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American/Curium Vitrification Process Development

A. P. Fellinger, M. A. Baich, B. J. Hardy, G. T. Jannik, T. M. Jones, J. E. Marra,
C. B. Miller, D. H. Miller, D. K. Peeler, T. K. Snyder, M. E. Stone, and D. C. Witt
Savannah River Technology Center
Westinghouse Savannah River Company
Aiken, SC 29808

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Abstract

The Savannah River Technology Center (SRTC) is conducting research and development to define the equipment design bases and process operating parameters for construction of a facility in the SRS F-Canyon Facility to vitrify an Americium (Am)-Curium (Cm) nitric acid solution. The final glass form will be placed in interim storage until it can be transported to the DOE Oak Ridge Complex for recovery of the Am-Cm from the glass.

Introduction

Technical problems associated with efforts to directly vitrify the nitric acid feed solution in a slab type Bushing Melter led to scoping studies of a batch operation that included a new pretreatment step as well as a new melter design. A previous paper describes the operating results and difficulties of the Am/Cm slab melter pilot system. [1] A second paper describes the potential of a batch vitrification alternative and the simplification of the melter system.[2] While a new induction heated, cylindrical melter was being installed, vitrification experiments with the product slurry from the new pretreatment step were carried out in a resistance heated platinum melter to validate the technical feasibility of the new flowsheet. This paper describes the preliminary process and discusses the test results of initial scoping studies.

Oxalic Pretreatment Process Description

An oxalic acid precipitation process completes pretreatment of the nitric acid feed stream prior to introduction of the material to the melter vessel. The precipitation pretreatment flowsheet is shown in Figure 1. The pretreatment includes a precipitation with the addition of 8 weight percent oxalic acid. The precipitated oxalates are settled and the liquid decanted. The precipitated oxalates are washed with 0.1 molar oxalic acid, and then allowed to settle. The wash solution is then decanted. A one-liter surrogate precipitation yields approximately 160 grams of feed solids. The washed oxalate precipitate is then combined in the melter vessel with a glass forming composition in the form of either frit, cullet, glass beads or raw batch chemicals. The glass forming composition (25SrABS) is shown in Table 1. Current operation of the Am-Cm pilot facilities is performed using a surrogate feed based on the 1993 sample results of the F-canyon Am/Cm solution using Erbium as a substitute for the actinide bearing material. Results of a 1998 sample have recently been obtained and the surrogate feed was revised to incorporate the new sample results (also shown in Table 1). Both surrogate feed compositions have been tested with no observed processing differences.

Table 1. Surrogate feed and 25SrABS glass former compositions

Oxide	Surrogate Feed 1993 Sample wt% oxide	Surrogate Feed 1998 Sample wt% oxide	25SrABS Glass Former wt% oxide
Al_2O_3	0.49	0.01	24.87
B_2O_3	-	-	13.54
CaO	0.03	-	-
Ce_2O_3	12.50	12.94	-
Cr_2O_3	0.20	-	-
Dy_2O_3	0.45	0.36	-
Er_2O_3 *	12.92	12.43	-
Eu_2O_3	1.24	1.56	-
Fe_2O_3	1.72	0.03	-
Gd_2O_3	3.09	3.98	-
Ho_2O_3	0.45	0.36	-
La_2O_3	10.89	15.05	25.00
Lu_2O_3	0.44	0.35	-
MnO	8.20	0.14	-
Nd_2O_3	26.53	32.80	-
Pr_2O_3	12.52	11.26	-
SiO_2	-	-	33.68
Sm_2O_3	6.19	7.49	-
SrO	-	-	2.91
Tb_2O_3	0.45	0.36	-
Tm_2O_3	0.60	0.53	-
Yb_2O_3	0.44	0.35	-
Total	98.86	100.00	100.00

* Er_2O_3 substituted for Am_2O_3 and Cm_2O_3 on weight percent basis.

Figure 1. Precipitation Pretreatment Flowsheet

Batch Vitrification Process Description

The batch vitrification processing includes the three distinct steps of drying, calcination and vitrification prior to draining the glass to a storage canister. Descriptions of the three steps are presented below.

The drying step removes the free aqueous fraction required to transfer the precipitated feed slurry to the melter and chemically bound waters of hydration. The drying step is expected to be complete by the time the bed temperature reaches 200°C. The amount of time required to dry a single batch varies between 1 - 4 hours depending upon the total batch size and flush water used. Water is the main constituent in the off-gas during the drying step. Oxalic acid, nitrous oxides and a small quantity of carbon monoxide and carbon dioxide are also evolved.

