

Process Testing to Support the Conceptual Design of a Plutonium Vitrification Facility

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ABSTRACT

In the aftermath of the Cold War, the United States Department of Energy (DOE) has identified up to 50 metric tonnes of excess plutonium that needs to be dispositioned. The bulk of the material is slated to be blended with uranium and fabricated into a Mixed Oxide (MOX) fuel for subsequent burning in commercial nuclear reactors. Excess plutonium-containing materials that are not suitable for fabrication into MOX fuel will need to be dispositioned via other means. A lanthanide borosilicate (LaBS) glass was identified as a preferred form for the disposition of the impure plutonium-containing feeds. The LaBS glass formulation uses a lanthanide borosilicate frit rather than the alkali borosilicate frit used to vitrify high level waste. The LaBS glass has been shown to be able to accommodate high quantities of fissile material (greater than 10 wt % elemental plutonium) and tolerate the impurities expected in the plutonium feed streams. A conceptual design effort is now underway at the Savannah River Site (SRS) to design a vitrification facility to immobilize the excess Pu feeds that are not slated for disposition via MOX fuel. The conceptual design phase is planned to complete in FY07. A test program was initiated at the Savannah River National Laboratory (SRNL) to provide input data to the conceptual design effort. A major component of this test effort involves vitrification process testing. A cylindrical induction melter (CIM) was developed for the vitrification of actinide feed streams. Due to the high temperatures required to incorporate high plutonium oxide contents into the glass by dissolution and melting, the melter vessel is constructed out of Pt/Rh alloy and can be operated at temperatures up to 1600° C. Additionally, the melter design is compact to facilitate installation in a glovebox (the size of the conceptual facility melter is approximately 6" in diameter by 18" tall). The CIM has proven to be a viable means to process the LaBS glass at processing temperatures of 1400-1500° C. In this paper, the offgas sampling tests conducted in the CIM to capture and analyze the particulate and vapors emitted from lanthanide borosilicate (LaBS) Frit X with HfO₂ as a surrogate for PuO₂ and added impurities are discussed. The tests with impurities added showed that alkali salts such as NaCl and KCl were substantially emitted into the offgas system as the salt particulate, HCl, or Cl₂. Retention of Na and K in the glass were about 80 and 55%, respectively. Chloride retention was about 35%; chloride remaining in the glass was 0.29-0.37 wt%. Overall, about 58-72% of the impurities added were volatilized. Virtually all of the particulate species were collected on the nominal 0.3 µm filter. The particulate was found to be as small as 0.2 µm and have an approximate median size of 0.5 µm. The particulate salt was also found to stick together by forming bridges between particles.

INTRODUCTION

The Department of Energy-Environmental Management (DOE-EM) plans to conduct the Plutonium Disposition Project (PDP) at the Savannah River Site (SRS). An important part of this project is to reduce the attractiveness of plutonium scrap by fabricating a durable plutonium glass form and immobilizing this Pu form within the high level waste (HLW) glass prepared in the Defense Waste Processing Facility (DWPF). In support of the previous Plutonium Immobilization Program (PIP), a glass formulation was developed that was capable of incorporating large amounts of actinides as well as accommodating any impurities that may be associated with Pu feed streams. The basis for the glass formulation was derived from commercial glasses that had high lanthanide loadings. A development effort led to a lanthanide borosilicate (LaBS) glass that accommodated significant quantities of actinides, tolerated impurities associated with the actinide feed streams and could be processed using established melter technologies [1]. A Cylindrical Induction Melter (CIM) was developed during the PIP for vitrification of the Pu LaBS glass. The CIM system consisted of an inductively heated platinum rhodium (Pt-Rh) containment vessel, an induction heating system, a control system and an offgas filtering system. Following the PIP, the CIM melter was extensively studied and refined in support of the Am/Cm vitrification development program [2].

Although significant testing has been conducted on the CIM in support of Am-Cm vitrification, the application to vitrification of Pu has not been extensively tested. Experimental studies on the vitrification of plutonium oxide surrogates were begun to support the PDP. In these studies, PuO₂ surrogate (HfO₂ as a surrogate for PuO₂) feed streams, some containing various impurities, and LaBS glass frit were fed to the CIM to produce the glass product. Thorough evaluation of melter operating parameters and melter performance for this application are required. Testing of the CIM with impurities that are likely to be present in the Pu feeds is also required to evaluate the effect of the impurities on the glass produced, to quantify the offgases produced during the vitrification process, and to begin the process of testing offgas treatment systems.

APPROACH

This paper discusses the melter offgas tests conducted in the CIM to capture and analyze the particulate and vapors emitted from lanthanide borosilicate (LaBS) Frit X with HfO₂ as a surrogate for PuO₂ and added impurities. It also includes data on glass chemistry and impurity retention in the glass. Prior to the impurity feed testing, several melter runs were conducted in the CIM to evaluate the melting behavior of LaBS Frit X glass and establish process conditions for vitrifying LaBS Frit X glass. These tests were also used to provide frit for subsequent testing as well as evaluating incorporation of HfO₂ (as a surrogate for PuO₂) at high loadings. A summary of the tests is shown in Table I. For brevity, only the impurity feed tests (CIM Runs #14 and #15) are discussed in this paper. The purpose of Run #14 (NaCl Run) was to sample the offgas emissions and fumes that are generated during the vitrification of the LaBS Frit X blended with NaCl. Run #15 (Rocky Flats feed) sampled the offgas emitted while vitrifying LaBS Frit X blended with simulated Rocky Flats Can B5495 impurities.

