Offgas Generation from the Disposition of Scrap Plutonium
by Vitrification - Simulant Tests

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ABSTRACT

INTRODUCTION & BACKGROUND

The Department of Energy Office of Environmental Management is supporting R&D for the conceptual design of the Plutonium Disposition Project at the Savannah River Site in Aiken, SC to reduce the attractiveness of plutonium scrap by fabricating a durable plutonium oxide glass form and immobilizing this form within the high-level waste glass prepared in the Defense Waste Processing Facility. A glass formulation was developed that is capable of incorporating large amounts of actinides as well as accommodating many impurities that may be associated with impure 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 **La**nthanide **B**oro**S**ilicate (LaBS) glass that accommodated significant quantities of actinides, tolerated impurities associated with the actinide feed streams and could be processed using established melter technologies.

A Cylindrical Induction Melter (CIM) was used for vitrification of the Pu LaBS glass. Induction melting for the immobilization of americium and curium (Am/Cm) in a glass matrix was first demonstrated in 1997. The induction melting system was developed to vitrify a non-radioactive Am/Cm simulant combined with a glass frit. Most of the development of the melter itself was completed as part of that work. This same melter system used for Am/Cm was used for the current work.

The CIM system used consisted of a 5 inch (12.7 cm) diameter inductively heated platinum-rhodium (Pt-Rh) containment vessel with a control system and offgas characterization. Scrap plutonium can contain numerous impurities including significant amounts of chlorides, fluorides, sodium, potassium, lead, gallium, chromium, and nickel. Smaller amounts of additional elements can also be present. The amount of chlorides present is unusually high for a melter feed. In commercial applications there is no reason to have chloride at such high concentrations. Because the melter operates at 1400-1475°C, many of the impurities present are extremely volatile. An alternative being considered is to pre-treat the impure PuO_2 by water washing to remove the soluble salts, which would significantly reduce the melter emissions. The disadvantage of the washing alternative is the criticality concerns of using water with plutonium.

In this paper, the testing that has been conducted at the Savannah River National Laboratory (SRNL) to demonstrate induction melting of impure plutonium simulants will be described. The work described concentrates on quantification of the gaseous and particulate emissions from the induction melter.

The Pt-Rh melter vessel is a cylinder with a conical bottom and a tubular drain as shown in Figure 1. A 5-inch (12.7 cm) diameter CIM was used for all of the emissions tests. A 6-inch (15.24 cm) diameter CIM, which is the size of the full-scale melter, has since been constructed for further testing. The 5-inch CIM is heated by three induction coils: one for the 5 inch cylinder, one for the conical section, and one for the ¼" (6.35 mm) drain tube. The 6-inch CIM is similar except the cylinder heater extends lower and also heats the cone. The induction heating system

is manufactured by Ameritherm™. The heating system is controlled by a PC to maintain a specific heat up profile and then maintain a constant energy input that maintains a constant temperature.

The CIM is operated in batch mode where the plutonium simulant and the glass-forming frit are first thoroughly mixed in an attrittor mill, then added to the melter. Hafnium oxide (HfO_2) is used as a simulant for the radioactive PuO_2. The melter is heated until the mixture begins to melt at about 1100°C, then completely melts at about 1400-1450°C. This temperature is maintained for about three hours. While the temperature is maintained at ~1400°C, an air bubbler is normally used to promote mixing of the glass-forming frit and the waste simulant.
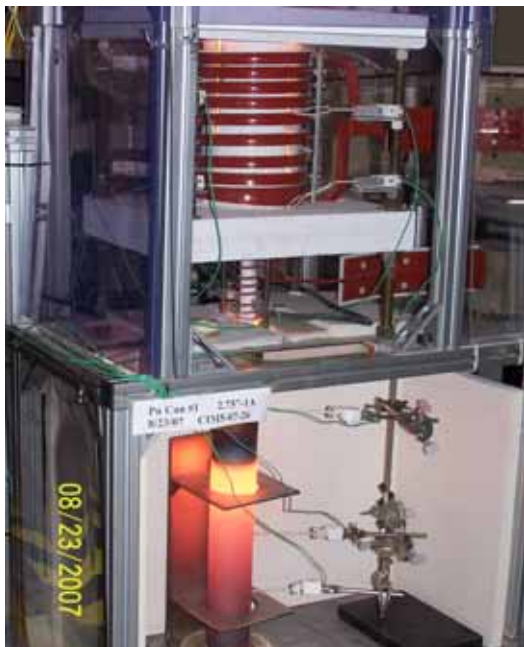

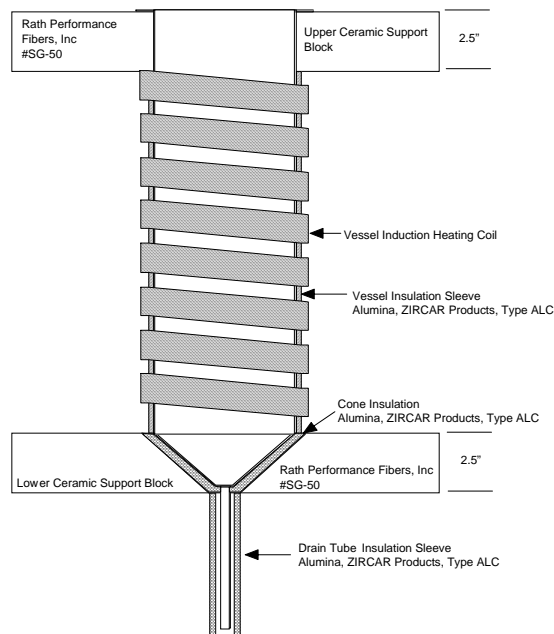**Figure 1. 5-Inch Cylindrical Induction
Melter Pouring Glass**

**Diagram of 6-Inch Cylindrical
Induction Melter**

EXPERIMENTAL
Measurements of emissions from the CIM with were conducted with several simulant feeds that approximated the compositions of actual scrap plutonium. A 'nominal' composition was chosen (B5495) along with two compositions (B5497 and B5439) that were significantly different in at least one component. The 'nominal' composition contained most of the components near the middle range of their extremes in the reported samples. The B5497 composition contained a high level of PbO and B5439 was high in CuO. These compositions are summarized in Table 1. The major impurities are highlighted in bold face. The LaBS frit contains lanthanides (Gd, Hf, La, Nd), boron, silicon, aluminum and strontium. The composition of this frit is shown in Table 2.

