The objective of this run was to evaluate the use of a reducing agent added to a well-mixed blend of frit and calcine to overcome foaming conditions (Blair and Lukacs 1980) in the melter. The LFCM was used because it is the largest melter and could be fitted with a solids feeder to add the dry material. Previous runs were made to test the theory that a well-mixed blend of frit and calcine (without a reducing agent) would not foam; but the results were unfavorable. Laboratory- and small-scale tests had shown positive results when adding a reducing agent such as cornstarch to the melter feed. However, an excess addition of cornstarch has shown a tendency to precipitate metals in the small-scale tests, and a maximum amount needed to be determined.

Results of Run #1 were encouraging in that melting rates of up to 90 kg/h were achieved with the addition of cornstarch equivalent to 1.0 wt% of the resulting glass. Foaming was evident at levels less than 0.75 wt%; severe foaming occurred at 0.5 wt%.

This run also pointed out the need to keep the plenum temperature of the melter low enough so that the cornstarch would not burn at the surface. This temperature is particularly crucial during startup when the melter surface is molten glass. Initial overfeeding and the use of a N₂ purge to the plenum helped to establish a desirable cold-cap condition.

Significantly different melting behavior was observed with the addition of cornstarch as compared to runs without cornstarch. Previous tests had indicated a well-formed cold cap with venting of off gases around the periphery. This test did not show this behavior, which indicates that gases were released above the viscous layer and are passing through the cold cap.

Metal formation on the melter floor was not found following this test.

(a) The calcine for this material was produced offsite by a spray-drying vendor.

Run #2--Full-Scale Spray Calciner

The objective of this run was to improve the mixing of calcine and glass formers as they are combined in the two step calcination/melter process by introducing some of the glass-forming chemicals into the spray calciner feed. Increasing levels of sodium metasilicate pentahydrate ($\text{Na}_2\text{OSiO}_2 \cdot 5\text{H}_2\text{O}$) were added to the feed to determine the ability of the calciner to operate without the $\text{Na}_2\text{OSiO}_2 \cdot 5\text{H}_2\text{O}$ sticking to the walls. Cornstarch was also added to the waste to determine if significant carbon losses from burning in the calciner would occur as the cornstarch passed through the heated chamber. Should this test (Run #2) prove successful, future melting tests would be conducted using a frit depleted in equivalent amounts of Na_2O and SiO_2 .

Testing was successful with $\text{Na}_2\text{OSiO}_2 \cdot 5\text{H}_2\text{O}$ levels up to 17.25 g/L. At levels of 35.51 g/L, the $\text{Na}_2\text{OSiO}_2 \cdot 5\text{H}_2\text{O}$ was sticking to the calciner walls. Normally calcine-to-frit weight distribution is 28 wt%:72 wt%, but by incorporating 17.25 g/L of $\text{Na}_2\text{OSiO}_2 \cdot 5\text{H}_2\text{O}$ into the calcine, the distribution changes from 32 wt%:68 wt%. This change does not appear to be a significant improvement.

Run #3--Calcine Feeding to ECM

The objective of this run was to test the melting behavior of the calcine produced at PNL in Run #2 in a small-scale ceramic melter. If successful, this would be the composition used for a large-scale, five-day run with the full-scale spray calciner and ceramic melter.

The results were encouraging. The calcine-frit mixture was melted at rates up to 7.5 kg/h without any foaming. Previous runs at 5 kg/h in this unit had shown significant foaming.

Run #4--Full-Scale Spray Calciner Coupled to the Ceramic Melter

The objective of this experiment was to demonstrate improved operation of the coupled, calciner, melter system with the large-scale equipment, using information from feed mixtures tested in Runs #2 and #3. Improvements in feed mixing were to be accomplished by: 1) adding sodium metasilicate pentahydrate to the feed, 2) using smaller-sized frit than the normal -20+80 mesh (50% 40-100 mesh and 50% 100 mesh), and 3) introducing frit to the melter from a

position higher in the calciner so the frit would fall through the off-gas stream and become entrained with the calcine and hopefully provide better mixing of fine frit and calcine. Cornstarch (equivalent to 1 wt% of the glass product) was also added. The feed concentration to the calciner was equivalent to 75.4 g of oxide/L.

The aforementioned changes were not able to overcome the glass-melt foaming that was caused by unstable melter operating parameters (glass temperature, power-step changes, power control and cold-cap stability). On the second day of the test, the amount of cornstarch in the feed was increased to 1.5 wt% since foaming was not being reduced; this amount was also insufficient. On the third day, cornstarch was blended with the frit rather than putting it in the calcine feed. After the third day of testing, it was found that fouling of the calciner barrel by the sodium metasilicate pentahydrate was occurring, and the operation was switched back to the normal frit and feed compositions and methods of feeding.

In previous tests, foaming had been substantially reduced by the addition of cornstarch. Foaming in Run #4, however, could not be controlled. This lack of control could have been caused by the cornstarch igniting before reaching the melter cold cap, and/or melter operating conditions could have overwhelmed any effect the cornstarch had.

Considerable corrosion of the calciner filters and melter was noted after this run resulting in a shutdown and inspection of the system. This inspection was fully documented (Dierks et al. 1980).

Feed and frit compositions for this test are shown in Table 5, and calciner and melter operating parameters are shown in Figures 9 and 10.

The canisters of glass made from this run were core drilled and glass samples were subjected to leach tests. The range of radial and axial sample leach rates for 24-h soxhlet tests was 2.28 to 2.78 wt% loss. This is equivalent to $9 \times 10^{-5} \text{ g/cm}^2$ a day.

Samples leached in pH4 solution ranged from 21.8 to 90.2 wt% loss with an average of 49.4 wt% loss. The pH4 results showed great variations from the top

TABLE 5. Waste Compositions Used for Run #4

Makeup Chemical ^(a)	Sodium Silicate Composition	Normal Composition
	TDS 211-SS, kg/1000 kg of Glass	TDS 211, kg/1000 kg of Glass
Fe(OH) ₃	195.4	195.4
Al ₂ O ₃ 3H ₂ O	49.0	49.0
MnO ₂	39.0	39.0
CaCO ₃	17.8	17.8
NiO 2H ₂ O	25.2	25.2
NaNO ₃	8.2	8.2
Na ₂ SO ₄	4.0	4.0
Zeolite	29.0	29.0
Na ₂ OSiO ₂ 5H ₂ O	74.9	---
Cornstarch	10.0	---
NaCl	4.8	4.8
NaF	0.5	0.5
TOTAL	457.8	372.8
<u>Frit Component</u>		
SiO ₂	398.1 (58.8) ^(b)	419.8 (58.3) ^(b)
Na ₂ O	126.6 (18.7)	148.3 (20.6)
Li ₂ O	31.8 (4.7)	31.7 (4.4)
B ₂ O ₃	79.9 (11.8)	79.9 (11.1)
CaO	40.6 (6.0)	40.3 (5.6)
TOTAL	677.0 (100.0)	720.0 (100.0)

(a) Water--enough to make 4286 L of slurry

(b) Percent frit weight.