Table I. Runs Performed To Process LaBS Frit X Materials

Date	Run Title	Material Processed in CIM
6/29/06	Run 1 Process Frit X Batch To Produce Cullet	2170 g Frit X Batch Chemicals
7/11/06	Run 2 Process Frit X Batch To Produce Cullet	2193 g Frit X Batch Chemicals
7/13/06	Run 3 Process Frit X Batch To Produce Cullet	3264 g Frit X Batch Chemicals
8/9/06	Run 4 Frit X With HfO ₂ Sub for 9.5 wt% PuO ₂	1849.2 g Frit X (140 mesh) with 150.8 g HfO ₂ blended in
8/16/06	Run 5 Frit X With HfO ₂ Sub for 9.5 wt% PuO ₂	1849.2 g Frit X (140 mesh) with 150.8 g HfO ₂ blended in
8/17/06	Run 6 Frit X With HfO ₂ Sub for 9.5 wt% PuO ₂	1849.2 g Frit X (140 mesh) with 150.8 g HfO ₂ blended in
8/24/06	Run 7 Fill Canister With LaBS Frit X Glass	6020 g LaBS Frit X cullet from Runs 4, 5 and 6
9/5/06	Run 8 Process Frit X Batch To Produce Cullet	3000 g Frit X Batch Chemicals
9/6/06	Run 9 Process Frit X Batch To Produce Cullet	3100 g Frit X Batch Chemicals
9/7/06	Run 10 Process Frit X Batch To Produce Cullet	2600 g Frit X Batch Chemicals
9/13/06	Run 11 Process Frit X Batch To Produce Cullet	2600 g Frit X Batch Chemicals
9/18/06	Run 12 Process Frit X Batch To Produce Cullet	3189 g Frit X Batch Chemicals
9/20/06	Run 13 Process Frit X Batch To Produce Cullet	3191 g Frit X Batch Chemicals
10/11/06	Run 14 Process Frit X with NaCl Impurity Addition aka "NaCl Run" or "Run 101006"	~3000 g Frit X / HfO ₂ / NaCl blend
10/26/06	Run 15 Process Frit X with Rocky Flats B5495 Addition aka "Rocky Flats Run" or "Run 102606")	2981 g Frit X / HfO ₂ / Rocky Flats Can B5495 surrogate blend
11/1/06	Run 16 Reprocess Run 15 Cullet Product aka "Remelt Run" or "Run 110106"	2833 g glass from Run 15

Melter Configuration and Setup

The CIM was prepared to support the LaBS glass pour testing. A photo of the CIM located at the Aiken County Technology Laboratory (ACTL) is shown in Figure 1. For the CIM to be in proper working order, the calibration of process thermocouples had to be performed to ensure that the melting process is prototypical. The CIM also had to be capable of maintaining the glass melt at a temperature of 1500°C for nominally 4 hours, then draining the glass product into an appropriate receipt container.

In advance of design and installation of an offgas filtering system, melter testing was conducted in the CIM using an existing fume hood configuration and glass compositions that contained no impurities (i.e. no hazardous species). These tests are designated as runs #1-13 in Table I. These tests provided initial data regarding melter operating performance and throughput. Specific objectives of these tests included evaluation of dry feed (powder) melting behavior, melter operation parameters (power input and temperature), melter pouring behavior, melter cycle time, melter structural behavior, and glass quality produced by the test runs. For brevity, these runs will not be further discussed.

Some form of an offgas system will be required for operating the CIM with Pu in a glovebox environment. The specific requirements of the offgas system are not known at this time. A primary goal of the current effort was to evaluate offgas emissions from extreme impurity feeds. Runs #14 and 15 (NaCl and Rocky Flats) were conducted to sample the offgas emissions that evolve during the vitrification of LaBS Frit X blended with HfO₂ (as a surrogate for PuO₂) and expected impurities. Modifications were made to the CIM to accommodate an EPA gas sampling train. Offgas sampling was performed using a modification of EPA Source Sampling Method 26 [3]. This EPA method is applicable for determining emissions of hydrogen halides (HCl, HBr, and HF) and halogens (Cl₂ and Br₂). It should be noted that bromine was not present in these tests.

The top of the melter was replaced with a 3/8" thick quartz plate with a 1" offgas vent hole and two smaller penetrations to accommodate the glass melt thermocouple and the bubbler. A 1" thick sheet of M-board insulation was placed on top of the quartz plate. A quartz cylinder was placed into the hole in M-board and quartz plate so that the offgases leaving the melter would not contact the M-board insulation. The offgases were collected by a Pyrex™ glass sampling funnel that was positioned above the melter vent penetration, and the balance of the glasswork and impinger vessels were positioned in close proximity to the melter by the addition of a new support platform (see Figure 1).