Table 1   Compositions of Feed Simulants

Component	NaCl Only	B5495 with Cl; bubbler	B5495 with Cl; no bubbler	B5495 no Cl; bubbler	B5497 no Cl; bubbler	B5439 no Cl; bubbler	B5495 no Cl; no bubbler
Sampling Method	26	26	26 29	29	29	29	26 29
HfO_2	75	61.9	61.5	81.1	62.3	76.9	81.0
Σ Impurities	25	38.1	38.5	18.9	37.7	23.1	19.0
Al_2O_3	0	0	1.13	1.49	1.73	0.96	1.49
$CaCl_2 \cdot 2H_2O$	0	1.92	1.36	0	0	0	0
CaF_2	0	2.65	0	0	0	0	0
Cr_2O_3	0	2.20	2.07	2.73	2.74	0.63	2.73
CuO	0	0.12	0.12	0.15	0.53	**11.82**	0.15
Fe_2O_3	0	1.20	1.13	1.49	3.58	0.69	1.49
Ga_2O_3	0	0	0	0	**5.44**	0	0
KCl	0	**10.87**	**10.22**	0	0	0	0
MgO	0	0	0	3.59	1.86	3.17	3.59
$MgOHCl$	0	**5.52**	**5.19**	0	0	0	0
MoO_3	0	0.25	0.23	0.30	0.27	0.27	0.30
$NaCl$	**25**	**10.63**	**9.99**	0	0	0	0
NaF	0	0	2.68	3.53	**6.91**	1.49	3.53
NiO	0	1.80	1.70	2.24	2.76	1.24	2.23
Na_3PO_4	0	0.28	0.27	0.35	1.23	0.31	0.35
PbO	0	0	0.00	0	**8.92**	0	0
SiO_2	0	0	1.81	0	0	2.07	2.39
WO_3	0	0.60	0.56	0.75	0.67	0.41	0.74

Table 2   Target and Measured Composition of Frit X

Element	Target (wt%)	Measured (wt%)	Oxide	Target (wt%)	Measured (wt%)
Al	5.29	6.18	Al_2O_3	10.00	11.67
B	4.04	3.91	B_2O_3	13.00	12.59
Gd	11.71	11.60	Gd_2O_3	13.50	13.37
Hf	5.94	5.54	HfO_2	7.00	6.53
La	16.20	16.10	La_2O_3	19.00	18.88
Nd	12.86	12.25	Nd_2O_3	15.00	14.29
Si	9.35	9.74	SiO_2	20.00	20.83
Sr	2.11	2.07	SrO	2.50	2.45
Cu	0	0.04	CuO	0	0.05
			TOTAL	100.0	100.6

The plutonium compounds reported in actual scrap, PuF_4 and PuO_2, were replaced by HfO_2 as a surrogate. The fluoride in the PuF_4 was added as either CaF_2 or NaF. The use of HfF_4 to simulate PuF_4 was rejected because the properties of HfF_4 and PuF_4 are not similar, and HfF_4 is very toxic and reactive. The reported compositions included excess unmatched chloride; this

chloride was added as additional NaCl. For several tests, the chlorides were not added to simulate possible compositions that would result from washing of the scrap plutonium oxide to remove soluble salts. Sodium fluoride, although soluble, was still added because PuF_4 would be insoluble. It was hypothesized that the flux of vaporizing salts might increase the emission rate of the metal oxides.

Quantitative measurements of the particulate and gaseous emissions were made both with and without chlorides present. Halide (HF, HCl, and Cl_2) emissions were measured with modified EPA Method 26. This method was extended to measure metals in both the particulate and scrub solutions, although this method is not the optimum method for these measurements. For some tests, modified EPA Method 29 was used to quantify particulate and gaseous metals emissions. The sampling method used for each of the runs is shown in Table 1. For the runs with the B5495 composition both with and without Cl and now bubbler, the first 90 minutes at 1400°C were sampled by Method 26 and the second 90 minutes by Method 29.

Tests were also performed to quantify the particle size distribution of the emitted particulate. Tests without the use of the air bubbler for mixing were also performed to determine if the emission rates were increased by use of the bubbler. For all tests, the entire offgas flow was sampled by the sampling train. The sampling system is shown in Figure 2.

In some tests, a cascade impactor was used to separate the particulate into size fractions. Scanning electron microscopy (SEM) and SEM-Energy Dispersive Spectroscopy (SEM-EDS) were used to examine the physical characteristics and elemental composition of the particulate collected as a function of particle size. The cascade impactor used was a Model CI-700K supplied by Apex Instruments; for most tests, a precollector was used. Typical collection periods were three minutes or less due to the high particulate load.