FIGURE 9. Calciner Operating Parameters Run #4

FIGURE 10. Ceramic Melter Operating Parameters Run #4

to the bottom of the canister. Leach rates were highest at the bottom where SiO_2 , Al_2O_3 and Fe_2O_3 were more concentrated.

Of interest from an effluent standpoint was the volatility of fluoride and chloride from the melter. Fluoride was not detected volatilizing from the melter. Chloride appeared to reach a solubility limit of 0.6 wt% in the glass while chloride concentrations in the calcine increased from 0.7 wt% to 5 wt% (average 1.83 wt%). Chloride appeared to accumulate in the melter system, possibly at rates up to 190 g/h, as material balances could not account for it leaving the system.

Table 6 shows anion analysis from off-gas samples taken during the run. The fluoride values appeared to be roughly that of tap water (~ 1 ppm), indicating either no fluoride contamination of the feed or low fluoride volatility. It was thought that fluoride might have contributed to the calciner/melter corrosion, but it did not appear to be significant. The glassware condensate samples did show chloride penetration of the calciner filters, especially at the beginning of the run, but it decreased as the run progressed. The venturi scrub solution samples showed chloride concentrations in the same range as the glassware concentrate (as expected). Most of the chloride was removed by the venturi and condenser as indicated by the low chloride concentrations in the downstream packed tower (see Figure 5 for off-gas schematic). The nitrate and nitrite numbers followed the same trends as the chloride numbers. The nitrate concentrations were high at the beginning and decreased as the run progressed. The venturi scrub samples were in the same range as the glassware samples, and most of the nitrate was removed before reaching the packed tower. The sulfate numbers show sulfate penetration of the filters, but it is not known whether it was as a particulate or as a SO_2 gas.

Table 7 shows chloride weight percentages in the calcine and glass. There is a high degree of variability in the calcine chloride concentrations. The average is 1.83 wt%. The glass chloride concentrations were low at the beginning of the run, indicating that the chloride may have volatilized from the melt during the idling period preceding the run. At the end of the run, the glass concentrations were constant at 0.6 wt%, while the feed concentrations continued to increase. These concentrations may indicate that the chloride

TABLE 6. Anion Concentrations from Off-Gas Sampling System During Run #4

Sample Type	Concentrations, ppm				
	F^{-} (a)	Cl^{-}	NO_2^{-}	NO_3^{-}	SO_4^{-}
Glassware condensate, 11/6/79	<0.44	124.0	---	710.0	8.3
Glassware condensate, 11/7/79	<1.5	15.0	---	8.6	36.0
Glassware condensate, 11/8/79	<0.47	4.0	7.9	2.5	9.2
Glassware condensate 11/9/79	<0.15	2.9	5.8	5.5	1.0
Venturi scrub solution, 11/5/79	<2.4	9.7	---	5.9	36.0
Venturi scrub solution, 11/7/79	<1.3	9.7	---	6.3	33.0
Packed tower scrub solution, 11/5/79	<0.17	0.35	0.5	0.19	1.2
Packed tower scrub solution, 11/7/79	<0.22	0.86	3.3	0.55	1.5

(a) Due to interference of a contaminant peak, the F^{-} values listed are approximate maximum values. Actual are probably 10 to 50% of the values listed.

solubility in the glass is limited to 0.6 wt%. The difference between the calcine and glass concentrations indicates that the chloride either accumulated in the calciner/melter or exited in the off gas. If no accumulation is assumed, then an average of 50.4 wt% of the chloride exited in the off gas. This does not agree with condensate analysis, however. If the chloride was in the off gas, the concentration of the condensate collected would have been 0.65 g chloride/L, but the analysis showed much lower values (~100 ppm).

Shown in Table 8 are results of additional gas samples taken downstream of the spray calciner filters and using the sampling system shown in Figure 11. As can be seen from the table, the noncondensable off-gas composition varies

TABLE 7. Chloride Concentrations in the Feed and Glass and Percent Difference for Run #4

Chloride in Calcine			Chloride in Glass			wt% (without frit)	% Difference
Date	Time	wt%	Date	Time	wt%		
11/5/79	0220	0.741	11/5/79	0330	<0.03	0.107	85.6
11/5/79	0730	0.647	11/5/79	0830	0.04	0.143	77.9
11/5/79	1300	0.741	11/5/79	1350	0.06	0.214	71.1
11/5/79	2145	0.706	11/5/79	2330	0.10	0.357	49.4
11/6/79	0200	0.823	11/6/79	0330	0.10	0.357	56.6
11/6/79	1000	0.706	11/6/79	0900	0.10	0.357	49.4
11/6/79	1400	0.894	11/6/79	1400	0.20	0.714	20.1
11/7/79	0015	0.941	11/7/79	0122	0.20	0.714	24.1
11/7/79	2000	0.706	11/7/79	2050	0.20	0.714	0.0
11/8/79	0621	3.76	11/8/79	0530	0.30	1.07	71.5
11/8/79	0840	3.65	11/8/79	0945	0.60	2.14	41.4
11/9/79	0005	4.47	11/8/79	2230	0.60	2.04	52.1
11/9/79	0200	5.06	11/9/79	0116	0.60	2.14	57.7
Average wt% dry		1.83	wt% w/o Frit			0.859	50.4

TABLE 8. Gas Samples From Run #4

Component (a)	Average Vol%	Standard Deviation	Air Vol%
CO ₂	0.073	0.045	0.052
O ₂	21.3	0.37	21.9
N ₂	77.2	0.64	77.0
CO	Trace 1 Sample	---	---
Ar	0.97	0.02	0.97
H ₂	<0.01	---	---
CH ₄	<0.01	---	---
NO _x	<0.01	---	---
SO ₂	<0.01	---	---

(a) HP 5840A Gas Chromatograph

FIGURE 11. Offgas Sampling System

little from air. This is because the total noncondensable flow was 90 scfm at a glass production rate of 60 kg/h and of that, 80 to 85 scfm was atomizing air.

Shown in Table 9 are results of the off-gas samples taken right at the melter surface. The composition of the off gas at the melt surface also varies little from air except higher CO and CO₂ levels. It appears that inleakage to this melter controls the melt surface atmosphere. No CO was found at the melt surface until cornstarch was mixed with the frit.

Run #5--Pilot-Scale Spray Calciner/In-Can Melter

The objective of this run was to test two waste feed components, anthracite coal and sodium EDTA, that had not previously been included in tests due to insufficient information on their behavior. Both components contain significant carbon and would obviously affect the melting behavior in the same manner as reducing agents that were being added for foam control. Scoping tests had shown little decomposition of these compounds during calcination; however, complete decomposition will occur during vitrification.

The results indicated different behavior of the two components. Coal appeared to burn as it fell past the hot canister walls of the in-can melter and completed its decomposition on the surface of the glass. The EDTA appeared to be dried and entrained with the calcine and frit and then decomposed under the glass surface, emitting flames as the gas bubbles contacted the atmosphere above the melt crust. No problems were foreseen in larger-scale tests using these constituents.

Run #6--Full-Scale Spray Calciner

This was a short-term test to determine the effects of higher-oxide equivalent loadings on the spray calciner. A feed slurry concentration of 144 g oxide/L was tested successfully. This concentration was over double that of previous runs. Although the system operated well for the short-term, the potential for abrasive wear on the feed system components needs to be considered before going to long-term operation. This run offered no significant data related to melting as it was aimed primarily at calciner throughput.