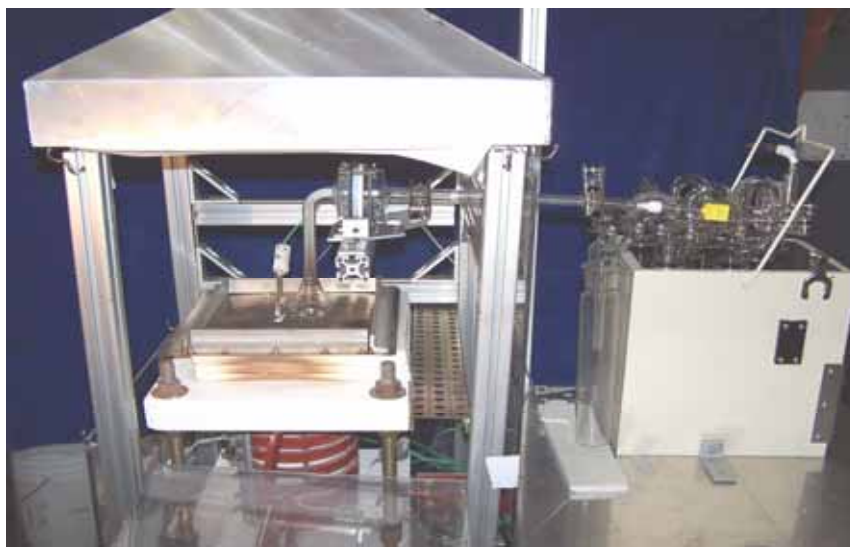


Figure 1. Melter and off-gas sample collection equipment.

A 3" diameter quartz fiber on Teflon™ mesh filter was used to collect particulate. The filter papers have 99.95% efficiency for dioctyl phthalate (DOP) particles at 0.3 μm. The offgas was then passed through an empty impinger, two water impingers, two 0.1N (0.05M) sulfuric acid (H₂SO₄) impingers, two 0.1N sodium hydroxide (NaOH) impingers, and then a silica gel impinger to remove any water vapor remaining in the gas. All except the empty impinger were kept at near 0 °C in an ice bath. The gas flowrate varied from around 4.25 L/min to 16.99 L/min (0.15 to 0.6 ft³/min (cfm)). The flowrate was measured with an orifice meter and a dry gas meter. A diagram of the offgas sampling system is shown in Figure 2.

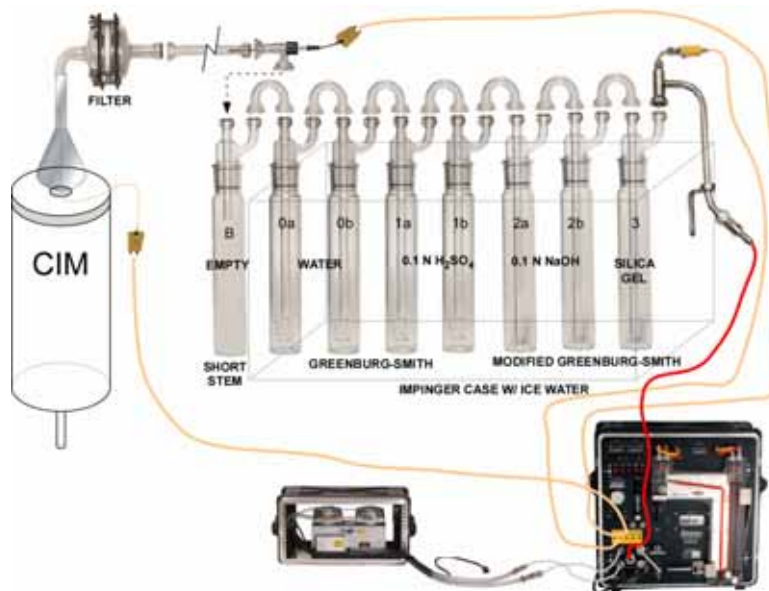


Figure 2. Schematic of modified EPA Method 26 sampling system.

Offgas Sampling System Operation

Because the stack sampling system collected the entire offgas from the melter, isokinetic sampling was not required, so control of the sampling rate was not critical so long as all of the offgas was collected. During filter and impinger changes, there were short (<5 minutes) periods where the offgas was not collected.

The particulate matter recovered from the filter and filter inlet were analyzed for halides, other anions, metals, and by Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM/EDS). This analysis is not part of EPA Method 26; these methods quantify only the hydrogen halides and halogens. There is no EPA method for halide salts. The total particulate mass was also measured approximately by weighing filter assembly before and after sampling.

The first empty impinger was used to protect the melter from accidental flow reversal in the sample system that could have resulted in water being sprayed onto the top of the melter. The empty impinger and the outlet of the filter were rinsed with water and analyzed with the water impinger contents.

The water impingers were added to the EPA method to help distinguish between chloride from HCl vapor and from NaCl, KCl, or other chloride salt; the EPA method is not designed to look for salts. Increases in the acidity of the water are directly indicative of the amount of HCl and HF in the offgas.

The halides were quantified by Ion Chromatography (IC); nitrate, sulfate, and phosphate were also measured by IC. Metals were quantified by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Samples containing solids were analyzed for total species by dissolving the solids with a few drops of HNO₃ and also for soluble species by first filtering out the solids.

The acid impingers are designed to remove the hydrogen halide vapors, while the basic impingers remove the halogens (Cl₂). Chlorine has a very low solubility in the acidic solutions and should pass through to the alkaline solution where it is hydrolyzed to form a proton (H⁺), the chloride ion, and hypochlorous acid (HClO):



Sodium thiosulfate is added to the alkaline solution to assure reaction with the hypochlorous acid to form a second halide ion such that two chloride ions are formed for each molecule of chlorine gas. Table II summarizes the offgas sample and analyses performed.