Particulate deposition on the offgas lines was examined in several tests to estimate the minimum temperature necessary to prevent deposition. These tests were conducted with a simple system consisting of a quartz tube contained within an electrical resistance heater. The offgas was drawn through this system for a period of time and the tube was then examined for particulate deposition. A sketch of the melter top head configuration is shown in Figure 3.
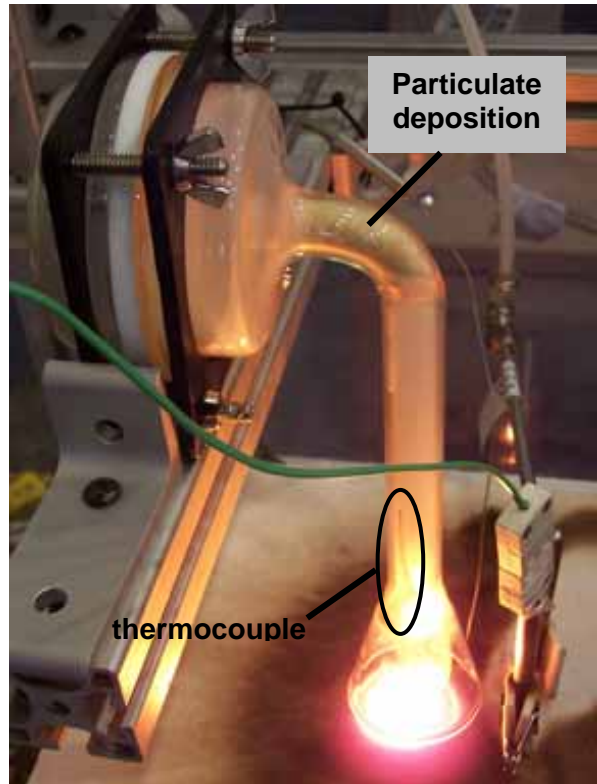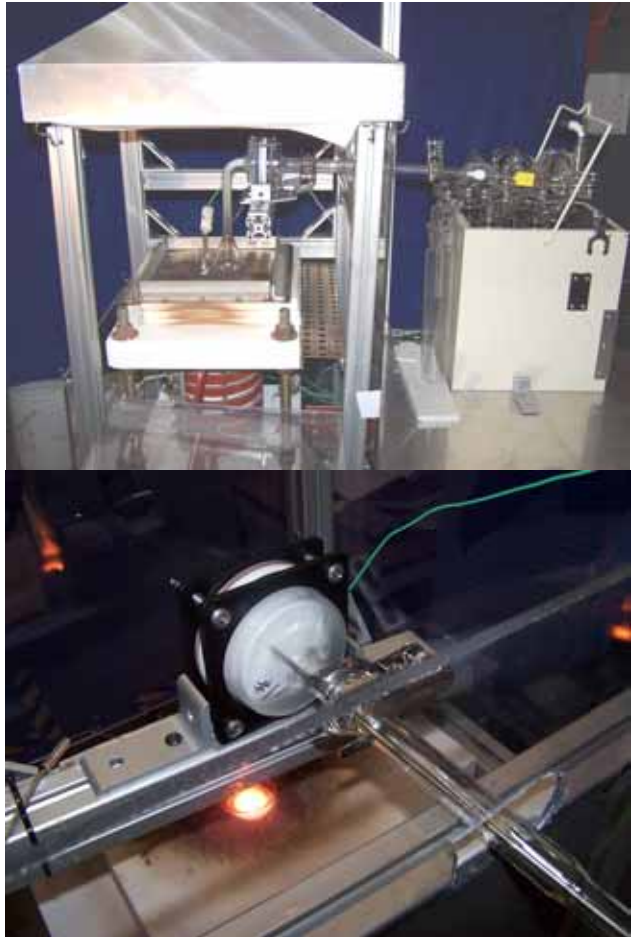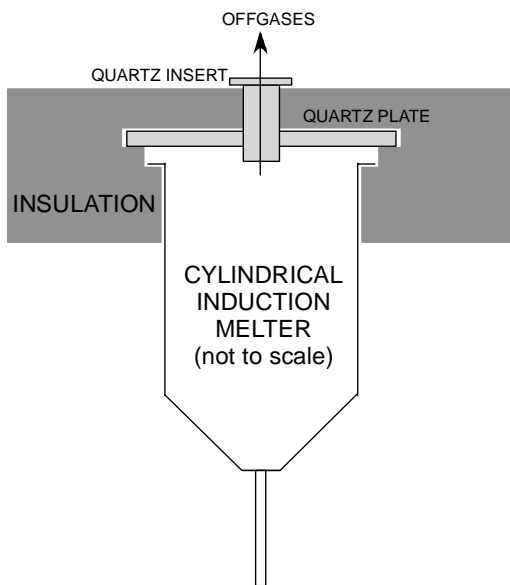
Figure 2   Offgas Sampling System Operation

Figure 3   Melter Top Head Configuration

RESULTS

Offgas Chemical Characterization and Rate

Measurements of the total particulate evolution, expressed as the normalized mass of particulate per mass of feed (or glass) per time (mg/kg/h), for the runs are shown in Figure 4. The evolution rates with chlorides present are about 100 times the rates with no chlorides as expected due to the much higher loading of volatile species in the feed. Use of the bubbler at 0.35 or 0.75 ft^3/h (9.9-21.2 L/h) increases the total particulate evolution rate by about three times with or without chlorides present. There is no significant difference in evolution rate at these two air purge rates. Figure 5 shows that the particulate evolution rate at 1400°C is fairly constant. During the heat up phase, the rate increases until the temperature reaches about 1100°C, where it then levels off. A significant number of the impurity species become volatile at this temperature. The presence of chlorides (NaCl and KCl) increased the particulate emissions by an order of magnitude over that measured with no chlorides.
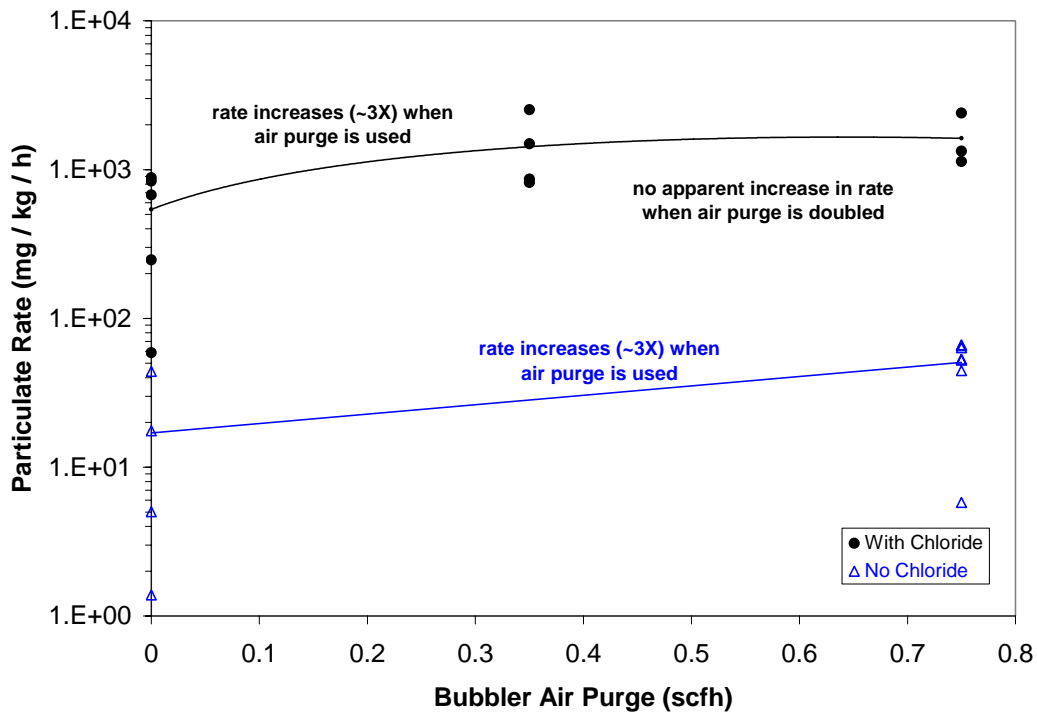

