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Americium/Curium Melter 2A Pilot Tests

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AMERICIUM/CURIUM MELTER 2A PILOT TESTS (U)

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ABSTRACT

Isotopes of americium (Am) and curium (Cm) were produced in the past at the Savannah River Site (SRS) for research, medical, and radiological applications. These highly radioactive and valuable isotopes have been stored in an SRS reprocessing facility for a number of years. Vitrification of this solution will allow the material to be more safely stored until it is transported to the DOE Oak Ridge Reservation for use in research and medical applications. To this end, the Am/Cm Melter 2A pilot system, a full-scale non-radioactive pilot plant of the system to be installed at the reprocessing facility, was designed, constructed and tested. The full-scale pilot system has a frit and aqueous feed delivery system, a dual zone bushing melter, and an off-gas treatment system. The main items which were tested included the melter feed system, the dual zone bushing melter, the drain tube with dual heating and cooling zones, glass compositions, and the off-gas system which used for the first time a film cooler/shorter melter plenum. Most of the process and equipment were proven to function properly, but several problems were found which will need further work. A system description and a discussion of test results will be given.

INTRODUCTION

Isotopes of americium (Am) and curium (Cm) were produced in the past at the Savannah River Site (SRS) for research, medical, and radiological applications. They have been stored in a nitric acid solution in a SRS reprocessing facility for a number of years. Vitrification of the americium/curium (Am/Cm) solution will allow the material to be more safely stored until it is transported to the DOE Oak Ridge Reservation. Oak Ridge is responsible for marketing radionuclides for research and medical applications. To this end, the Am/Cm Melter 2A bushing melter pilot system was installed and tested at the SRS.

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A bushing melter was chosen because of its small size and its shape (which could be needed for future criticality requirements if other radioisotopes such as plutonium were subsequently vitrified in the same system). Platinum/rhodium bushing melters are commonly used in the glass industry, especially in the manufacture of fiber glass. In these industrial applications, however, either molten glass or dry feed is delivered to the bushing. There has never been a bushing melter which was designed for the additional requirements of slurry feeding. Slurry feeding greatly increases the level of difficulty for glass melting as higher power requirements are needed at the upper portion of the bushing. An off-gas system is also required to treat any volatile or entrained components coming out of the melter. In addition, the numerous remote operation requirements for this radioactive feed had never been attempted to be met before.

PROCESS DESCRIPTION

The Melter 2A system is a full-scale pilot plant of the actual system to be installed at the SRS. It comprises a feed delivery system, a dual zone bushing melter, a split power supply and an off-gas treatment system (see Figure 1). The main differences between this and the previous Am/Cm system are a re-designed dual zone melter, a shorter melter plenum, an off-gas film cooler, and PC control/monitoring of the process.