Table II. Offgas Sample Preparation and Analyses

Sample	Preparation	Analyses
Filter – Particulate	None	total mass XRD SEM/EDS
Filter – Particulate	dilution & dissolution (acidification)	IC (except nitrate) ICP-AES
Filter – Particulate	dilution & filtration	IC ICP-AES
Water Impingers (+ empty impinger)	Dilution	Total Acid IC ICP-AES
Acid Impingers	Dilution	Total Acid IC (except sulfate) ICP-AES (except sulfur)
Basic Impingers	Dilution	IC
Basic Impingers	reaction with sodium thiosulfate	IC (except sulfate)

Impurity Feed Test Compositions

The melter coupled with the offgas sampling system was utilized for impurity feed testing to demonstrate processing of the impurity feed compositions and identify any challenges associated with specific feeds by analysis of the particulate and fume samples collected. Specific objectives of this testing included evaluation of: melter operation parameters, offgas behavior, melter structural behavior, and glass quality produced from the impurity feeds tested. In this initial phase, limited impurity feed testing was completed. It is anticipated that extensive follow-on testing will be conducted in a future task.

Melter feed was batched using LaBS Frit X frit, HfO₂ as a surrogate for PuO₂ on an equivalent molar basis, and impurity components anticipated for the various feed streams. The Frit X composition is given in Table III. Run #14 involved a high NaCl loading designed to evaluate a NaCl content near the extreme in the feed. Run #15 targeted a Rocky Flats Can B5495 feed that was thought to typify a high salt content impurity feed. Table IV shows the composition of the impurity melter feeds.

Table III. Nominal LaBS Frit X Batch Composition

Oxide	Mass %
Al ₂ O ₃	10.00
B ₂ O ₃	13.00
Gd ₂ O ₃	13.50
HfO ₂	7.00
La ₂ O ₃	19.00
Nd ₂ O ₃	15.00
SiO ₂	20.00
SrO	2.50

Table IV. Feed Compositions for Impurity Test Runs

Component	NaCl Run		Rocky Flats Run	
	Mass (g)	Wt% in Feed	Mass (g)	Wt% in Feed
Total Initial Feed	3000 (2981)[†]	NA	2981	NA
Frit X	2700	90.0	2733.3	91.7
HfO ₂ *	225	7.5	153.4	5.14
Σ Impurities	75.0	2.5	94.28	3.16
CaCl ₂ •2H ₂ O	0	0	4.76	0.16
CaF ₂	0	0	6.56	0.22
Cr ₂ O ₃	0	0	5.46	0.18
CuO	0	0	0.304	0.01
Fe ₂ O ₃	0	0	2.98	0.10
KCl	0	0	26.93	0.90
MgOHCl	0	0	13.68	0.46
MoO ₃	0	0	0.609	0.02
NaCl	75.0	2.5	26.33	0.88
NiO	0	0	4.47	0.15
Na ₃ PO ₄	0	0	0.703	0.024
WO ₃	0	0	1.49	0.05

Some approximations to the actual composition of the Rocky Flats feed had to be made. The Pu content is a combination of PuO₂ and PuF₄; HfO₂ is used as a surrogate for PuO₂ in the simulant tests, but HfF₄ was not available. To add more fluorine (F), CaF₂ was added, which resulted in the Ca content of the simulant being about 3.6 times higher than the target. The actual frit content of the total feed was 91.7 wt% versus the target 90.0 wt%. This difference was due to unintentionally leaving out the Pu from PuF₄ and not adding an equivalent amount of Hf for the Pu. The amount of HfO₂ added was equivalent to the amount of PuO₂ present on a molar basis.

Magnesium chloride MgCl₂ cannot be added in the anhydrous form due to its hygroscopic nature; only the hexahydrate can be used in non-inerted atmospheres. Because this impure Pu stream has been fired at high temperature, it was deemed likely that the MgO and MgCl₂ could have formed the hydroxychloride MgOHCl, so MgOHCl was used in place of the MgO and MgCl₂. MgOHCl is also much easier to handle as it is a refractory non-hygroscopic solid. Use of MgOHCl resulted in the chloride content of the simulant being about 20% higher than the target.

Anhydrous sodium phosphate Na₃PO₄ was substituted for phosphorus pentoxide P₂O₅, again due to the hygroscopic nature of P₂O₅. This substitution resulted in 3% more Na than the target. Calcium chloride dihydrate CaCl₂•2H₂O was used rather than the anhydrous form because the anhydrous material was not available.

Overall, the impurities accounted for about 38 wt% of the simulated Pu feed compared to the target value of about 29.4 wt%. The difference is due to the substitutions described above. The Pu stream is assumed to be completely dry, but the actual amount of water associated with it is not known. No additional water was added to the simulant other than any water that was associated with the reagents and any water that may have been adsorbed during handling in the laboratory.

Glass Analyses

To perform cation analyses, the collected glass samples were prepared in duplicate using a sodium peroxide/sodium hydroxide (Na₂O₂/NaOH) fusion with an HCl uptake. The dissolutions were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Fluoride and chloride contents were determined using a sodium peroxide/sodium hydroxide fusion with water uptake followed by analysis using Ion Chromatography (IC).

RESULTS AND DISCUSSION

Chronology of NaCl Run

The NaCl Run processed approximately 3000 g of feed which was charged into the CIM, resulting in an 8.5" bed height (of 14" total in the CIM vessel). The material was subjected to a standard heating schedule for CIM processing of LaBS frit, including 30 minutes initial heating at minimum induction heating power input, followed by a nominal 10°C per minute temperature increase to approximately 1400°C. Air bubbling was then initiated at 21.24 L/h (0.75 scfh) to homogenize the glass for an additional 3 hours at nominally 1400°C. During glass pouring, glass samples were collected at the initiation of pouring, mid-way into the pour, and as the final glass drips were deposited. Glass composition analyses were not completed on the final glass drip sample due to the small sample size. The offgas was sampled throughout the entire vitrification run.