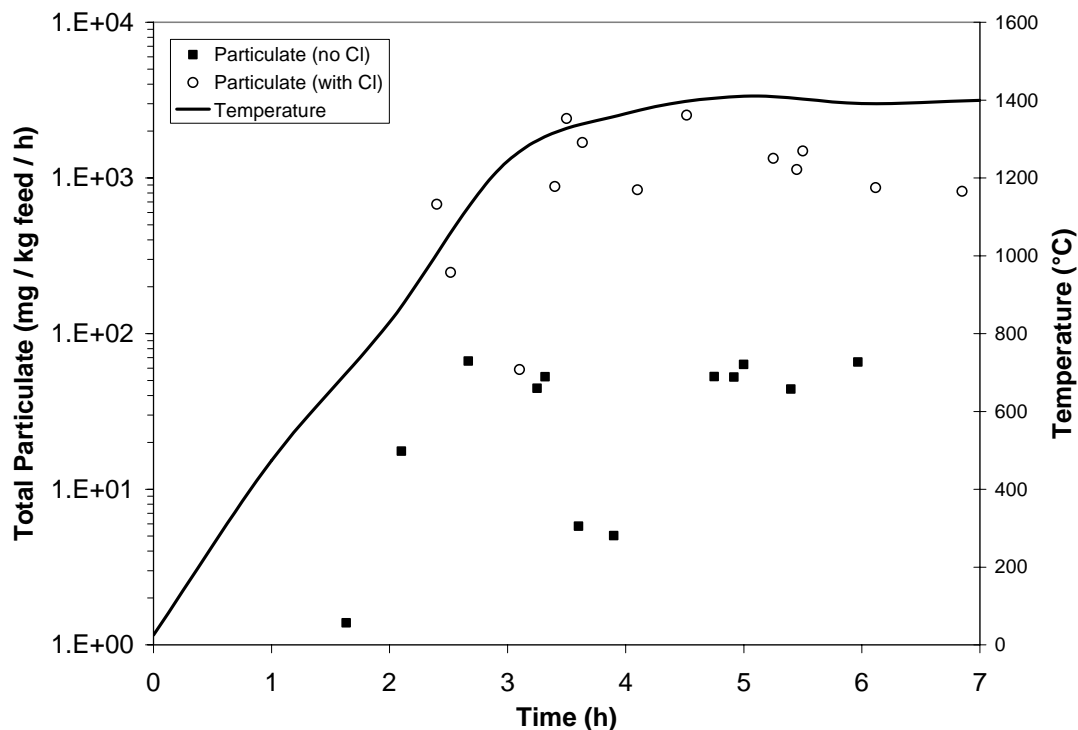**Figure 4   Particulate Evolution Rates**

Figure 5   Particulate Evolution versus Time

Figure 7 shows the evolution rates of the elemental species in the melter feeds in both the particulate and impinger portions of the Method 29 and Method 26 samples. The graphs are divided into particulate and impinger categories, and then into sub-categories based on the elements. The metals are Al, Cr, Cu, Fe, Mg, Mo, Ni, P, and B. The glass former elements are Al, Gd, Hf, La, Nd, Sr, and Si; B is also a glass former element, but it is known to be much more volatile than the other glass formers. The salt category includes Na, K, F, and Cl. All of the evolution values shown are in mg/(kg in feed)/h, so these are all normalized on the amount in the feed.

For particulate, the Na, K, and Cl rates were all about 10^5 (mg/kg/h) with NaCl and KCl in the feed, whereas the Na rate was about 10^3-10^4 with no NaCl or KCl added. This result is similar to that found for total particulate. The most volatile metals species, Cr, Cu, Fe, Mo, and Ni had evolution rates of 10^3-10^5 when the feed contained the chlorides. Without chlorides, these rates were 10^0-10^3, as were the other metals (Al, Mg, P, B) with or without chlorides. For the glass former species, Al and Sr were more volatile than the lanthanides at 10^1-10^2. The evolution of B was 10^2-10^3. The remaining frit species (lanthanides and Si) had the lowest rates at 10^{-1} to 10^1. Any emission of lanthanides is a concern because these would also contain Pu in radioactive service. The Pu emissions would need to be contained and a disposal path or method determined.

The higher volatility for Al was unexpected due to the refractory nature of Al_2O_3 and of Al in glass melts. Because the Al volatility was significantly increased by the presence of Cl, it may be that the Al was emitted as a volatile chloride such as $AlCl_3$.

The impinger data are the amount of each species that passed through the filter. The filter was located within about one foot of the melter exit. Some species that passed to the impingers may

not have if the offgas line been longer, allowing additional condensation of these species. The impinger data show that all metals except the lanthanides had emission rates of about 10^0-10^2, with a few element with higher values (Mo, Fe, Cr). The lanthanide species emission rates were 10^{-2}-10^1. As expected, the rates for Cl and F were significantly higher than the metals, showing that a portion of these halides were emitted as HCl (and maybe Cl_2) and HF in addition to NaCl and NaF. Overall, except for Cl and F, the amount of each species found in the particulate on the filters was about 100 times higher than that found in the impingers.

The percentage of each species found in the particulate fraction and the mean amounts of species remaining in the glass product are shown in Table 3. The lanthanides Gd, Hf, La, and Nd emissions were at least 99.4% particulate which is consistent with the refractive nature of their oxides. As previously mentioned, the low value of 62.3% for Al was unexpected. The Si value was also low; neither Method 26 nor 29 are designed to measure silicon or boron well due to using borosilicate glass. Both Cl and F had low particulate percentages as would be expected.

The percentages remaining in the feed are indicative of a combination of the overall volatility and entrainment of each species. For most elements, the amount emitted was higher with chlorides present than without, and higher with use of the bubbler. In some cases, the data indicate the opposite, but these values are generally very close and in some cases the amounts of each species were so low that the measurement uncertainty overwhelmed the apparent differences. Notably, Cl, F, Na, and K had significantly more evolved when the bubbler was used. More Na and K were emitted when Cl was present.

The quartz offgas line insert was removed after each run and examined. After a B5495 run with chlorides, there was a buildup of reddish brown crystals inside the offgas line. A photo of the offgas line is shown in Figure 6.