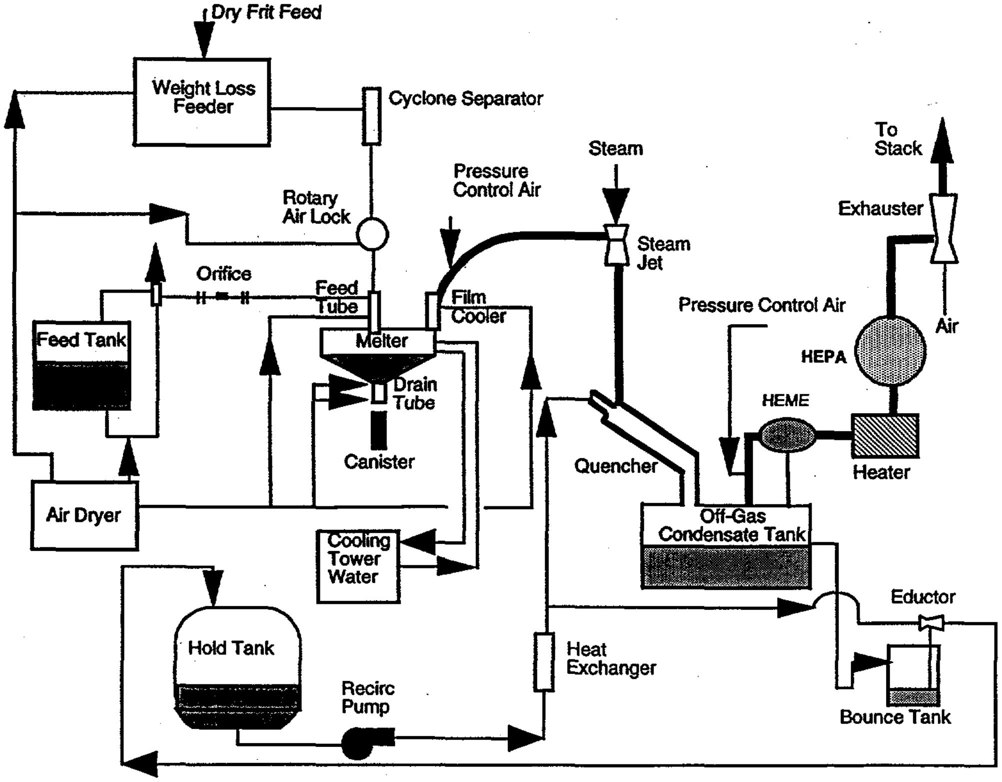

Figure 1. Am/Cm Melter 2A bushing melter pilot system schematic

A surrogate (non-radioactive) Am/Cm nitric acid feed solution, along with glass forming frit, are fed to the melter in two separate streams in a carefully controlled mass flow ratio. The feed is introduced into the vapor space of the bushing melter which is equipped with a top plenum to contain the melter off-gasses. The glass melt flows from the bottom of the melter by gravity through a heated drain tube into a stainless steel canister[1].

The melter vessel is a 90% platinum/10% rhodium alloy, bottom-sloped, rectangular vessel which acts like a resistance heater when current is passed through it. The melter is about 28 cm tall, 25.4 cm wide, and 7 cm deep. Two sets of platinum screens are located just below the melt line to aid in melting the feed. The melter is operated at about 1350° to 1500°C. The glass flows by gravity from the bottom of the melter through a 80% platinum/20% rhodium heated drain tube (nominal 0.5 cm inner diameter) into a stainless steel canister. Glass pouring is stopped by applying cooling air to the upper and lower portions of the drain tube.

As the melter is fed and the liquid is vaporized, the expanding gasses are drawn through a film cooler into the off-gas treatment system by a steam jet. The steam jet, coupled with a control air purge that is introduced into the off-gas system between the film cooler and the steam jet, maintains a target melter plenum pressure that is negative with respect to ambient pressure. The vapor exiting the steam jet enters a quencher where it is cooled and scrubbed of particulate entrained into the off-gas system during melter feeding. The condensate drains to the off-gas condensate overflow tank (COT). Overflow from the COT goes to the Bounce Tank. The vapor exits the top of the COT and is drawn through a High Efficiency Mist Eliminator (HEME), a High Efficiency Particulate Airfilter (HEPA) pre-heater and a HEPA by an air jet. The pre-heater raises the off-gas temperature above the dew point prior to entering the HEPA filter to prevent condensation on the HEPA. The air jet discharges the treated off-gas to the atmosphere through a stack.

TEST PLAN DESCRIPTION

Testing was planned in three phases as described below. Melter 2A performance was planned to be evaluated using Frit 25SrABS-F (the frit developed that has a lower liquidus than the original reference Frit B2000) which enabled operating the melter at a lower temperature and correspondingly provided a greater temperature delta between operating temperature and the temperature at which the integrity of the platinum begins to be potentially compromised. However, during Phase 2 testing severe foaming was encountered when a nitric acid solution was fed to the melter which had been initially inventoried with 50SrABS Hybrid glass (a surrogate glass representing the product of vitrification of the Frit 25SrABS-F and a surrogate feed). As a consequence, it was necessary to depart from the original experimental plan and consequently several of the Phase 2 and Phase 3 test objectives were not met. The compositions of the various feed streams are shown in Tables I and II. B1000 is a leaded glass that represents the vitrification product of Frit B2000 and a surrogate feed.

Table I. Major components of Am/Cm surrogate feed solution

Component	Equivalent oxide weight percent
Lanthanum	11.23
Cerium	12.90
Praseodymium	12.90
Neodymium	27.35
Samarium	6.34
Europium	1.25
Gadolinium	3.22
Erbium	12.90
Iron	2.19
Manganese	8.34

Table II. Compositions of various Am/Cm frits and glasses

(Note: all values in weight percent oxide)

Oxide	B2000	25SrABS-F	B1000	50SrABS-H
SiO_2	44.0	33.7	28.9	21.9
B_2O_3	9.2	13.5	3.0	8.8
Al_2O_3	6.0	24.9	17.3	16.4
La_2O_3	7.1	25.0	14.8	20.2
PbO	24.3	---	9.1	---
BaO	9.0	---	3.5	---
SrO	---	2.9	---	1.9
Re_2O_3			15.6	22.3
CeO_2			6.8	4.5
Fe_2O_3			---	0.8
MnO_2			---	2.9
Cr_2O_3			---	0.1
Others			---	0.2