Offgas Analysis of NaCl run

Table V shows the offgas species collected in the NaCl Run. Based on the chemical analyses, about 1.79 wt% of the feed was volatilized to the offgas system, while the amount volatilized based on the feed and glass masses was 1.82 wt%. These amounts correspond to an impurity loss of ~72% of the added 2.5 wt%. The DFs for boron and Sr were the highest for the frit components. The species with NA for the decontamination factor were not intentionally added to the feed, but some were present nonetheless. The elements K, Fe, and Cu were present at higher than expected amounts. The K may have been an impurity in the NaCl used. The source of Fe may be from blending of the frit and HfO₂ in ferrous metal equipment or from the HfO₂ used (99% pure). Frit analysis (prior to blending) showed no detectable Fe. The HfO₂ has not been analyzed for impurities. The Cu could have come from frit screening on brass sieves. Brass contains both Cu and Zn, and Zn was found in the offgas particulate even though it was not added; the ratio of Zn:Cu was 0.25 which is in the range of a typical brass.

Offgas Particulate Analysis from NaCl Run

Offgas particulate collected on the filter from the NaCl Run was also examined by SEM/EDS. These photographs are shown in Figure 3. The predominant features in these micrographs were small spherical salt particles (these particles were identified to contain Na and Cl by EDS). The salt particles were as small as 0.2 µm and that they were agglomerated. It appears that a median size may be around 0.5 µm. "Photo 8" in Figure 3 shows that there were some cubic particles that suggest entrained NaCl.

Table V. Offgas Species from NaCl Impurity Run (shaded components are Frit X species)

	Offgas Particulate (mg/kg glass)	Offgas Scrubbers Total (mg/kg glass)	Offgas Total (mg/kg glass)	Offgas / Feed (wt%)	Decontamination Factor**
Mass Loss (Feed – Glass)	NA	NA	18171	1.82	NA
Mass Measured	3354	NA	NA	NA	NA
Σ Elements	6725	6041	12767	1.79	55.8
Cl	3973	6028	10001	64.4	1.55
Na	2632	0	2632	26.1	3.83
B †	42.1	5.65	47.7	0.13	756
Sr	18.1	0.085	18.1	0.095	1052
Al	1.00	0.100	1.10	0.0019	5.16E+04
La	1.59	0	1.59	0.0011	9.31E+04
Nd	1.07	0	1.07	0.00095	1.06E+05
Hf	1.08	0.006	1.09	0.00093	1.07E+05
Gd	0.826	0	0.826	0.00077	1.30E+05
Si †	0.234	0.128	0.363	0.00040	2.48E+05
K	24.7	0.178	24.8	NA	NA
Fe	12.3	0.029	12.3	NA	NA
Cu	8.85	0.041	8.89	NA	NA
Zn	2.30	0	2.30	NA	NA
Ca	1.70	0.180	1.88	NA	NA
Ni	1.08	0	1.08	NA	NA
S	0.905	4.31	5.21	NA	NA
W	0.725	0.044	0.769	NA	NA
Pb	0.668	0	0.668	NA	NA
Cr	0.331	0.013	0.345	NA	NA
Mo	0.266	0.027	0.293	NA	NA
Mg	0.245	0	0.245	NA	NA
P	0	0	0	NA	NA
F	0	2.77	2.77	NA	NA

† B & Si in scrubbers possibly from glassware

** Decontamination Factor = Concentration of specie in batch/Total offgas concentration of specie

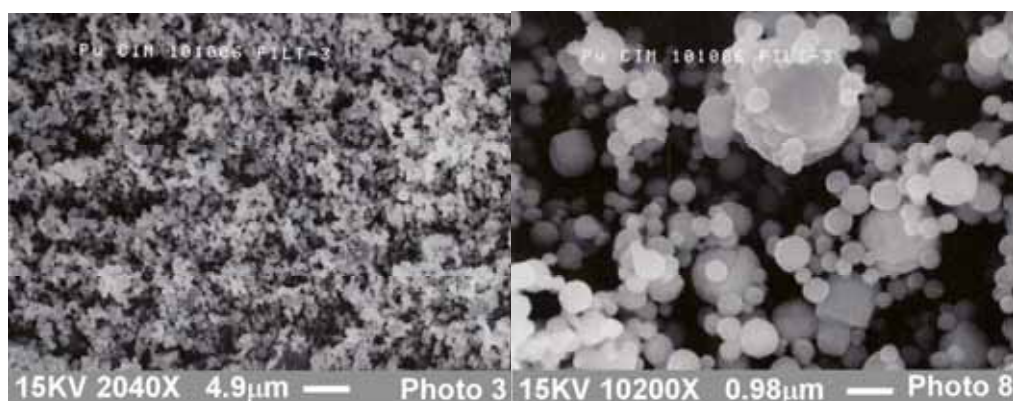


Figure 3. SEM micrographs of salt particles collected on the filter from the NaCl Run.

Chronology of Rocky Flats B5495 Run

The Rocky Flats Run processed a 2981 g batch consisting of LaBS Frit X with chemical additions representative of a Rocky Flats Can B5495 composition. The same heating and sampling schedule was followed as was employed with the previous NaCl addition test. The offgas was sampled throughout the entire vitrification run. Particulate and vapors were still evident by visual observation at the completion of three hours air bubbling at 1450°C. Part way through the run, the bubbler air flow was reduced to about 9.91 L/h (0.35 scfh) to see if the lower flowrate would visibly change the appearance of the offgas particulate emissions. No noticeable change occurred. During glass pouring, glass samples were collected at the initiation of pouring, mid-way into the pour, and as the final glass drips were deposited. Glass analyses were not conducted on the final glass drip sample.