TABLE 9. Noncondensable Gas Samples Taken From Melter Surface

<u>Component</u>	<u>Average Vol%</u>	<u>Standard Deviation</u>	<u>Air Vol%</u>
CO ₂	0.667	0.436	0.052
O ₂	21.7	0.750	21.9
N ₂	77.1	0.60	77.0
CO	0.012	0.016	---
Ar	0.97	0.03	0.97
H ₂	0.01 (one sample)	---	---
CH ₄	<0.01	---	---
NO _x	<0.01	---	---
SO ₂	<0.01	---	---

Run #7--Full-Scale Spray Calciner/In-Can Melter

The objective of this test was to produce two cans of glass on the full-scale equipment using feed containing cornstarch, tetra sodium EDTA and anthracite coal. These three carbon-containing compounds have been identified as likely to be in the waste at the Savannah River Plant. A similar waste composition had been tested on the pilot-scale system as previously reported in Run #5. The canisters of glass would be produced at two different temperatures--1050°C and 1150°C. The latter would use a can made from Inconel-601 due to the high-temperature requirement. Although foaming had not been a serious problem in the ICM process as compared to the joule-heated ceramic melter, it has limited the maximum, fill height of cans. The experiment also assessed the reducing agents effects on foaming, feed rate and glass quality.

The first canister was fed at 75 kg/h while being held at 1050°C. These rates were higher than expected and are believed to be partly due to the added heat of combustion of the organics. The filling rate was consistent even near the top of the can, which usually has a much lower feed rate.

The second canister was fed at 100 kg/h. However, after five hours, a failure in the frit-feeder circuitry resulted in erroneous frit addition rates and compromised the results of the test. Operating data for Run #7 is shown in Table 10 and Figures 12, 13 and 14.

TABLE 10. Summary of Spray Calciner In-Can Melting Run #7^(a)

	Run Number	Run Number
	FS-ICM-26	FS-ICM-27
	<u>3/4/80</u>	<u>3/6/80</u>
<u>Canister Description</u>		
Diameter, in.	24	24
Length, in.	84	84
Wall thickness, in.	5/8	1/4
Material	304L-SS	Inconel 601
Fins	None	None
<u>Batch</u>		
Waste type	SRL TDS (modified)	
Waste form	Spray Calcine	
Waste oxide-to-frit ratio	28:72	38:62
Frit type	211	
Frit form, mesh	-80, +20	
Additives	None	
Batch preparation	None	
<u>Operating Parameters</u>		
Time at melt temperature, h	24	19
Surface temperature range, °C	1060 to 1080	1130 to 1150
Nominal melt temperature, °C	1075	1150
Batch feed method	Continuous	Continuous
Batch conditioning	None	None
Maximum batch feedrate, kg/h	75	100
Melting rate, kg/h	75	74
Maximum power consumption, kW	76	102
Glass cooling rate, °C/h		
1000 to 700°C	100	130
700 to 400°C	Not available	80
<u>Product Description</u>		
Type	SRL TDS (modified) with Frit 211	
Weight, kg	1136	1024
Unfired material, kg	25	1.7

(a) The off-gas treatment consisted of filters, condenser, and scrubber.

FIGURE 12. Calciner Operating Parameters Run #7

FIGURE 13. Time Summary Run #7 (Nominal Temperature: 1075°C)

FIGURE 14. Time Summary Run #7 (Nominal Temperature: 1150°C)

Both cans showed evidence of significant combustion at the glass surface and periodic pressurizations of the system were experienced.

Both cans contained metallic spheres on the bottom. The compound was identified as nickel subsulfide (Ni_3S_2) with traces of iron, lead and zinc. Lead and zinc are impurities in the feed-makeup chemicals. The exposed interior walls of the can were coated with salts, primarily sodium chloride and traces of other alkali-metal chlorides.

The glass composition in both cans showed less variation from top to bottom than previously found. Crystal content of the cans ranged from 5% to 10% each of spinel $(\text{Ni, Mn})\text{Fe}_2\text{O}_4$ and acmite $\text{NaFe}(\text{SiO}_3)_2$. Generally, crystal content was greater near the bottom of the cans, as would be expected due to settling.

Leach-rate data on core samples of the cans was also uniform, unlike previous runs. For the can filled at 1050°C , the soxhlet test results ranged from 1.90 wt% to 5.82 wt% with an average of 3.33 wt%. For the can heated at 1150°C , the results ranged from 1.78 wt% to 3.42 wt% with an average of 2.42 wt%. Samples from the can heated at 1050°C were placed in a pH4 solution and the leach rates from these samples ranged from 74.87 to 92.63 wt% with an average of 85.23 wt%. Leach rates for the can heated at 1150°C ranged from 74.64 wt% to 94.80 wt% with an average of 84.07 wt%.

Detailed off-gas sampling was done at the sintered-metal filter outlet from the spray calciner.

A sampling system for organic compounds was used to determine if any of the coal or EDTA was not oxidized completely to CO or to CO_2 .

Results of the noncondensable gas analysis from the gas chromatograph and mass spectrometry are presented in Table 11 for samples taken while processing.

As can be seen from the table, the decrease in O_2 concentrations (24% less than air) and the presence of CO and H_2 indicate a reducing atmosphere in the calciner/in-can melter system. This was born out by the fact that metals reduced out of the glass and that foaming was not rate-limiting during operation. Assuming the only O_2 source in the calciner is from atomizing air (no inleakage

TABLE 11. Average Composition of Noncondensable Off-Gases From Filter Outlet (Dry Basis) Run #7

<u>Component</u>	<u>Average Vol%</u>	<u>Standard Deviation</u>	<u>Air, Vol%</u>
CO ₂	1.22	0.369	0.052
O ₂	16.6	4.5	21.9
N ₂	80.4	6.0	77.0
CO	0.02	0.02	---
Ar	0.93	---	0.97
H ₂	0.07 (2 samples)	---	---
CH ₄	<0.01	---	---
NO _x	0.383	---	---
SO ₂	<0.01	---	---

at the frit feeder and canister connection), the O₂ concentration in the calciner on a wet basis could have been as low as 1 to 2 vol%.

The only alkane found in samples was a small amount (~2 ppm) of hexane in one filter-outlet sample. Two other organic compounds were identified in five samples: benzene and CF₃Cl. Since the instrument was not calibrated for these compounds, quantitative concentrations could not be determined. However, an estimation of their concentrations would range from 0.1 to 3000 ppm. Relative differences between the samples indicate the benzene was 12 to 135 times more concentrated in the can-outlet samples while the CF₃Cl was fairly constant (ratios of can-outlet samples to filter-outlet samples ranged between 1 and 2). This difference may indicate a fluorocarbon contamination of the sampling bags.

During the filling of the sampling bags, a green liquid condensed in the bag. After the organic analysis was completed, approximately 10 ml of the liquid was analyzed for feed and frit elements. The analysis showed a very high chloride content: 51 g/L. The sample also contained large amounts of iron (18 g/L), nickel (2.1 g/L), sodium (10 g/L), and chromium (2.6 g/L). Calculating the equivalence per liter of sample indicated that the metals were present as chlorides. Of importance is the chromium, which is probably present as CrCl₃, and is probably from a chloride attack of the stainless steel can.