Phase 1 covered the startup of the melter and focused on characterizing the performance of the zoned power supply. Temperatures of the glass pool, the platinum vessel and external surfaces of the melter assembly were measured during steady state and transitional periods of melter operation. Phase 2 testing was designed to characterize the response of the zoned power supply to aqueous feeding, obtain some measure of the rate of glass production achievable with the power supply and evaluate the capability of the off-gas system to control the pressure in the melter plenum. Initially, only a nitric acid solution was to be used during feed simulations. Ultimately, it was planned to feed 50SrABS Hybrid frit along with the nitric acid solution. Phase 3 testing was to determine nominal and maximum rates of vitrification while feeding the reference frit (25SrABS-F) and a surrogate feed solution (a nitric acid solution containing lanthanides and actinide stand-ins) compositionally identical to the feed solution projected for actual radioactive operation.

TEST RESULTS

Melter 2A Startup -Phase 1

The melter was initially charged with 50SrABS Hybrid glass cullet prior to heatup. With both zones in manual control, the melter was energized and a nominal heatup rate corresponding to 2°C/min was initiated. Upon reaching 1350°C, both zones were placed in automatic temperature control. Zone 1 (upper) and Zone 2 (lower) required 249 volts/44.3 amps (primary) and 231 volts/12.5 amps respectively to maintain the control temperature setpoint in both zones at 1350°C. Because of the foaming problem (and splattering of solids) encountered once nitric acid feeding was initiated, it was difficult to sustain any significant feed rates and correspondingly not possible to meet the test objective of quantifying vitrification rate capacity of the system. Consequently, the remainder of the original experimental plan was abandoned and subsequent efforts were directed at trying to determine the cause of the foaming (see Foaming section).

Glass Pouring

One of the test goals during the performance assessment of Melter 2A was to thoroughly characterize the glass draining process and develop the process operating parameters. The three main objectives of the glass pouring experiments were to (1) demonstrate the effectiveness of the two zone resistance drain tube heater on starting and stopping the flow of glass; (2) determine the reproducibility of the starting and stopping process; and (3) identify the values of process parameters required for acceptable glass pouring. Twenty-one glass pours were done with Melter 2A during this testing. Of those twenty-one pours, nine pours were with a glass of the 50SrABS Hybrid glass composition, seven of the 25SrABS-F/surrogate feed composition, and five pours of the Frit B2000/surrogate glass composition. The melter temperature was adjusted as required, based upon the temperature-viscosity relationship for the composition of the glass being poured.

Glass pouring began with gradual movement of the cold glass plug at the extreme tip end of the drain tube upon removal of the tip cooling air. Melter Zone 2 temperature setpoints were 1350°C to 1380°C for SrABS glass (1450°C to 1480°C for Frit B2000 glass), and pours transitioned from glass droplets to a steady stream of glass within seconds. Temperatures of Melter Zone 2 and the drain tube were found to be critical. For example, when the melter Zone 2 temperature was maintained at 1380°C (versus 1350°C) for 50SrABS glass, a steady glass stream immediately followed the cold glass plug as it disengaged from the drain tube without any glass droplets. This type of pour initiation is needed to minimize the chance of glass pluggage or the formation of glass stringers (thin fibers) during pouring. In each case, the drain tube was heated to 1350°C or higher prior to initiation of glass pouring.

To stop the glass pouring, 2800 l/hr cooling air was applied to the upper portion of the drain tube for 80 seconds, with 450 l/hr air being applied to the lower tip end of the tube 60 seconds after the initial application of the upper cooling air. Power input was also reduced to the drain tube heater assembly when the cooling air was applied to stop the glass pouring. The lower tip cooling air was continuously applied at 450 l/hr flow to maintain the cold glass plug until the next glass pour was initiated. The upper drain tube cooling air remained off until needed to stop the next glass pour. In general, the glass pouring tests showed that the dual zone heating and cooling performed quite well. Optimization of the process, however, is still needed and is being done.

FOAMING

Severe foaming was encountered during Phase 2 testing when the melter began to be fed with a nitric acid solution and SrABS frit. The foaming problem rendered completion of the original experimental plan of little value. Subsequent testing focused on developing an understanding of the cause for the foaming and compositionally characterizing the foam layer using the reference frit, 25SrABS-F. In an effort to develop an understanding of the cause of the foaming, a series of feed cycle simulations using 25SrABS-F frit under the following conditions were conducted:

- Surrogate Feed of Varying Nitric Acid Concentrations (0.16M to 3.2M)
- Surrogate Feed Without Manganese
- Surrogate Feed Without Metal Oxides (Mn, Fe, Cr, Ni)
- Deionized Water as the Feed Solution

These cycles were chosen based on past SRS experience with nitric acid feed and redox conditions which can cause foaming. Twenty-seven feeding cycles were made with 25SrABS-F frit. A 3.2 Molar nitric acid surrogate solution was prepared and fed at 2.6 l/hr with the 25SrABS-F frit at 0.5 kg/hr to build the glass inventory within the melter. As the liquid feed rate varied between 2.4 and 2.8 l/hr for the different solutions fed, the frit feed rate was adjusted to balance the surrogate components being fed with the liquid. With the exception of feeding deionized water only, all combinations using liquid surrogate feeds foamed and splattered.