Offgas Analysis of Rocky Flats B5495 Impurity Run

The amounts of each offgas species (element) collected per kg of glass produced in the Rocky Flats Run are shown in Table VI. The fraction as wt% of each species present in the feed that was evolved to the offgas is also given. Based on the chemical analyses, about 1.72 wt% of the feed was volatilized to the offgas system; based on the mass loss from the feed to glass (feed mass minus glass mass), the amount volatilized is estimated to be 1.92 wt%. Of the total impurity addition of 3.16 wt%, the offgas species constitute 54-61% of the impurities. The major constituents in the offgas particulate were Cl, K, and Na, while Cl and F predominated in the offgas scrub solutions. The losses of Na and Cl were similar to the values found for the NaCl Run. All of the frit components were found in very low concentrations in the offgas. Except for Hf and boron (B), all were less than 0.03 wt% in the offgas. Hf is likely to be higher due to physical entrainment of HfO₂ particles while boron is higher due to the known volatility of boron at the melter temperatures. To check whether physical entrainment of HfO₂ is likely, particle size analysis of the HfO₂ will be performed. The decontamination factors (DF) for the melter to offgas are also given. The sum of the elements for the particulate (6541 mg/kg) was very close to the particulate mass measured (6051 mg/kg).

The offgas scrub solutions contained primarily HCl and HF, with a small amount of alkali. Overall, the amount of alkali and other metals found in the scrubbers was very small, indicating that the particulate filter efficiency was high. Subtracting the Cl and F from the offgas scrubber total and adding back Cl equivalent to the Na and K present (balance Na⁺ & K⁺ with Cl⁻) gives about 90 mg “non HCl or HF”/kg glass in the scrub solutions. This means that other than HCl and HF, only about 0.8% (90/11582) of the species volatilized were collected in the scrub solutions while 99.2% were collected on the filter.

Table VI. Offgas Species from Rocky Flats B5495 Impurity Run (shaded components are Frit X species)

	Offgas Particulate (mg/kg glass)	Offgas Scrubbers Total (mg/kg glass)	Offgas Total (mg/kg glass)	Offgas / Feed (wt%)	Decontamination Factor**
Mass Loss (Feed - Glass)	NA	NA	19146	1.92	NA
Mass Measured	6051	NA	NA	NA	NA
Σ Elements	6541	5565	12107	1.72	58.0
Cl + F	3098	5510	8608	62.0	1.61
K + Na	2830	29.7	2860	34.2	2.93
Cl	3086	5337	8422	65.9	1.52
Cu	47.8	0.50	48.3	58.2	1.72
K	2101	17.8	2118	43.9	2.28
Mo	32.0	1.60	33.6	24.3	4.12
Na	730	11.9	742	20.9	4.77
Ni	241	2.71	243	20.2	4.94
F	12.2	173	185	17.0	5.89
Fe	24.4	0.45	24.8	3.48	28.7
Cr	37.9	6.09	43.9	3.44	29.1
W	5.50	0.19	5.69	1.41	71.1
Ca	2.10	0.20	2.30	0.52	192
P	0.09	0	0.09	0.20	510
B †	52.1	7.38	59.5	0.16	614
Hf	156	0.03	156	0.16	615
Mg	0.64	0	0.64	0.043	2316
Sr	5.73	0.11	5.85	0.030	3309
Si †	0.26	4.76	5.03	0.0055	1.81E+04
Al	1.33	0.24	1.57	0.0027	3.66E+04
La	0.59	0	0.59	0.00039	2.56E+05
Gd	0.31	0	0.31	0.00029	3.46E+05
Nd	0.31	0	0.31	0.00027	3.69E+05
Pb*	0.54	0	0.54	NA	NA
S*	1.11	1.78	2.89	NA	NA
Zn*	3.54	0	3.54	NA	NA

* not added to feed † B & Si in scrubbers possibly from glassware

** Decontamination Factor = Concentration of specie in batch/Total offgas concentration of specie

Glass Composition Analyses

The predicted and measured glass compositions for the NaCl and Rocky Flats Runs are shown in Table VII. The table gives the composition predicted from subtracting the measured offgas species from the feed. Elements that deviated more than 25% from the predicted composition are shown in bold in the “% Difference” column.

For the NaCl Run, all species except Cl were within 25% of the predicted concentrations. The measured chloride in the glass was lower than predicted because the measured total chloride in the offgas was probably lower than the actual amount in the offgas. Small amounts of Ca, Cu, Fe, and Zr were found in the the NaCl Run glass even though none was intentionally added in the Frit X, HfO₂, or impurity NaCl. In the Rocky Flats Run, the Ca, Cu, Fe, and Zr were again higher than the amounts added to the feed; in fact, the Ca, Cu and Fe present as impurities were higher than the intended amount to be added. The source of Zr is most likely the HfO₂ used as the surrogate for PuO₂ and for the frit; ZrO₂ is an impurity at up to 1.5 wt% in HfO₂. As mentioned previously, the source of Fe is probably processing in ferrous metal equipment, while the Cu could have come from frit screening on brass sieves. Brass contains both Cu and Zn, but Zn would not be found in the glass due to its volatility. Reanalysis of the Frit X for impurities is pending.