Figure 6   Offgas Line Showing Deposits

The crystalline deposits were analyzed by X-Ray Diffraction and X-Ray Fluorescence and were also dissolved and analyzed for elements. The crystals were identified as a mixture of KCl, NiO, and what appears to be a solid solution of metal borates with a ludwigite-like structure such as bonaccordite $(Ni_2)^{+4}(Fe)^{+3}(BO_5)^{-7}$. Bonaccordite is a reddish brown crystal. The formation of crystals such as these could eventually cause plugging of the offgas line.
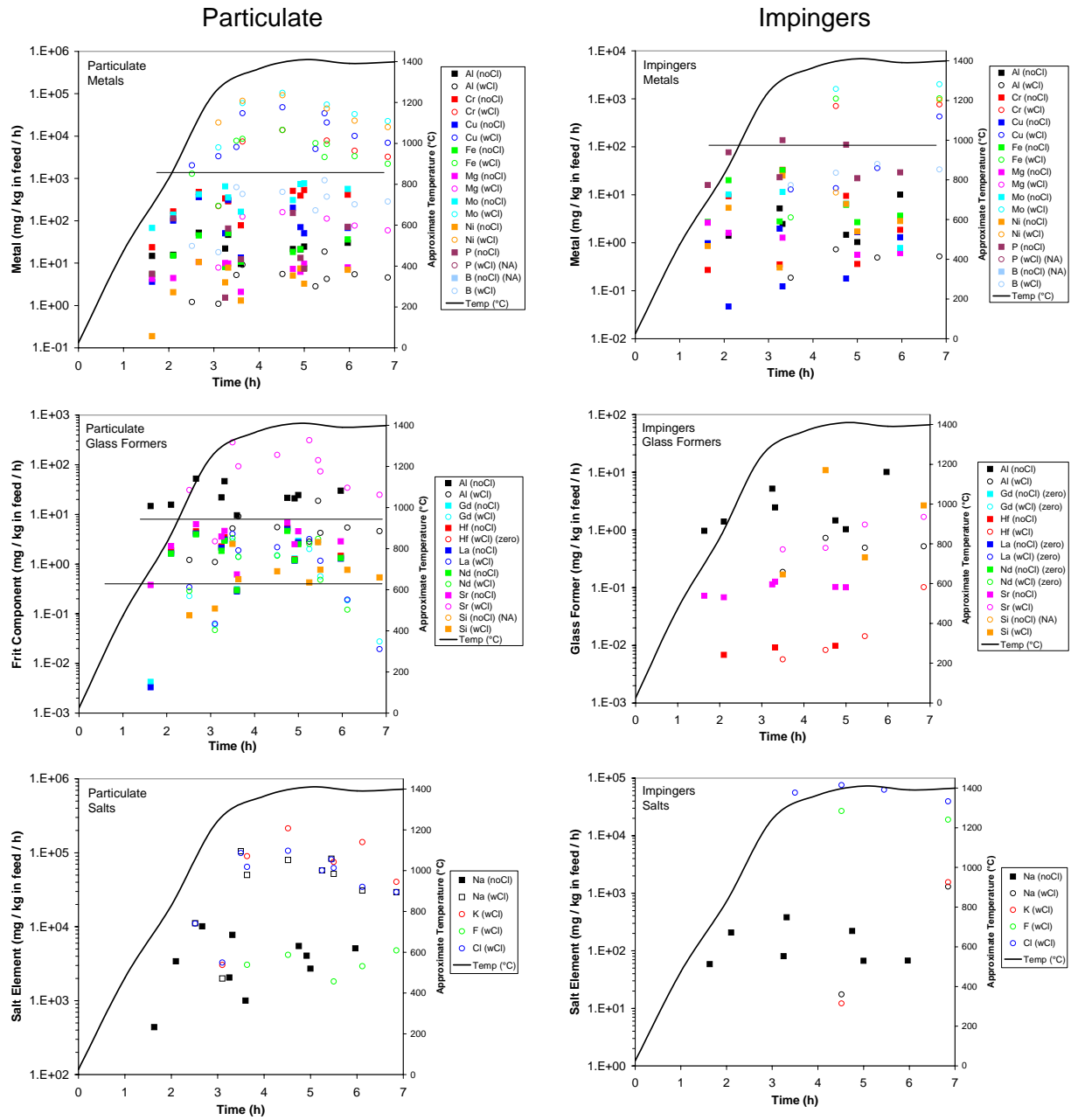
Figure 7   Element Evolution Rates for Particulate and Impinger Samples

Table 3   Emission Percentages

Average Percentage of Emissions as Particulate

Element	*Al*	*B*	Ca	Cr	Cu
	62.3	*73.7*	64.7	90.1	98.0

Fe	*Gd*	*Hf*	K	*La*	Mg
68.4	*99.4*	*99.93*	99.7	*~100*	76.7

Mo	Na	*Nd*	Ni	P	Pb
98.3	96.3	*~100*	74.8	50.4	~100

Si	*Sr*	W	Zr	Cl	F
47.1	*98.1*	68.8	66.7	36	7.3

$\left(\dfrac{\text{Particulate}}{\text{Total Emissions}}\right)$

Average Percentage Remaining in Glass Product

	Total	*Al*	*B*	Ca	Cr	Cu
no Cl	99.988	*99.992*	*99.975*	99.96	99.9	99.96
with Cl	99.7	*99.998*	*99.91*	99.68	98.49	90.8
no bubbler	99.94	*99.999*	*99.97*	99.75	99.71	94.1
with bubbler	99.8	*99.991*	*99.86*	99.91	99.0	97.3

	Fe	*Gd*	*Hf*	K	*La*	Mg
no Cl	99.988	*>99.998*	*>99.998*	>99.9999	*>99.998*	>99.995
with Cl	98.4	*99.9995*	*>99.999*	84.6	*>99.999*	>99.96
no bubbler	99.7	*99.9998*	*>99.9999*	98.9	*>99.9999*	99.9996
with bubbler	98.9	*99.9991*	*99.9991*	56.1	*99.9991*	99.987

	Mo	Na	*Nd*	Ni	P	Pb
no Cl:	99.8	98.9	*99.9993*	99.996	99.95	99.85
with Cl:	86.9	86.7	*99.9994*	89.5	99.90	NC
no bubbler	94.7	98.0	*>99.9999*	97.8	99.90	NC
with bubbler	92.7	89.8	*99.9993*	93.8	99.95	99.8

	Si	*Sr*	W	Zr	Cl	F
no Cl:	*99.97*	*99.9986*	99.99	99.94	NC	NC
with Cl:	*99.98*	*99.97*	99.8	99.998	57.6	89.1
no bubbler	*99.96*	*99.998*	99.91	99.993	93.3	98.9
with bubbler	*99.997*	*99.97*	99.986	99.93	39.8	79.2