A NO_x monitor was used to determine decontamination factors for the primary off-gas system. The results are summarized in Table 12. The sintered-metal filter-outlet numbers are slightly lower than the values based on the theoretical feed concentration (5280 compared with 3830). This probably indicates that the feed was slightly deficient in nitrate or that the inleakage to the system was larger than the average value of 50 scfm during sampling.

The NO_x decontamination factors for the venturi scrubber and packed-tower are low. This is because NO_x is not soluble in the water scrub solution and the off-gas velocity is too high to allow sufficient contact time. Overall system efficiency for NO_x is $\sim 20\%$.

Condensate samples and scrub-solution samples from the filter-outlet sampling system were analyzed for the elements in the feed and frit. The average condensate analysis is shown in Table 13. Also included in the table is the average, venturi scrub-solution analysis for comparison because this solution should have the same analysis as does the condensate. As can be seen from the table, the venturi scrub solution is higher in almost every component indicating a calcine carryover from previous runs. Condensate pH ranged between 9 and 10 indicating it was slightly basic. During Run #4 with the spray calciner/ceramic melter, when the sintered filters failed, the pH was slightly acidic (pH from 4 to 7).

Table 14 shows the theoretical feed plus the frit wt% for each component, the wt% for each component from the combined the condensate and scrub-solution analysis, and the percent of volatility. As can be seen from Table 14, B_2O_3 , Na_2O and CaO appear to be volatile, while Li_2O , MnO_2 , SiO_2 and Fe_2O_3 appear to be removed more efficiently than the feed and frit as a whole. It is not understood why Fe_2O_3 was removed more efficiently because its particle size was small compared with the large frit particles (Li_2O and SiO_2).

Average off-gas flow leaving the filters was $422 \text{ ft}^3/\text{min}$ at 189°C and 10-in. H_2O vacuum. Of this flow, ~ 50 scfm was from inleakage mainly around the filter housing. Since sampling at the filters was only 45% of isokinetic, higher than actual particulate concentrations were observed. The particulate leaving the filters was 2.77 g/h , resulting in a decontamination factor of at least 2.70×10^4 .

TABLE 12. NO and NO_x^(a) Levels From the 1050°C Canister

Range	Quantity, ppm					
	Sintered-Metal- Filter Outlet		Venturi Outlet		Packed- Tower Outlet	
	NO, 2000 to 3100	NO _x , 3600 to 4500	NO, 3000 to 3200	NO _x , 3000 to 3800	NO, 2600	NO _x , 3000 to 3700
Average	2660	3830	3120	3670	2600	3310
Average decontamination factor	---	---	1.0	1.05	1.20	1.11

(a) On a dry basis.

TABLE 13. Average Condensate and Venturi Scrub-Solution Analysis

Component	Average Condensate, g/L	Standard Deviation, g/L	Average Venturi Scrub-Solution g/L	Standard Deviation, g/L
Al ₂ O ₃	2 x 10 ⁻⁵	4 x 10 ⁻⁵	4.8 x 10 ⁻⁴	1.83 x 10 ⁻⁴
B ₂ O ₃	4.45 x 10 ⁻⁴	4.7 x 10 ⁻⁴	9.07 x 10 ⁻⁴	1.91 x 10 ⁻⁴
CaO	2.02 x 10 ⁻³	2.28 x 10 ⁻³	5.25 x 10 ⁻³	2.64 x 10 ⁻³
Fe ₂ O ₃	1 x 10 ⁻⁵	---	6.7 x 10 ⁻⁵	1.5 x 10 ⁻⁵
Li ₂ O	2.9 x 10 ⁻⁵	2.2 x 10 ⁻⁵	6.0 x 10 ⁻⁵	9 x 10 ⁻⁶
Na ₂ O	1.33 x 10 ⁻³	6.04 x 10 ⁻⁴	1.6 x 10 ⁻³	5.73 x 10 ⁻⁴
MnO ₂	9 x 10 ⁻⁶	6 x 10 ⁻⁶	5 x 10 ⁻⁶	6 x 10 ⁻⁶
NiO	6.1 x 10 ⁻⁵	1.21 x 10 ⁻³	9.7 x 10 ⁻⁵	2.1 x 10 ⁻⁵
SiO ₂	8.67 x 10 ⁻⁴	9.55 x 10 ⁻⁴	2.8 x 10 ⁻³	7.9 x 10 ⁻⁴
SrO	1.5 x 10 ⁻⁵	1.0 x 10 ⁻⁵	---	---
Cs	<4 x 10 ⁻⁶	---	---	---
TOTAL	4.8 x 10 ⁻³	---	1.13 x 10 ⁻²	---

The manufacturer's specifications on the ejector venturi used in the off-gas system is a decontamination factor of 10 for particles larger than 1 μm. Assuming that 23% of the mass of particulates is <1 μm (Hanson 1980) the overall venturi decontamination factor for particulates is 3.3. Based on this

TABLE 14. Theoretical Weight % of Feed Plus Frit, Oxide Weight % Taken From the Filter Outlet Sampling Cart, and Percent Volatility

<u>Component</u>	<u>Theoretical Feed and Frit, wt%</u>	<u>Filter Outlet Sampling, wt%</u>	<u>Volatility, %</u>
Al ₂ O ₃	3.70	3.2	---
B ₂ O ₃	7.99	23.5	0.007
CaO	5.06	24.5	0.02
Fe ₂ O ₃	14.6	3.03	(a)
Li ₂ O	3.18	0.26	(a)
Na ₂ O	15.4	24.3	0.01
MnO ₂	3.9	0.19	(a)
NiO	1.7	1.5	---
SiO ₂	44	19.4	(a)
SrO	0.01	0.18	0.06 ^(b)
Cs ₂ O	0.02	0.04	---

- (a) Lower values from the sampling compared with the theoretical values indicate a larger decontamination factor for these components.
- (b) This number appears to be in error since the SrO boiling point is 3000°C, and it should not be volatile.

decontamination factor, the average particulate-mass flow rate to the packed tower was 0.86 g/h. The packed-tower scrub-solution tank was operated as a closed system so that particulate accumulation could be observed. The accumulation rates for each component are listed in Table 15.

For the components in the feed and frit that are not in Table 14, no accumulation was observed. Of the 0.86 g/h entering the packed tower, 0.47 g/h entered the scrub solution, leaving 0.39 g/h in the exiting off gas. The resultant particulate decontamination factor was ~2 for the packed tower.

The results of sampling this system have been summarized in the flowsheet presented in Figure 15.

TABLE 15. Accumulation Rate of Each Component in the Packed-Tower Scrub Solution

<u>Component</u>	<u>Accumulation Rate, g/h</u>
Na ₂ O	0.245
B ₂ O ₃	0.06
CaO	0.06
Al ₂ O ₃	0.02
SiO ₂	0.05
Li ₂ O	0.02
NiO	<u>0.01</u>
TOTAL	0.47

Run #8--Experimental Ceramic Melter

With the high feed rates achieved using the feed composition containing coal, NaEDTA and cornstarch in the ICM process, it was necessary to check the composition by using the reference ceramic melter process. This short-term scoping run tested the composition from Run #7 above.