The Na was also higher than predicted, but only by 27.5%. Na was definitely found in the offgas as NaCl, so the total amount of Na added may have also been higher than intended. Both Ni and Cr were low; both were found to be volatile and were found in both the offgas particulate samples and in offgas line deposits (detected via SEM/EDS analyses). The amounts of each of these in the offgas line deposits were not accounted for in the material balance; these deposits may account for the missing Cr and Ni. The balance on chloride was good, with both the measured and predicted concentration in the glass being about 0.4 wt%.

Fluoride and chloride were measured in the glass using a sodium peroxide/sodium hydroxide fusion with water uptake that does not dissolve all of the fused product. It appears that fluoride does not dissolve in the water uptake. For test glasses made with CaF₂, the calcium was present at a molar ratio of Ca:F of 1:2 and much less than expected fluoride was found in the glass. Analysis of glasses with fluoride in significant excess over calcium give slightly low fluoride measurements. If the fluoride is bound to the calcium in the fusion, the water uptake is not likely to dissolve it, resulting in low measurements of fluoride. Analytical method development will be required to accurately quantify fluoride in the presence of excess calcium.

Table VII. Predicted and Measured Compositions of Glasses Produced from the NaCl and Rocky Flats Runs

	NaCl Run			Rocky Flats Run		
	Predicted From (Feed – Offgas) (wt%)	Measured (mean of 2) (wt%)	% Difference (Meas.-Calc.)	Predicted From (Feed – Offgas) (wt%)	Measured (mean of 2) (wt%)	% Difference (Meas.-Calc.)
Al	5.58	5.49	-1.69	5.70	5.61	-1.56
B	3.53	3.54	0.27	3.60	3.67	1.88
Ca		0.090	NA	0.044	0.213	79.5
Cr		<0.01	NA	0.122	0.092	-32.0
Cu		0.031	NA	0	0.048	92.8
Fe		0.049	NA	0.068	0.088	22.9
Gd	10.49	10.65	1.52	10.71	10.65	-0.55
Hf	11.39	11.20	-1.7	9.49	9.56	0.74
K		<0.1	NA	0.268	0.289	7.34
La	14.56	14.75	1.31	14.86	14.70	-1.10
Mg		<0.01	NA	0.146	0.117	-24.7
Mn		<0.01	NA	0	<0.01	NA
Mo		<0.01	NA	0.010	0.012	11.7
Na	0.730	0.724	-0.8	0.276	0.381	27.5
Nd	11.08	11.30	1.98	11.31	11.40	0.81
Ni		<0.01	NA	0.095	0.065	-46.2
P		<0.1	NA	0.0045	<0.1	NA
Si	8.80	8.93	1.44	8.99	9.10	1.28
Sr	1.87	1.88	0.41	1.91	1.89	-1.21
W		<0.1	NA	0.039	<0.1	NA
Zr		0.025	NA	0	0.045	NA
Cl	0.543	0.293	-85.7	0.431	0.374	-15.1
F		<0.02	NA	0.090	NA	NA
TOTAL	68.57	68.95	0.55	68.16	68.31	0.21

Table VIII shows the predicted composition of the Rocky Flats Run glass assuming incorporation into the glass of 1) all impurities; 2) only the cation (metal impurities) plus phosphorus; 3) no impurities; and 4) impurities predicted by the material balance (feed – offgas); these values are compared to the measured values. This comparison is presented on both elemental and oxide bases. Analyses of these data clearly show the good retention of most species in the glass.

Table VIII. Elemental and Oxide Concentrations Predicted and Measured for Glass from the Rocky Flats Run

Element	Cation					Oxide	Cation				
	All Impurities (wt%)	Impurities + P (wt%)	No Impurities (wt%)	Feed – Offgas (wt%)	Measured Mean (wt%)		All Impurities (wt%)	Impurities + P (wt%)	No Impurities (wt%)	Feed – Offgas (wt%)	Measured Mean (wt%)
Al	5.63	5.70	5.81	5.70	5.61	Al₂O₃	10.63	10.78	10.99	10.77	10.60
B	3.56	3.61	3.68	3.60	3.67	B₂O₃	11.47	11.63	11.85	11.60	11.83
Ca	0.043	0.044	0	0.044	0.213	CaO	0.060	0.061	0	0.061	0.298
Cr	0.125	0.126	0	0.122	0.092	Cr₂O₃	0.182	0.184	0	0.178	0.135
Cu	0.008	0.008	0	0.003	0.048	CuO	0.010	0.010	0	0.004	0.060
Fe	0.070	0.071	0	0.068	0.088	Fe₂O₃	0.099	0.101	0	0.097	0.126
Gd	10.57	10.72	10.92	10.71	10.65	Gd₂O₃	12.18	12.35	12.59	12.34	12.28
Hf	9.38	9.51	9.69	9.49	9.56	HfO₂	11.06	11.21	11.43	11.19	11.27
K	0.471	0.477	0	0.268	0.289	K₂O	0.567	0.575	0	0.323	0.348
La	14.67	14.87	15.16	14.86	14.70	La₂O₃	17.21	17.44	17.78	17.43	17.24
Mg	0.144	0.146	0	0.146	0.117	MgO	0.239	0.243	0	0.242	0.194
Mo	0.014	0.014	0	0.010	0.012	MoO₃	0.020	0.021	0	0.016	0.018
Na	0.345	0.350	0	0.276	0.381	Na₂O	0.465	0.472	0	0.373	0.514
Nd	11.16	11.32	11.53	11.31	11.40	Nd₂O₃	13.02	13.20	13.45	13.19	13.30
Ni	0.117	0.119	0	0.095	0.065	NiO	0.149	0.151	0	0.121	0.082
P	0.004	0.004	0	0.004	<0.1	P₂O₅	0.010	0.010	0	0.010	<
Si	8.87	8.99	9.17	8.99	9.10	SiO₂	18.98	19.24	19.61	19.22	19.47
Sr	1.89	1.91	1.95	1.91	1.89	SrO	2.23	2.26	2.30	2.26	2.23
W	0.039	0.040	0	0.039	<0.1	WO₃	0.050	0.050	0	0.050	<
Zr	0	0	0	0	0.045	ZrO₂	0	0	0	0	0.061
Cl	1.25	0	0	0.431	0.374	Cl	1.25	0	0	0.431	0.374
F	0.107	0	0	0.090	NA	F	0.107	0	0	0.090	NA
TOTAL	68.47	68.04	67.92	68.16	68.31	TOTAL	100	100	100	100	100.43