NC: not calculated (insufficient data)   *red italics: frit component*

Particle Size Measurements

The low emission of the lanthanide species and high percentage as particulate is consistent with evolution by entrainment. In the cascade impactor tests, the particles emitted were separated by size and it was possible to distinguish the method of emission for some of the species. The cascade impactor filter papers were examined by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). Figures 8-11 show SEM micrographs of some of the deposits collected. Glass spheres were typically found on stages 1 and 2, although some salts were sometimes found. The presence of the glass spheres is most likely due to entrainment of

glass from the melt. The bubbler flow rate was usually 0.75 std. ft^3/h (21.2 L/h), which at the melt temperature of ~1425°C, is 4.3 std. ft^2/h (122 L/h), so it is not surprising that there was some entrainment. However, as the percentages remaining in the feed show, the total amount of glass emitted was small compared to the emissions of the other metals and salts.
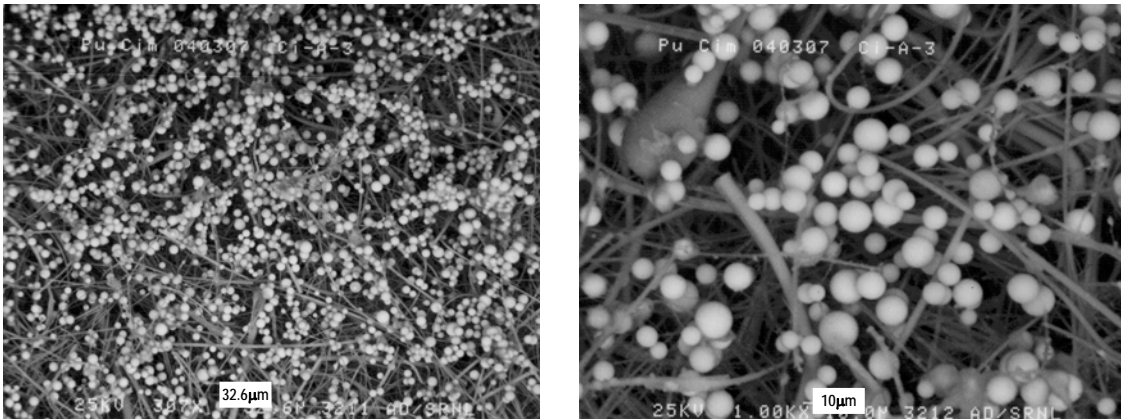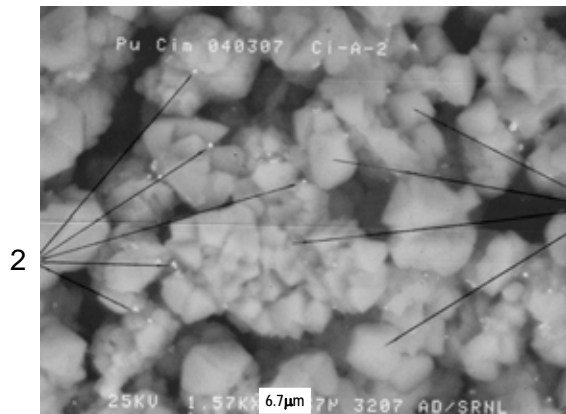

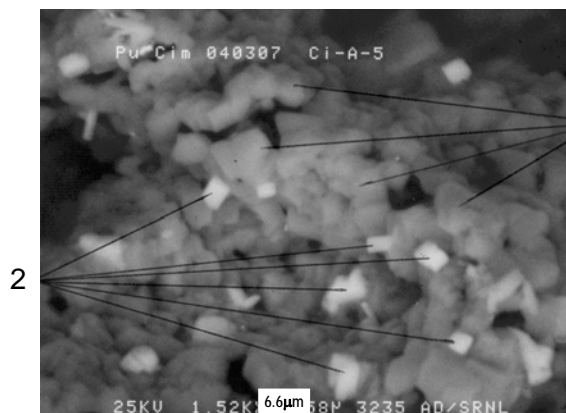**Figure 8   Deposits of Glass Spheres on Stages 1 and 2**

$D_{50} \sim 3\ \mu m$

1. Bulk deposits are KCl and K_2CO_3

2. Small dots are PbO

Stage 4 is similar.

Figure 9   Deposits from Stage 3 for B5495 with NaCl & KCl Simulant

$D_{50} \sim 0.9\ \mu m$

1. Bulk deposits are K_2CO_3

2. Cubes are NaCl

Figure 10 Deposits from Stage 5 for B5495 with NaCl & KCl Simulant

1. Bulk amorphous deposits are K_2CO_3

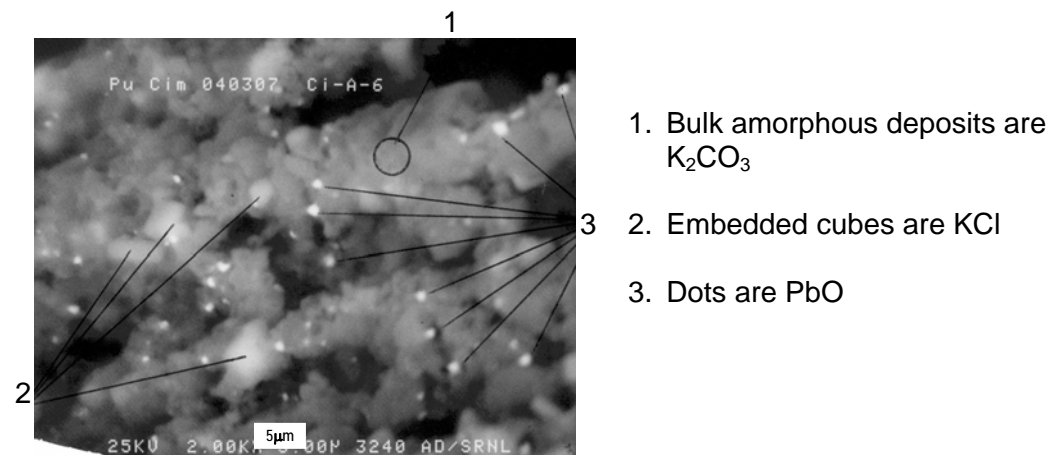2. Embedded cubes are KCl

3. Dots are PbO

Figure 11 Deposits from Stage 6 for B5495 with NaCl & KCl Simulant

For simulant with NaCl and KCl, Figure 9 shows that the majority of the particulate deposits on the stage 3 was KCl and K_2CO_3. These deposits are significantly larger than the 3 μm D_{50} of the impactor stage. From this result and the appearance of the deposits, it is apparent that these deposits are agglomerated or crystallized material. The presence of K_2CO_3 was unexpected and it is believed that the actual emission was K_2O and that its affinity for absorbing water to form KOH resulted in ultimately forming K_2CO_3; the formation of K_2CO_3 may have occurred during sample storage. The small dots of PbO are significantly smaller than the D_{50} for this stage. The catch of the PbO particles smaller than the D_{50} shows that the agglomeration of bulk particulate is effective in trapping smaller particles. As shown in Figure 2, the offgas sampling line before the filter for Method 26 or 29 became quickly coated in sticky, agglomerated particulate. This tendency to stick to the walls would make cyclones and similar particulate removal devices ineffective.