The calcine-frit mixture produced during Run #7 was fed to the experimental ceramic melter for six hours at rates near 10 kg/h or 181 kg/h-m². These were very high rates and no reduction of metals was detected in the melter cavity. The only unusual aspect of the run was the appearance of flames on regions where the cold cap was thin. Results of this run were very encouraging for operating a joule-heated melter with waste containing significant amounts of organic components.

Run #9--Advanced Glass-Forms Melter

A scaled-up test using the high organic-containing calcine/frit was performed in this larger joule-heated ceramic melter to establish rates and to demonstrate operation on a larger scale. This melter has 0.24 m² of surface area while the experimental ceramic melter has 0.054 m²; thus, the advanced glass forms melter is ~4.4 times bigger.

FIGURE 15. Off-Gas Flowsheet Based on Run #7

Approximately 288 kg of glass was produced in 10 h at rates of 116 kg/h-m² or 28 kg/h. Rates of up to 145 kg/h-m² were demonstrated for several hours, and no indication of metal precipitation was noted. Again, these results were very encouraging for continued ceramic melter tests with high organic levels.

Run #10--Advanced Glass-Forms Melter

This was a repeat of Run #9 with some modifications made to the equipment to reduce the entrainment of fine particulates, such as calcine, in the off-gas (high inleakage corrected from Run #9). Rates of 109 to 124 kg/h-m² were attained for the test. Excess CO₂ was noted in the off gas, indicating that combustion was occurring. A stable, thin foam-like layer with periodic small flames projecting from this layer was noted around the cold cap in all these runs. No interruption of processing resulted from the foam layer.

Run #11--Full-Scale Spray Calciner

The purpose of this run was to generate large quantities of calcine for shipment to the sponsor for tests at his plant. It also provided an excellent opportunity to gather calciner-operating data. Determining the maximum calciner capacity at a wall temperature of 400°C, was necessary because tests were being considered in which all the glass-forming frit would be put in the feed to the calciner to maximize the mixing potential as compared to the partial frit addition that was tested in Run #7. Laboratory tests had shown that the material would stick to the walls at 400°C.

As expected, the calciner capacity depended greatly on wall temperature. This test indicated that 50 L/h was the maximum rate that could be achieved with a 400°C wall temperature and a 200°C filter-outlet temperature. During this run approximately 19,000 L of feed was calcined at temperatures of 400 to 700°C. Operating data was correlated with that of other calciner tests to develop capacity correlations (Larson 1980).

Run #12--Pilot-Scale Spray Calciner

To further test the calcining of a mixture of waste and frit, a run was made on the pilot-scale spray calciner using increasing amounts of frit. Frit

was added to the feed at concentrations of 63.7 g of frit/L (33% of the required glass amount) to 192 g of frit/L (100% of the required amount).

The calciner operated well at all compositions in the short-term test. Off-gas temperatures were lower than desirable ($\sim 130^{\circ}\text{C}$ versus 200°C); however, the results were encouraging enough to warrant a further test with the in-can melter coupled to the calciner.

Run #13--Pilot-Scale Spray Calciner/In-Can Melter

The objective of this run was to demonstrate the processing of the well-mixed glass formers and waste components (frit-in-feed) as described above with the pilot-scale spray calciner/in-can melter system. If mixing is an important parameter in glass quality, this run would provide an opportunity to evaluate that aspect. Operating conditions were set for slurry to be processed at 15 to 20 L/h at a calciner-barrel temperature of 400°C . The net glass-melting rate would be 5 kg/h with the in-can melter at $\sim 1050^{\circ}\text{C}$.

The results indicate that, although a well-mixed feed was used and the glass appeared homogeneous, stratification of the components in the glass was occurring. Leach rates were not significantly improved, as the soxhlet test ranged from 1.56 wt% to 2.03 wt% (bottom to top), and the pH4 leach test was 70.75 wt% to 87.92 wt%. There was approximately 5% to 10% spinel near the bottom of the canister, but there was none at the top.

Run #14A and #14B Full-Scale Spray Calciner/In-Can Melter

Although the pilot-scale run (Run #13) with frit-in-the-feed was not totally successful in improving product quality, it was decided to repeat it on the full-scale. In addition, a full-scale canister would be made that would attempt to mix the glass in the canister by sparging the glass as it melted. This method would be tested while running the process in the conventional mode using a separate frit-entry stream. Thus, the two mixing concepts could be compared.

The problem to overcome was the collection of a high iron-crystalline phase in the bottom of the ICM canisters. By sparging the can, the crystal phase might mix throughout the can, or it may dissolve. In the frit-in-the-

feed mode, prior mixing of components may reduce the formation of the spinels. A drawback to the frit-in-the-feed mode is the low, processing rates expected, which are due to the 400°C calciner wall temperature limit. Rates of up to ~25 kg/h were anticipated for the second can while the first can should melt at rates three to four times as fast. A summary of the operating data is presented in Table 16.

The first canister was filled in a similar manner to the first can filled in Run #7 except that the sparge step was added. The Run Plan called for filling the entire canister at one rate and stopping the fill when foam or glass reached the top. The previous can from Run #7 was run at 75 kg/h and gave every indication that higher rates could be achieved. This run was at 85 kg/h, and the canister was filled equally well. Indications from the power usage show that this rate is close to the limit at the top of the can; however, faster fill rates could be achieved in the bottom two-thirds of the canister. The glass agitation was increased at the end of the run by increasing the sparge rate, and this successfully pulled down most of the clinkers that were present at the top of the canister. This action did not however give a clean top on the cooled glass because material spalled off the interior canister walls. The top was clean and smooth after the canister surface was vacuumed. The can was sparged at the high flow rate for 45 min, then the sparger and ICM furnace were turned off for cooldown.

The second canister was filled with the calcine slurry, which contained powdered frit. Because of the low stick point of the frit, the calciner barrel temperature was held to 400°C. This limited the production rate to 17 kg/h. The low rate should have assisted in the mixing because the calcine melts as it is added, and the melted glass has a long "soak" time at 1070°C as the rest of the canister is filled. Convection should be minimized because of the isothermal condition of the canister. Product results are notable only in the lack of change from earlier ICM canisters. The large concentration gradients and crystallinity are indistinguishable from the earlier cans. This indicates that either the amount of mixing only approximated the level of natural mixing in the can and that much greater mixing is necessary to achieve a homogeneous product, or that the gradients could be formed by crystal formation and collection motivated by convection currents in the glass. The vigorous sparge mixing