The glass compositions on an elemental and an oxide basis for the NaCl and Rocky Flats Runs are compared in Table IX. The oxide totals for both were very close to the expected 100%. The Hf content of the NaCl Run glass was higher than the Rocky Flats Run glass as expected due to a higher target value.

Table IX. Measured Compositions of Glass from the NaCl and Rocky Flats Runs

Element	Oxide	NaCl Run				Rocky Flats Run			
		Sample 1 (wt%)	Sample 2 (wt%)	Mean	Oxides (wt%)	Sample 1 (wt%)	Sample 2 (wt%)	Mean	Oxides (wt%)
Al	Al ₂ O ₃	5.52	5.47	5.49	10.37	5.56	5.67	5.61	10.60
B	B ₂ O ₃	3.54	3.54	3.54	11.40	3.64	3.71	3.67	11.83
Ca	CaO	0.103	0.078	0.090	0.126	0.195	0.231	0.213	0.298
Cr	Cr ₂ O ₃	<0.01	<0.01	<0.01	0	0.093	0.092	0.092	0.135
Cu	CuO	0.031	0.032	0.031	0.039	0.056	0.040	0.048	0.060
Fe	Fe ₂ O ₃	0.052	0.047	0.049	0.070	0.086	0.091	0.088	0.126
Gd	Gd ₂ O ₃	10.65	10.65	10.65	12.28	10.80	10.50	10.65	12.28
Hf	HfO ₂	11.10	11.30	11.20	13.21	9.56	9.56	9.56	11.30
K	K ₂ O	<0.1	<0.1	<0.1	0	0.282	0.296	0.289	0.348
La	La ₂ O ₃	14.75	14.75	14.75	17.30	14.95	14.45	14.70	17.24
Mg	MgO	<0.01	<0.01	<0.01	0	0.110	0.125	0.117	0.194
Mo	MoO ₃	<0.01	<0.01	<0.01	0	0.012	0.012	0.012	0.018
Na	Na ₂ O	0.723	0.725	0.724	0.976	0.427	0.336	0.381	0.514
Nd	Nd ₂ O ₃	11.35	11.25	11.30	13.18	11.35	11.45	11.40	13.30
Ni	NiO	<0.01	<0.01	<0.01	0	0.060	0.070	0.065	0.082
P	P ₂ O ₅	<0.1	<0.1	<0.1	0	<0.1	<0.1	<0.1	0
Si	SiO ₂	8.96	8.90	8.93	19.10	9.03	9.18	9.10	19.47
Sr	SrO	1.88	1.88	1.88	2.22	1.92	1.86	1.89	2.23
W	WO ₃	<0.1	<0.1	<0.1	0	<0.1	<0.1	<0.1	0
Zr	ZrO ₂	0.025	0.025	0.025	0.034	0.069	0.021	0.045	0.061
Cl	Cl	0.294	0.291	0.293	0.293	0.370	0.379	0.374	0.374
F*	F	<0.02	<0.02	<0.02	0	<0.02	<0.02	NA	0
TOTAL		100.6				100.4			

CONCLUSIONS

The following summarizes the results of these tests and conclusions that can be drawn:

- The melter operated effectively in producing a homogenous glass product. The glass batch was readily melted and poured from the melter.
- The glass composition analytical data indicated good retention of most species in the glass.
- Approximately 72% of NaCl added as an impurity at 2.5 wt% in the feed was emitted into the offgas as particulate NaCl, HCl, or Cl₂.
- About 54-61% of the Rocky Flats Can 5495 impurity mixture added at 3.16 wt% in the feed was emitted into the offgas as particulate or vapor.
- Particulate generated was mostly NaCl and KCl (these were the major impurities added).
- Offgas vapors consisted of HCl, Cl₂, and HF. HCl and Cl₂ could not be totally distinguished.
- Feed entrainment as indicated by frit elements in the offgas particulate was <0.03 wt% except for Sr (<0.1 wt%), B (0.13-0.16 wt%), and Hf (0.16 wt%). Sr and B are the most volatile components of the frit. HfO₂ surrogate may have been entrained.
- Chloride (Cl) in the glass ranged from 0.29-0.37 wt%.
- Approximately 99.2 wt% of volatilized species (excluding HCl, Cl₂, HF) were collected on the nominal 0.3 μm filter.
- Particulate generated was mostly spherical salt particles as small as 0.2 μm, with an approximate median size of about 0.5 μm. Larger agglomerates may have also been present.

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