Stage 5, shown in Figure 10, contained mostly K_2CO_3 with embedded cubic crystals of NaCl. Again, all of the deposits here were larger than the D_{50} of the stage, indicating that the crystals found grew in size on the stage. The image of stage 6 shown in Figure 11 again shows the bulk material to be K_2CO_3 with embedded KCl and PbO. Based on the size of the crystals found, it seems very possible that the crystals were grown from gas phase deposition of the salt species onto the crystal surfaces resulting in crystals much larger than the D_{50} of the impactor stage. Both agglomeration and deposition to form crystals should aid in the removal of the particulate from the offgas stream because larger particles are easier to remove. However, the agglomeration or deposition must occur on the correct surfaces; the offgas line is not a desirable location for deposition.

There are several factors contributing to the deposition of salts within the impactor. The impactor was used to sample the entire offgas stream from right at the exit of the melter, as shown in Figure 12. This close-coupled sampling did not allow the offgas species to completely react or condense before entering the impactor. There was also a temperature gradient (140-280°C inlet, 30°C outlet) within the impactor that could cause different species to condense along the length of the impactor as the offgas cooled. The impactor was intentionally placed at the melter exit rather than far downstream an offgas line because it was known that a significant amount of particulate would deposit on the offgas line unless the temperature was maintained above about 300°C.
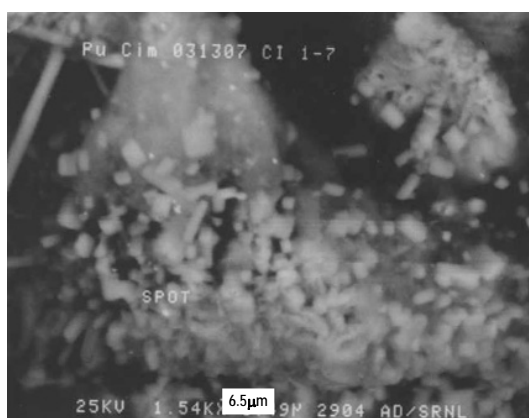
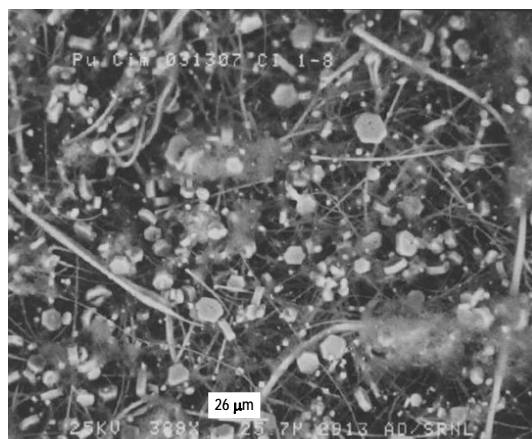Impactor normally used with precollector insulated.

Figure 12 Cascade Impactor in Use
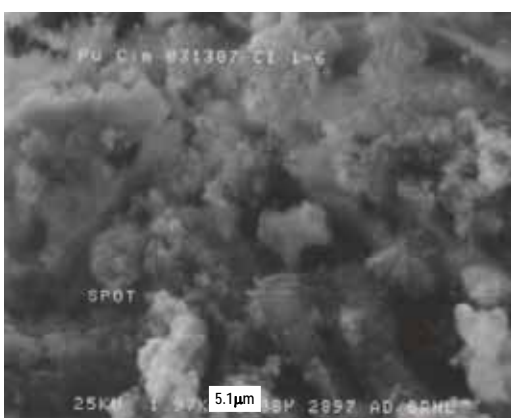
Stage 6

Stage 7

Absolute Filter

Stage 6: mostly amorphous NaF

Stage 5 similar

Stage 7: amorphous NaF and crystalline Na_2SiF_6

Absolute: mostly crystalline Na_2SiF_6 with amorphous NaF

All have small amounts of Cr, Cu, and K_2CO_3

Figure 13 Typical Deposits on Stages 6, 7, and Absolute Filter for B5495 with No NaCl or KCl

The deposits found for the B5495 simulant with no chlorides are shown for stages 6, 7, and the absolute filter in Figure 13. Because the no chloride runs had no K or Cl, there were no deposits of potassium species found. Only NaF with traces of metals were found on stages 5 and 6. These deposits were very amorphous and were consistent with the D_{50} of these stages. No

solids were measured on stages 3 and 4; stages 1 and 2 had only glass spheres present. However, stage 7 and the absolute filter both contained large crystals of hexagonal Na_2SiF_6. The absolute stage had the largest crystals indicating that a vapor deposition mechanism probably grew these crystals on the surface of the filter paper. Very little Si was ever found in any of the particulate deposits, so the source of the Si in the Na_2SiF_6 may have been the Si in the quartz filter paper.

Several tests were performed with feed containing NaCl and KCl to examine the deposition of particulate on the offgas line surface. In these tests, the offgas was drawn through a heated quartz tube at about 0.5 std. ft^3/min (14.2 L/min) for 30-60 minutes. The quartz tube was maintained at various temperatures to determine the minimum temperature necessary to prevent deposition. This minimum temperature was found to be about 315°C.

Effects of the Reduction of Oxides

In the run the B5439 composition that was high in CuO (11.8 wt% of simulant), there was a glass bed volume expansion that occurred when the glass temperature reached 1100°C. This volume expansion raised a layer of glass up to the top of the melter somewhat like a balloon expanding. Figure 14 shows the top of the melter after this run with partially melted glass deposited because of the lower temperature at the top of the melter. It is apparent from the opaqueness of the glass that some material that has not been incorporated into the glass matrix still remained.

Cupric oxide, CuO, reduces to cuprous oxide, Cu_2O, at about 1100°C to release O_2.[1,2] The release of oxygen from the CuO would account for the observed bed expansion. The thermal radiation transmittance of CuO-containing glasses is lower than other glasses, which can cause higher temperature gradients in the glass.[3] A skin of colder glass could have formed on top of the melt and trapped the oxygen evolved, resulting in the 'balloon' of glass that formed. A test in an oven showed that glass with CuO generated numerous large bubbles compared to glass without CuO.

A similar problem occurred early in the Am/Cm melter program where cerium (Ce) was used as a simulant for the Am/Cm. Cerium oxide Ce_2O_3 reduced to CeO_2 above about 1100°C and released oxygen. Other oxides (Fe_2O_3, Cr_2O_3, Ni_2O_3, SnO_2) would cause similar behavior by reducing to release oxygen at temperatures of about 1100°C. The simulants contained smaller amounts of Cr_2O_3 (<2.5%) but no bed expansions were noticed.

Figure 14 Residual Glass from Glass Excursion

Another unusual occurrence with the B5439 run was that the outlet line from the filters to the impingers became coated with fine particulate during the entire run. These solids appear to have condensed out of the vapor after the filter rather than passing through the filter or through a leak. The analysis of the impinger samples, which include these outlet lines, did not show any unusual concentration of any particular species compared to other runs. No other runs had particulate deposition on this part of the sample system. This deposition beyond the filter has implications for the design of an effective offgas treatment system for this process.