Calcination decomposes the precipitated solids to carbonates and oxides and is expected to occur as the bed temperature is raised from 200°C to ~700°C. The amount of time required to calcine a single batch is a function of the heating rate and the total batch size. Proposed heating rates are in the range of 4-10°C/min and at the current rate of ~8°C/min would require approximately one hour to complete. During the calcination step, carbon monoxide (CO) and carbon dioxide (CO_2) are evolved from the oxalate decomposition.

Vitrification occurs as the oxides and the 25SrABS glass composition begins to soften and melt to form a low viscosity glass. The softening point of the 25SrABS composition when combined with the oxides is around 1100°C. It is known that cerium oxide (CeO_2) will reduce at high temperatures in lanthanide borosilicate glass. The thermal reduction of cerium ($Ce^{+4} \Rightarrow Ce^{+3}$), which liberates oxygen, begins at about 1140°C and is complete at about 1300°C.[2] The liberation of oxygen during the transition of high to low viscosity glass results in a small frothy bubble accumulation at the glass surface. The time to complete the vitrification step may include a hold period to fine the bubbles before the vitrified glass is drained from the melter into a stainless steel canister.

Early testing of the drying, calcination, and vitrification steps was conducted in a test facility known as the Drain Tube Test Stand (DTTS). The DTTS melter was originally designed and built for de-coupled glass draining tests in early 1997. The 11" high, open top cylindrical melter is constructed of 90 percent platinum and 10 percent rhodium alloy with an inside diameter of 2.5". The melter is heated by passing an electric current through the platinum/rhodium shell.

Experimental Description

In early 1998, Phase I of batch flowsheet development studies was completed in the DTTS melter vessel. Laboratory scale crucible tests were completed in parallel with these larger scale DTTS tests.

Phase I tests conducted in the DTTS melter were designed to identify the technical issues associated with the sequential drying, calcination and vitrification of an oxalate slurry feed in a cylindrical melter. The identification of a technical issue, that of volume expansion/high temperature bubble formation, drove additional testing to identify process parameter variations to eliminate/mitigate the expansions. The increase in volume occurred as the batch transitioned from the calcination step (oxides and unmelted cullet) to the vitrification step (a molten glass). Batch volume increases were isolated to two mechanisms, a sintered frit cap that trapped expanding air and evolving gases, and a frothy bubble accumulation due to the thermally induced reduction of cerium. Testing was also designed to evaluate the effects of heating rates, hold times and glass processing temperature on volume expansions, pour characteristics and product glass quality.

Results

Volume Expansion - Sintered Frit Cap

The first mechanism for volume expansion associated with sequential drying, calcination and vitrification in the batch flowsheet focused on a frit size phenomena. The process was isolated as a porous sintered frit cap that evolved from unmelted 25SrABS frit particles and expanding gases below the cap surface.

Initial testing of the batch flowsheet added a pre-dried oxalate feed to 25SrABS glass composition frit sized to -80 +200 mesh. The dry mixture was mechanically mixed and then added to the DTTS melter. The batch was heated at approximately 4°C per minute to a target vitrification temperature of 1350°C. At approximately 1120°C the height of the batch bed surface in the melter increased from a vitrified volume of about 140cc to 804cc, or greater than 5X. The domed, sintered surface was fairly thick, approximately one inch at its thickest point. The sintered material was porous and light, and cooled quickly near the open top of the melter vessel, effectively sealing evolving gases. Subsequent analysis showed that the material was primarily frit (25SrABS frit rich) but was also comprised of the oxides from the incoming feed.

Prior testing in the DTTS melter during pour characterization studies revealed a pattern to the sintered surface volume expansion noted in initial batch vitrification tests. Approximately one quarter of the previous melter runs that used small frit sizes (-14 +30 and -80 +200 mesh sizes) resulted in the sintered bed expansion. However, the sintered bed expansion had not been observed with the use of cullet (premelted glass poured into water). A batch was prepared as described above with a 25SrABS cullet composition recipe added in place of the frit. No sintered frit surface increase was noted in this run and over 20 like it using cullet. However, solving this problem revealed a second problem. Repeatably between 1140°C and 1200°C the bed would begin to pulse as large bubbles were released from beneath a bed surface of surrogate feed oxides and high viscosity glass (>500 poise at this temperature), identifying the second mechanism of volume expansion.

Volume Expansion - High Temperature Bubble Formation

The elimination of the sintered bed surface expansion revealed that the volume increase was also due to the evolution of gas at high temperature. This was evidenced by the presence of a pulsing oxide/cullet bed at ~1140°C, before the batch became a low viscosity molten glass pool. As the bed temperature continued to increase, the batch materials (cullet and oxides) began to soften and trap the evolving gas in small bubbles. The layer of bubbles insulated the melt pool below it which resulted in a extremely rapid increase in the bed/glass temperature (60C+ per minute), perpetuating the problem by providing a higher rate of gas evolution. As the high viscosity glass trapped more of the evolving gas in bubbles, the bubbles quickly accumulated over the bed surface and subsequently resulted in an overall increase of the batch volume. As the bubbles accumulated and increased in height, the cooling effect of the open top melter sealed the top layer of bubbles into a thin high viscosity layer of foamy glass. The accumulation of the bubbles formed at high temperature has been measured to increase the melted glass volume by two to three times.