TABLE 16. Summary of Full-Scale Spray Calciner/In-Can Melting Run #14A,B

	<u>Run 14A</u> <u>(8/22/80)</u>	<u>Run 14B</u> <u>(8/25/80 to 8/27/80)</u>
<u>Canister Features</u>		
Number	180	181
Diameter, in.	24	24
Length, in.	72	72
Wall thickness, in.	0.5	0.5
Material	304L SS	304L SS
Fins	0	0
<u>Batch Description</u>		
Waste type	Modified TDS	Modified TDS
Waste form	Calcine	Calcine
Waste oxide-to-frit ratio	28:72	28:72
Frit type	211	211
Frit form	-200 mesh	-200 mesh
Additives	Cornstarch, Coal and Na-EDTA	Cornstarch, Coal and Na-EDTA
Preparation	Air Sparge	Frit Added to SC Feed
<u>Operating Parameters</u>		
Time at melt temperature, h	16	66
Surface temperature range	1000°C to 1050°C	1050°C to 1070°C
Nominal melt temperature	1070°C	1070°C
Coupled to	FSSC	FSSC
Off-gas treatment	Filters, condenser, scrubber	Filters, condenser scrubber

TABLE 16. (contd)

Operating Parameters (contd)

Frit feed method	Solids Feeder	Frit in the Feed
Batch conditioning	None	None
Maximum batch feed rate, kg/h	85	18
Melting rate, kg/h	81	12
Maximum power consumption kW	90	55
Glass-Cooling range, °C/h		
1000 to 700°C	17	25
700 to 400°C	14	14

Product Properties

Type	TDS-211	TDS-211
Weight, kg	1164	806
Unfired material, kg	NA	NA

of the first canister at the end of that run made it appear to the observer that the canister was well-mixed. This leaves only a separation mechanism that occurs during the cooldown to explain the condition of ICM canisters. These cans as well as previous cans contained small metal nodules spread throughout the glass and larger metal buttons near the bottom. These buttons had been analyzed and were found to be between 71% and 74% nickel. This material is reported to be Ni_3S_2 , which is a metalloid called nickel subsulfide and is known as the mineral heaslewoodite. Its melting point is listed as 790°C in the literature (Weast 1968).

Run #15--Pilot-Scale Spray Calciner

This run was performed to produce small quantities of calcine, each depleted in a key element suspected of contributing to the foaming being encountered in recent vitrification tests. Calcine, depleted in Fe, Mn, Ni and EDTA, respectively, would be produced for laboratory studies. The results were inconclusive because of cross contamination of the calcines.

Run #16--Pilot-Scale Spray Calciner

The objective of this test was to try a new concept to reduce the oxidation state of the multivalent cations in the calcine during the spray calcination step. Calcine would be produced while using nitrogen atomization instead of air. Calcine would also be produced using 50 g of urea/L added to the feed along with the nitrogen atomization.

Although the volume percent of oxygen in the off gas decreased with N_2 atomization (22.1 vol% to 18.6 vol%), and with N_2 plus urea (22.2 vol% to 18.6 vol%), the resultant melting properties of the calcine did not significantly change. Air inleakage to the system may contribute to higher O_2 levels than might be expected.

The off gas from Run #16 was analyzed with a gas chromatograph. The purpose of the sampling was to determine the changes in the O_2 concentration when N_2 was used as the atomizing gas, and when urea was added to the feed.

Table 17 shows the general trend that appeared. When air was used to atomize the feed, the O_2 concentration decreased below the normal air sample concentration. When N_2 was used for atomizing the feed, the O_2 concentration showed a larger reduction. When urea was added to the feed (with N_2 for atomizing), the O_2 concentration decreased even further.

The O_2 concentration, when calcining with only MnO_2 as feed and with air as atomizing gas, had a higher O_2 concentration than the air sample. The same pattern appeared in the MnO_2 feed that was evident in the defense-type feed. The O_2 concentration dropped when N_2 was used for atomizing gas, and the concentration dropped even further when urea was added to the MnO_2 feed (with N_2 for atomizing gas).

The extent of the effect on the O_2 concentration caused by the different feed conditions was probably greater than that shown, as a dampening of the effect on the O_2 concentration was due to the large amount of inleakage into the spray calciner. Assuming that all of the O_2 was from the inleakage air, the flow rate of inleakage was 10 scfm.

TABLE 17. Noncondensable Off-Gas for Run #16

Feed	Atomizing Gas	O ₂ , Vol%	N ₂ , Vol%	CO ₂ , Vol%	O ₂ to N ₂ Ratio
MnO ₂	Air	21.8	67.0		1:3.1
MnO ₂	N ₂	17.9	72.4		1:4.0
MnO ₂ + urea	N ₂	17.6	74.1	0.037	1:4.2
Defense type	Air	22.2	76.5		1:3.4
Defense type	N ₂	20.8	74.1		1:3.6
Defense type + urea	N ₂	18.6	73.9	0.062	1:4.0
Air sample		22.4	70.6		1:3.2

NOTE: The numbers do not add up to 100 because H₂O and NO_x were not included in the analysis.

B. DIRECT LIQUID FEEDING TESTS

Run #17--Experimental Ceramic Melter

As an alternative to the two-step calcination/vitrification process being investigated at PNL, a single-step direct-liquid-feeding method has been investigated for radioactive wastes from power reactors (Buelte and Chapman 1978; Buelte and Chapman 1979). This method appeared to be directly transferrable to the defense-waste immobilization program. Following a series of laboratory-scale tests to study the direct liquid feeding of defense waste, a short run on PNL's small, experimental, ceramic melter was undertaken. These laboratory tests showed that melt foaming was a problem with liquid feeding, as it had been with calcine feeding to the ceramic melters, and that reducing agents were necessary. Pacific Northwest Laboratory was successful in using 1% to 2% corn-starch in the calcine-fed process. Other conclusions from the lab tests were that premelted Frit-211 was the preferred form to add to the glass formers, and that using 2-wt% dry solids of bentonite^(a) was helpful in keeping the feed solids such as MnO₂, SiO₂ and Frit-211 in suspension. These were the conditions set for the first test on the ECM.

(a) Colloidal aluminum silicate clay of the sodium bentonite variety.

Results of this first twelve-hour test on the ECM were encouraging. No foaming problems occurred; however, there were a considerable number of problems with the feed delivery. The glass product was of good quality based on visual inspection. A 6-cm-thick cold cap formed and appeared to have good insulating qualities. A water-cooled feed nozzle functioned well while delivering feed to the center of the tank surface.

Run #18--Full-Scale Liquid-Fed Ceramic Melter

The encouraging results of the small-scale (ECM) run (Run #17) led to a full-scale test on the LFCM. The purpose of this test was to establish operating conditions, to evaluate product quality, to characterize effluents, and to determine what equipment modifications were necessary since the full-scale melter was scheduled to be disassembled and rebuilt following this run. The disassembly was necessary because the melter was at the end of its useful life. After more than three years of testing with power reactor wastes, this melter was to be rebuilt for subsequent testing with defense waste.

The same feed conditions that had been tested on the ECM were planned for the LFCM, including 1-wt% cornstarch, 2-wt% bentonite, -200-mesh frit, and 362.9 g of oxide/L (see Table 18). Feed density was $\sim 1.25 \text{ g/cm}^3$. Coal and Na_4EDTA were not added to the feed at the time of these tests, and cornstarch was added purposely as a foaming reductant. Cornstarch is also a constituent in the actual plant feed.