Proposed Offgas System Designs

Based on the characterization results, several possible alternative offgas treatment system designs were proposed for future testing. All of the designs are dry systems without any wet scrubbing equipment. Wet systems were not considered due to the criticality concerns with the plutonium and the desire to avoid a secondary wet waste stream. A dry secondary waste stream that would be a transuranic (TRU) waste could possibly be disposed at the Waste Isolation Pilot Plant (WIPP) in New Mexico. One of the proposed systems is shown in Figure 15.
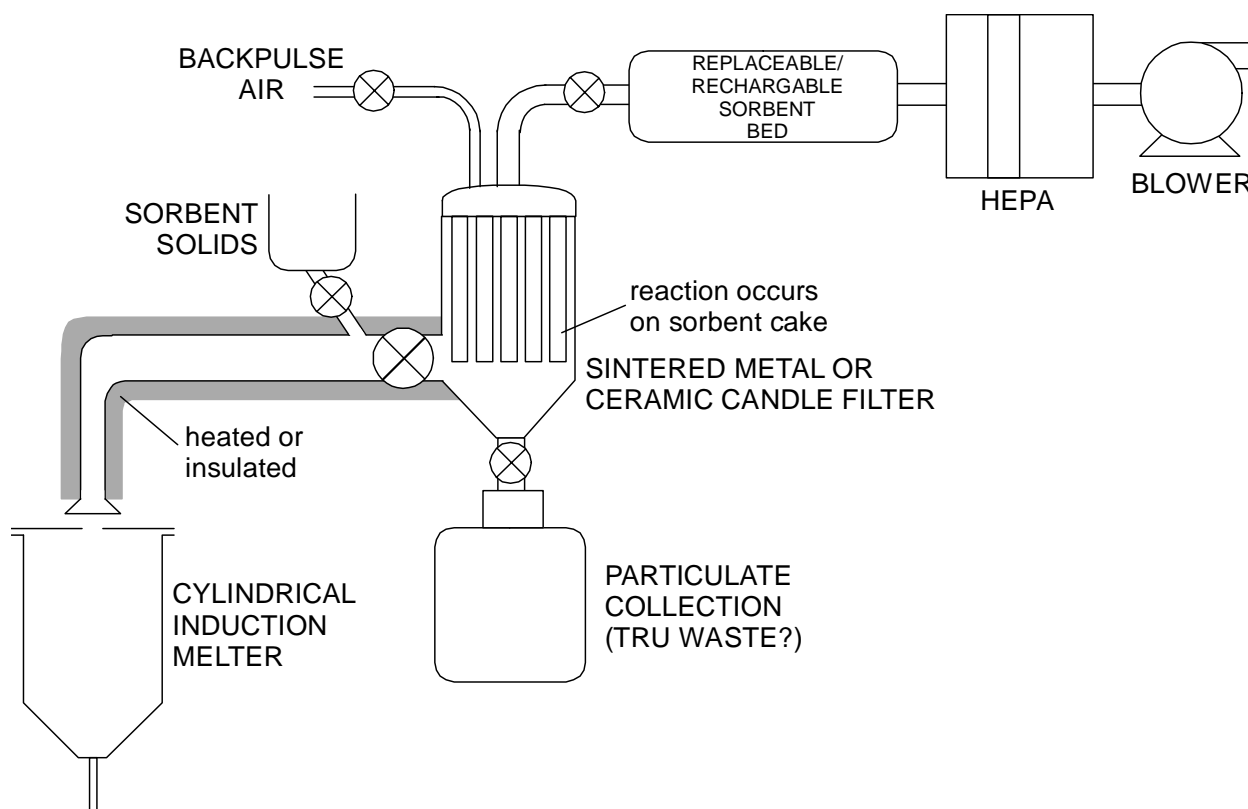

Figure 15 Possible Offgas Treatment System

The proposed offgas systems all utilize a sorbent medium to react with the acid gases. In the system shown in Figure 15, the offgas is kept above 315°C in the offgas line to prevent deposition of solids before the filter. The sorbent solids added could be sodium bicarbonate, sodium carbonate, or other solid that could neutralize the acid gases. The sorbent and any particulate emitted would be collected on a sintered metal or ceramic filter. A backpulse would be used to dislodge the solids into the particulate collection system. An replaceable fixed sorbent bed could be used downstream to remove any remaining acid gases. The entire system

will be located inside a radiological glove box that is vented via a HEPA filter, so the HEPA and blower may not be necessary. At this time, this test system has not been constructed for testing pending a decision by the Department of Energy about the future use of vitrification for plutonium treatment.

CONCLUSIONS

The following are some of conclusions that were drawn from this work:

1. The particulate evolution rate was about 10-100 times higher for the chloride containing feeds compared to those with no chlorides.
2. The most volatile species are K, Na, and Cl. The next most volatile are F, Mo, Fe, Cr, and Ni.
3. Most of the Cl is evolved as HCl, lesser amounts as NaCl and KCl, and some as Cl_2.
4. Most of the F is evolved as HF, with the remainder as NaF.
5. Use of the bubbler at 0.35 ft^3/h (9.9 L/h) or higher results in emissions that are increased by about a factor of 3. This increase include the lanthanide frit species indicating that entrainment of glass particles is increased.
6. The volatility of frit species is: B>Sr>Al. The emissions of these are significantly higher than the lanthanides.
7. The emissions of lanthanides are totally due to entrainment of glass particles.
8. The lanthanides are retained in the glass at >99.999%.
9. The particulate generated agglomerates and crystallizes easily, resulting in larger particles that should be easier to remove.
10. The stickiness of the particulate results in significant deposition on surfaces such that cyclones or similar devices may be ineffective.
11. The agglomeration of the particulate aids in the removal of submicron particulate (e.g, PbO).
12. The minimum temperature to prevent deposition of particulate is about 315°C.
13. Cupric oxide (CuO) in high enough concentrations may cause expansion of the glass melt due to reduction to Cu_2O to release of O_2. Other oxides that reduce at increased temperatures may have similar behavior.

REFERENCES

1 E. Mack, G.G. Osterdorf, H.M. Kraner, *Vapor Pressure of Copper Oxide and of Copper*, **J. Am. Chem. Soc., 45(3)**, 617-623, (1923).
2 F.H. Smyth, H.S. Roberts, *The System Cupric Oxide, Cuprous Oxide, Oxygen*, **J. Am. Chem. Soc., 42**, 2582 (1920).
3 M.B. Volf, **Chemical Approach to Glass, Glass Science and Technology 7**, Elsevier, 1984.