A review of the literature revealed that cerium is thermally reduced from a +4 valence state a +3 at temperatures in the 1120°C to 1200°C range. Three tests were conducted to validate the hypothesis of a temperature induced cerium reduction. The first test, which removed cerium from the surrogate feed, resulted in no bubbles and no volume expansion. The second test doubled the cerium of the incoming surrogate feed. This test resulted in a volume expansion to the top of the melter vessel (approximately a 5X increase from the melted glass volume) that consisted of small, active bubbles between temperatures of 1160°C and 1460°C. A third test was performed to vitrify a batch in an inert atmosphere and sample the off-gas with a gas chromatograph. This test validated the hypothesis that the gas evolved at high temperature was oxygen. With cerium being a major component of the incoming feed, oxygen liberation had to be dealt with. The "double cerium" test described above is currently considered a bounding case with respect to the process. Americium, the other waste component with the potential to undergo thermal reduction, is not judged to be a significant contribution to oxygen evolution.[3]

Effects of Processing Variations on Volume Expansion

It is theorized that a key to mitigating the volume expansion is to control the vertical location of glass softening and cerium reduction. Heating from the top down, that is providing a vertical temperature profile with a hot top and cooler bottom, would appear to provide a lower viscosity glass near the top allowing for oxygen to escape. The DTTS vessel provides such a temperature profile with a hot spot approximately one inch above the calcined bed surface and a cool bottom. Temperatures of the platinum bottom are approximately 200°C to 240°C cooler than the platinum wall during the heat up. When the batch was intentionally segregated with the cullet on the bottom and the oxalate slurry batched on the top of the cullet, the temperature profile in the DTTS melter allowed for the sequential redox of cerium while fluxing and melting the glass from the top down. This resulted in minimal bubbles and significantly reduced the severity of the bubble accumulation to less than a twice the final glass volume.

Several other processing variables can be adjusted to reduce the tendency for bubble formation and/or remove the bubbles after formation. Heating rates were varied between 1°C per minute and 10°C per minute during various steps of the process. It was determined, however, that there was no significant advantage to slowing the heating rate to reduce the rate of gas evolution. 8°C per minute was proven adequate for mitigating the volume expansion (<2X) when cullet was used, while still maintaining a reasonable batch cycle time (less than ten hours for all three batch vitrification sub-steps). Hold periods at temperature as well as higher temperatures can be utilized to fine the bubbles from the melt. Hold times from 1 hour to 18 hours were evaluated while varying the glass temperature from 1370°C to 1450°C. Dip samples revealed a significant reduction in the presence of bubbles after four hours when the glass was held at 1370°C. At a glass temperature of 1450°C a two hour hold was adequate to arrive at the same end point.

Conclusion

The successful demonstration of sequential drying, calcining and vitrifying an oxalate slurry in a the DTTS melter vessel provided the basis for testing on a larger scale in a cylindrical induction heated melter. Sintered frit cap expansions were eliminated with the use of cullet and volume expansions due to high temperature bubble formation (oxygen liberation from cerium reduction) were mitigated in the DTTS melter vessel through a vessel temperature profile that effectively separated the softening point of the glass cullet and the evolving oxygen from cerium reduction. An increased processing temperature of 1470°C and a two hour hold time to fine the glass reduced bubbles in the poured glass to an acceptable level. The success of the preliminary process demonstrations provided a workable process that was directly applicable to the newly installed Cylindrical Induction Melter system, making the batch flowsheet the preferred option for vitrification of the americium/curium feed stream.

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References

1. M.E. Smith, A.P. Fellinger, T.M. Jones, C.B. Miller, D.H. Miller, T.K. Snyder, M.E. Stone, and D.C. Witt, "Americium/Curium Melter 2A Pilot Tests (U)," submitted for publication in the *Proceedings of the International Symposium on Waste Management Technologies in Ceramic and Nuclear Industries*, The American Ceramic Society, May 1998.
2. J. E. Marra, M. A. Baich, A. P. Fellinger, B. J. Hardy, T. M. Jones, C. B. Miller, D. H. Miller, D. K. Peeler, T. K. Snyder, M. E. Stone, J. C. Whitehouse, and D. C. Witt, "Americium-Curium Vitrification Pilot Tests - Part II," to be published in the *Proceedings of the International Symposium on Waste Management Technologies in Ceramic and Nuclear Industries*, The American Ceramic Society, May 1998.
3. Henry Schreiber (private communication).