The melter was operated for 45 hours of actual feeding with an on-stream factor of 69%. Initial operation was unstable due to foaming and erratic feed-system operation. The cornstarch level was increased to 2 wt%, and the bulk glass temperature was raised from 1050°C to 1130°C during the run, which resulted in the last 19 hours of operation being quite successful. Melting rates of up to 40 kg/h or 38.1 kg/h-m^2 were achieved. Liquid-feed rates of 105 L/h were determined to be too high while rates of 80 L/h were acceptable. Operating conditions are shown in Figures 16, 17 and 18.

Samples of the cold cap showed significant chemical variations, indicating that segregation was occurring. However, glass samples taken at the melter cold cap (called batch) interface and from the exit glass stream showed little

TABLE 18. Feed Composition for Run #18

Components			Quantity, kg/L
Waste	Fe(OH) ₃		.0700 kg/L
	Al(OH) ₃		.0175
	MnO ₂		.0140
	CaCO ₃		.0064
	Ni(OH) ₂		.0075
	NaNO ₃		.0029
	Na ₂ SO ₄		.0014
	Zeolite (Linde Ion Siv IE-95)		.0104
	RuNO(NO ₃) ₃	Trace Elements	0.204 (g/L)
	Sb ₂ O ₃		0.0791 (g/L)
	TeO ₂		0.0241 (g/L)
	Cs ₂ CO ₃		0.237 (g/L)
	Sr(NO ₃) ₂		0.166 (g/L)
Frit	SiO ₂	58.3 wt%	Premelted Frit (-200 mesh)
	Na ₂ O	20.6	
	B ₂ O ₃	11.1	
	CaO	5.0	
	Li ₂ O	4.4	
Suspending Agent Bentonite			.0078
Reducing Agent Cornstarch			.0036

FIGURE 16. Run #18--Glass Temperatures

FIGURE 17. Run #18--Electrode Temperatures

FIGURE 18. Run #18--Power and Resistance Levels

compositional variation from the feed. Thus, the segregation in the batch cover disappeared as the melting occurred. The canister of glass that was produced was very uniform as far as chemical composition. The crystal formation was estimated at about half that seen in calcine-coupled operations. It must be kept in mind that, although the canisters are roughly the same size as the anticipated plant canisters, the fill rates are considerably lower, which has a significant effect on crystal formation and thermal behavior. A detailed evaluation of the off gas was made (Oma and Nelson 1980) and is reported elsewhere. An energy balance of the melter system was made during this run and is summarized in Figure 19.

Run #19--Experimental Ceramic Melter Tests

A short series of liquid-feeding experiments were completed on the ECM during the period the LFCM was being rebuilt. This series was to examine different operating parameters including frit size, batch chemical^(a) addition versus frit addition, and pulse-type feeding versus continuous feeding. The feed composition used included coal and ~1.5 wt% cornstarch; Na₄EDTA was eliminated from the flowsheet by the sponsor. The reasons for the additional tests were: 1) the feed composition had changed somewhat and had become more concentrated; 2) additional tests performed following earlier lab-scale work had resulted in bridging of the cold cap; therefore the glass additive needed to be re-evaluated; 3) data was needed to evaluate the merits of running a cold cap with less than 100% surface coverage; and 4) the feed-slurry delivery technique to the melter needed development.

There was great difficulty in feeding the concentrated waste slurry with pilot-scale pumps. The larger frit sizes (-20+80 mesh) were the most difficult to handle, and dilution was needed in many cases. During pulse feeding, the feed nozzle became plugged due to the higher plenum temperatures inherent with that type of operation. Concentrated feeds tended not to melt well while pulse feeding because of the inability of the thick slurry to spread over the melter surface as well as the formulation of slow-melting "islands". Cold caps with the frit additive tended to be more impermeable than with batch chemicals.

(a) Glass-forming additives in the form of chemical compounds rather than premelted glass-frit oxides.

FIGURE 19. Energy Balance of the Full-Scale LFCM

Some foaming was noted in the runs; however, this was not considered a problem. High-carbonate batch chemicals were delivered to the melter with the least difficulty and appeared to melt successfully unless an overfeeding occurred, at which point an extremely hard, cold cap would develop.

At the sponsor's request, batch chemicals were eliminated in future tests due to their belief that a possibility of makeup errors existed. The sponsor also did not want to run a melter with a complete cold cap, and this reduced the importance of permeability of the off-gas vapors.

Run #20--Liquid Fed Ceramic Melter

Following the rebuilding of the liquid-fed ceramic melter and the series of small-scale ECM tests, a five-day run was planned to establish a baseline capacity. It was also planned to test a method of increasing the capacity by supplying additional heat to the system via lid heaters. The concentration of the waste had been increased and was to be equivalent to ~ 511 g of oxide/L (including frit). A target capacity of 39 kg/h-m^2 was set. It was anticipated that the lid heat along with the addition of coal in the feed would minimize any foaming problems.

Initial operation of the new melter system was plagued by typical startup problems inherent in any new equipment. Some fairly serious problems with the feed system were encountered, however, as the thicker slurry was not compatible with existing feed systems used for acidic power-reactor wastes. Modifications were made to allow the run to continue, although satisfactory feeding was never fully attained.

The run lasted for five days. During this test it was shown that the majority ($\sim 2/3$) of the radiant heat from the lid was being lost as superheated steam rather than being absorbed in the melter cold cap. Particulate loading in the off gas was high, and a plug occurred in a 15.2 cm (6 in.) diameter off-gas line.

The glass rate for this test during stable operation was $\sim 35.5 \text{ kg/h-m}^2$, equivalent to a slurry rate of 82 L/h. A higher rate of 42 kg/h-m^2 (95 L/h slurry rate) was attempted; however, at this upper rate, the melter surface was 100% covered and bridging of the cold cap occurred.

A summary of the data from the run is shown in Figures 20 through 25. Cesium analysis of the off-gas samples taken from the melter was made and the decontamination factors are shown in Table 19. Sampling was performed only when the melter was receiving feed.

During the run, 5.9 kg of material formed a plug in the off-gas line between the melter and the sampling nozzle. The plug was located about 3 m from the melter lid in a horizontal section of the off-gas line inside a flanged joint. The temperature of the off gas near the plug during feeding usually was between 400°C and 600°C. The material forming the plug accounted for 0.16 wt% of the total oxides fed before the shutdown. This corresponds to a decontamination factor of 630.

An analysis of the material in the plug and a comparison of this material to a typical feed composition are given in Table 20. Species with a higher concentration in the plug are not necessarily more volatile than the other species. Some components may be entrained more easily than others depending on their particle size. In the case of iron and nickel, their high concentration may be due to a corroding, steel, flex hose upstream from the plug.

Results of an ion-chromatography analysis are shown in Tables 21 and 22. These results show an increase in Cl^- , F^- and $\text{SO}_4^{=}$ during the run. This may be caused by an enrichment of the anions in the melt during continuous feeding. The melter operation was not interrupted by loss of feed between sampling periods 3, 4 and 5, but it was interrupted between sampling periods 1, 2 and 3.