Analysis of samples of the foamy, porous cold cap formed by feeding the 25SrABS-F frit with liquid nitric acid surrogate feed indicated the presence of rare earth oxides. Mass spectrometry analysis of gas trapped in the pores of the cold cap samples detected nitrogen and oxygen. The foaming mechanism postulated from this information was the decomposition of the rare earth nitrates to an oxide. This decomposition liberates NO_x gas which is trapped in the viscous cold cap. This foam layer then acts as an insulating blanket which in turn reduces the melting efficiency of the bushing. If feeding is continued, the bushing cannot melt the additional feed and the entire melt pool becomes covered with a cold cap. This theory was backed by the finding that the addition of just nitric acid to an SrABS glass melt pool produced a thin, non-porous oxide layer due to the extraction of the lanthanides from the glass. This extraction first converts the rare earths to a nitrate form and then quickly decomposes these nitrates to an oxide layer on the glass surface. This decomposition results in the liberation of gases which then attempt to rise out of the melt pool/cold cap. Without a cold cap, however, there was no viscous layer to trap these gases, and therefore these rare earth oxides were re-dissolved into the glass fairly rapidly.

The next logical step was to determine compositional differences in the two glass systems that would cause one to foam and the other to not foam. This comparison of the 25SrABS-F frit and the B2000 frit (see Table II) showed that the La_2O_3 weight percent was much higher in the 25SrABS-F frit (25% versus 7%). This higher lanthanide content would contribute to the foaming problem in two ways. First, there would be more lanthanide nitrates to decompose. Secondly, the lanthanides in the SrABS glass are one of the main fluxes to lower the viscosity of the glass (B2000 frit uses lead as its main flux). Therefore, extraction of the lanthanides would cause the viscosity of the cold cap/upper melt pool to increase much more for the SrABS glass than the leaded glass. The high viscosity cold cap would then make it much more difficult for the gases formed to escape.

Following the decision to abandon the SrABS glass system and resume testing with the original leaded glass, the melter was inventoried with Frit B1000 glass (a glass simulant compositionally similar to the vitrified product of the proper blend of Frit B2000 and the surrogate feed). This glass matrix has a liquidus of around 1350°C and accordingly requires a glass processing temperature in the 1425°C to 1450°C range. As previously experienced with Frit B1000 tests with a previous melter, no foaming was observed while feeding Frit B1000 with 2.8 M nitric acid. The cold cap produced by the frit and liquid feed melted into glass within 25 minutes after stopping feed. Feeding 0.87 M nitric acid surrogate solution by itself onto the Frit B1000 molten glass surface for 10 minutes also showed no evidence of foaming.

Frit B2000 together with surrogate feed was next fed onto the pool of Frit B1000 glass. After feeding for 30 minutes at 0.5 kg/hr frit addition and 2.7 l/hr of 0.87 M nitric acid surrogate, the B2000 composition feed was observed to form a normal cold cap which eventually spread across the entire glass surface. Many small bubbles could be seen breaking the upper surface of the crusty cold cap, but no foaming was detected. The upper zone of the melter was increased to 1470°C and the lower zone increased to 1500°C. Additional feeding of B2000 frit and surrogate liquid feed produced a normal appearing cold cap which allowed gasses to pass through without creating foam. The cold cap was incorporated into the molten glass within 30 to 45 minutes after feeding was stopped. Subsequent assessment of melter 2A with the B2000 system was halted because of pluggage problems with the off-gas HEME filter. Initial assessment of the causes of the HEME pluggage were lead volatilization during vitrification and the inability of the scrubber to effectively scrub out the lead aerosols and HEME design deficiencies (see next section).