TABLE 19. Cesium Decontamination Factors, Run #20

Sampling Period	Decontamination Factors	
	Without Plug Material	With Plug Material
1	66	54
2	100	70
3	44	38
4	38	36
5	32	30

FIGURE 20. Glass Temperatures of the Full-Scale LFCM

FIGURE 21. Electrode Temperatures of the Full-Scale LFCM

FIGURE 22. Electrode Resistance and Power of the Full-Scale LFCM

FIGURE 23. Lid Heater Total Power of the Full-Scale LFCM

FIGURE 24. Feed Rate of the Full-Scale LFCM

FIGURE 25. Glass Rate of the Full-Scale LFCM

TABLE 20. Composition of Material From Off-Gas Plug

Oxide	Average wt% in Plug	wt% Feed 9/18 Date 2030 Time	Ratio wt% Plug/ wt% Feed
Al ₂ O ₃	1.67	2.96	0.56
B ₂ O ₃	4.62	3.78	1.22
CaO	4.40	4.62	0.95
Fe ₂ O ₃	20.3	10.9	1.86
Li ₂ O	2.02	2.42	0.83
MgO	0.22	0.11	2.00
MnO ₂	1.21	3.67	0.32
Na ₂ O	16.9	13.0	1.30
NiO	2.49	1.32	1.89
RuO ₂	0.30	0.01	0.30
SiO ₂	31.0	35.0	0.89
SrO	0.04	0.02	2.0
TeO ₂	0.07	0.004	17.5
TiO ₂	0.07	0.03	2.33
ZnO	0.08	0.04	2.0
Cs ₂ O	0.26	0.04	6.5

TABLE 21. Ion Concentration in the Off Gas

Sample Period	Concentration, $\mu\text{g}/\text{std. L of Wet Off Gas}$			
	Cl ⁻	NO ₃ ⁻	F ⁻	SO ₄ ⁼
1	100.0	30.0	22.0	5.7
2	92.0	61.0	29.0	6.5
3	106.0	92.0	26.0	10.6
4	199.0	96.0	27.0	18.9
5	275.0	50.0	72.0	22.3

The results may also be due to other melter variables such as cold-cap size and melt temperatures, or feed composition.

Data on the particle size and the mass loading in the off gas was obtained by an aerosol spectrometer. The average, mass loading of the off gas during

TABLE 22. Ion Concentration in the Condensate

Sample Period	Concentration, $\mu\text{g}/\text{std. L of Wet Off Gas}$			
	Cl^-	NO_3^-	F^-	$\text{SO}_4^{=}$
1	197	90	60	17
2	274	200	92	21
3	174	215	57	25
4	353	213	58	42
5	585	113	152	50

steady operation was 2.5×10^{-3} g/scf of off gas. The actual loading was probably greater because the spectrometer does not detect particles below $0.32 \mu\text{m}$ in dia, and it assumes that all the particles are spherical with a density of $4.0 \text{ g}/\text{cm}^3$.

The decontamination factors for the run have been calculated, and the results are shown in Table 23. The decontamination factors were defined as the component's mass, which entered the melter in the feed, divided by its mass in the off gas. Five sampling periods were used, and each period lasted about 10 h. The decontamination factors shown in Table 23 are a combination of the mass collected in the off-gas sampling equipment multiplied by the fraction of the off gas sampled and the mass of the plug that formed in front of the sampling nozzle.

The off-gas samples were analyzed by ICP and X-ray fluorescence and elemental masses were produced. The elements analyzed were assumed to be oxides, therefore a total particulate decontamination factor could be approximated by a total oxide decontamination factor. An analysis of the plug material showed that 90% of the plug mass could be accounted for when oxides are assumed to be the main elements.

Chromium was detected in the off gas but not in the feed. As an oxide, the chromium mass loading was approximately $0.1 \text{ mg}/\text{scfm}$ or $5 \text{ mg}/\text{min}$.

The chromium comes from the construction materials of the melter and the off-gas piping. A stainless steel flex hose corroded during the run and is believed to be the main source of chromium. The flex-hose corrosion also increased the amount of iron and nickel in the off gas.

TABLE 23. Off-Gas Decontamination Factors

Compound	Range of Decontamination Factors		Average Decontamination Factors
	Minimum	Maximum	
Al_2O_3	3750	7730	4907
B_2O_3	177	530	259
CaO	544	954	741
$\text{CdO}^{(a)}$	120	562	343
Cs_2O	30	70	40
Fe_2O_3	330	948	419
Li_2O	691	1120	923
MgO	340	640	485
MnO_2	551	2450	1585
Na_2O	286	402	336
NiO	330	520	430
RuO_2	1.3	27	7
$\text{Sb}_2\text{O}_3^{(a)}$	310	580	481
SeO_2	80	430	218
SiO_2	631	1200	940
SrO	252	521	378
TeO_2	49	77	61
TiO_2	282	2294	1102
ZnO	294	361	346
Cl^-	9	32	17
TOTAL OXIDE DECONTAMINATION FACTOR			564

(a) Due to limitations of the analyzing equipment, the decontamination factors reported are minimum values based on the ICP detection limit.

V. PRODUCT DATA

Glass product from the process test is subjected to leach-rate tests to evaluate its durability. As previously mentioned, the processing Frit-211 was not intended to provide optimum durability but rather to allow melting of the waste in all processes. Table 24 compares leach rates from several of the tests. The process glass from the ceramic melter appears to be slightly better than that from the in-can melter. Other qualitative observations also favor the ceramic melter glass whether from a calcine-fed or liquid-fed process. Cracking of the glass at the canister/glass interface is always less in the ceramic melter, as the glass was poured into carbon steel cans whereas the ICM process uses stainless steel cans.

Shown in Figure 26 are process rates for the different processes tested at PNL. The rate is specified as the kilograms of glass melted per hour per square meter of melter surface (kg/h-m^2), and ranges are shown for several sizes of vitrification equipment used. As expected, high rates are achieved when a dry powder is fed to a melter.

TABLE 24. Process Leach Rate Comparison Wt% Loss

	Soxhlet Test		pH4 Test	
	Range	Ave.	Range	Ave.
Run 4 FSSC/CM	2.28 to 2.78	2.36	21.8 to 90.2	49.44
Run 7 FSSC/ICM				
1050°C can	1.90 to 5.82	3.33	74.87 to 92.63	85.23
1150°C can	1.78 to 3.42	2.42	74.64 to 94.80	84.07
Run 13 FSSC/ICM (2 Samples)	1.56 to 2.03	1.80	70.75 to 87.93	79.34
Run 18 LFCM--Grab Samples From Pour	1.54 to 2.53	1.84	70.2 to 87.5	77.44
Run 14 FSSC/ICM				
#A	2.09 to 6.00	3.79	57.6 to 83.9	74.90
#B	1.53 to 1.82	1.66	84.2 to 94.6	88.6
Run 20 LFCM				
Can #1	1.58 to 4.77	2.63	N.A.	> 80%
Can #2	1.54 to 5.08	1.97	N.A.	> 80%

(a) The numbers correspond to the run numbers used in Table 3.

FIGURE 26. Melting Rate Comparison

ABBREVIATIONS

AGFM Advanced Glass-Forms Melter
CM Ceramic Melter
ECM Experimental Ceramic Melter
LFCM Liquid Fed Ceramic Melter
ICM In-Can Melter
SC Spray Calciner
TDS Denotes the Type of Defense Waste Feed Tested
PS Pilot Scale
FS Full Scale

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