EQUIPMENT PROBLEMS

Film Cooler Pluggage

The film cooler is designed to cool the off-gas stream and walls of the off-gas piping to minimize the amount of deposit formation at the inlet to the off-gas system. Process air flows through slots in the film cooler into the off-gas stream. The slots are designed to provide a laminar flow of cooling air along the walls of the film cooler. The film cooler was operated with air flows of 39-41 kg/hr during operation with the SrABS frit. The airflow was increased during operation with B2000 frit to 59 kg/hr (because of the previous pluggage experience and higher melter operating temperatures). The airflow to the film cooler was sufficient to prevent damage to the Inconel insert, but not its ceramic gasket and Inconel spacer. During operation at 1350°C, the spacer showed signs of corrosion along the bottom edge. The spacer was slightly deformed when the operating temperature was increased to 1450°C, and required repair prior to re-installation. The ceramic gasket was heavily damaged during operation with leaded glass (Frit B1000) at 1450°C. Large sections along the bottom edge were found missing. The exit temperature of the film cooler ranged from 80°C while idling with SrABS glass to a high of 220°C during feeding with surrogate feed and B2000 frit.

Deposition occurred on all exposed surfaces of the film cooler insert, spacer, ceramic gasket, and downstream piping. The piping downstream of the film cooler contained a 0.16 cm layer of deposits and was cleaned on two different occasions. Deposits on the film cooler insert and downstream piping were friable and easily removed by mechanical scraping and/or water rinse. Deposits on the film cooler gasket and metal spacer were not friable. The ceramic gasket could not be cleaned and was replaced each time that it was removed. The metal spacer was cleaned with a water rinse each time. During SrABS operation, the deposits were rare earth borates and oxides which were caused by splatter from the cold cap. The deposits formed during B2000 frit feeding were lead borates and oxides due to volatilization.

HEME Pluggage / HEPA Pluggage

The quencher/scrubber is designed to condense the majority of condensables from the off gas and to scrub entrained particles from the off-gas line gas. This prolongs the life expectancy of the downstream HEME and HEPA filters. HEME and HEPA performance were acceptable during operation with SrABS glass. However, during operation with the leaded glass (Frit B2000 and B1000 glass), the HEME plugged six times and the HEPA plugged twice (HEPA plugged only after HEME was removed). Analysis of the HEME flushes and condensate indicate that a majority of the lead volatilized from the melter was collecting on the HEME filter with relatively small amounts collecting in the condensate. HEME flush sample analyses indicated that the original HEME plugged after accumulating 20 grams of lead, while replacement HEME filters plugged with less than 5 grams.

Lead oxide volatilization creates sub-micron particles entrained in the off-gas. Sub-micron particles are not effectively removed by the existing quencher, therefore these particles pass through the quencher and collect on the HEME. When the HEME was removed, these particles collected on the HEPA filter. The quantity of lead measured on the HEME was less than that expected to cause pluggage. Particle size distribution and chemical composition of the solids exiting the melter's film cooler and entering the HEME have been determined for the leaded glass. The main findings are as follows:

- During melter idling (non-feeding), virtually all of the particulate exiting the melter and just before the HEME is in the submicron range (0.25 microns) and is mostly PbO.
- Reduction of the idling melter glass temperature from 1450°C to 1150°C resulted in a particulate evolution rate of only 2% as that at 1450°C. In addition, lead volatility was reduced to a level below the detection limit of the test.
- Feeding the melter at 1450°C (as compared to idling) resulted in a eight fold particulate increase at the melter exit. Most of the particles were in the 0.91 to 9.2 micron range and had about the same composition as the feed. The B and Pb were still in the submicron range.
- Melter feeding at 1450°C (compared to idling) resulted in a 36% reduction in Pb volatility.

CONCLUSIONS/RECOMMENDATIONS

The following is a list of the conclusions and recommendations based on the M2A testing to date:

- The dual zone Melter 2A worked quite well and was able to achieve acceptable melt rates when used with the non-foaming leaded glass.
- SrABS glass tended to foam to the point that operation with this glass is not practical. The Frit B1000 leaded glass did not foam. Subsequent work was done to understand the foaming mechanism. The reference glass composition is now the leaded glass.
- The current film cooler design did not prevent off-gas pluggage when used with air flows of 41-59 kg/hr. The film cooler deposits consisted mostly of lanthanide oxides and borates. Lead oxide deposits occurred when leaded glass was present in the bushing melter.
- The dual zone drain tube heater with dual cooling air locations worked quite well for the initiation and stoppage of glass pours. Optimization of this process, however, is still needed.
- The off-gas HEME and HEPA plugged several times during the tests. It is recommended that further testing be done to solve this problem.

REFERENCES

[1] T.M. Jones, B. J. Hardy, and M.E. Smith, "Americium/Curium Bushing Melter Drain Tests (U)," WSRC-MS-97-0168, presented at the *21st Annual Actinide Separations Conference*, Charleston, SC, June 26, 1997.