WSRC-MS-98-00864, Rev. 1

Americium-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

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

Abstract

The successful demonstration of sequentially *drying*, *calcining* and *vitrifying* an oxalate slurry in the Drain Tube Test Stand (DTTS) vessel provided the process basis for testing on a larger scale in a cylindrical induction heated melter. A single processing issue, that of batch volume expansion, was encountered during the initial stages of testing. The increase in batch volume centered on a sintered frit cap and high temperature bubble formation. The formation of a sintered frit cap expansion was eliminated with the use of cullet. 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 any remaining bubbles successfully reduced bubbles in the poured glass to an acceptable level. The success of the preliminary process demonstrations provided a workable process basis that was directly applicable to the newly installed Cylindrical Induction Melter (CIM) system, making the batch flowsheet the preferred option for vitrification of the americium-curium surrogate feed stream.

Introduction

The Savannah River Technology Center (SRTC) is developing the equipment design bases and process operating parameters to vitrify a nitric acid solution containing isotopes of americium and curium (Am-Cm). The final glass form will be placed in interim storage until it can be transported to the U.S. Department of Energy's Oak Ridge National Laboratory for recovery of the Am-Cm from the glass. 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. Operating results and difficulties of the continuous feed Am-Cm slab melter pilot system have been documented by Smith, et.al.[1] The alternative of batch vitrification and the simplification of the melter system are described by Marra, et.al.[2] While a new induction-heated cylindrical melter was being installed, vitrification experiments with the product slurry from a 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 of the nitric acid feed stream will be the only "in-cell" pretreatment step before the feed material is introduced 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 (primarily rare earth oxalates) are settled and the free liquid decanted. The precipitated oxalates are washed with 0.1 molar oxalic acid, and again allowed to settle before the wash solution is decanted. A 1.0 liter surrogate precipitation yields approximately 160 grams of oxalate solids. The washed oxalate precipitate is then combined in the melter vessel with a glass-forming composition of either frit, cullet, glass beads or raw batch chemicals.

Figure 1. Precipitation Pretreatment Flowsheet

Current operations at the Am-Cm pilot facility are performed using two different surrogate feed compositions. The first surrogate feed was based on 1993 sample results of the F-canyon Am-Cm solution and used erbium as a substitute for both americium and curium. Recently, results of a 1998 sample have been obtained and the surrogate feed revised to incorporate the new sample results. Both surrogate compositions have been tested with no observed processing differences. The baseline glass forming composition (25SrABS) and the two surrogate feed compositions are shown in Table 1.

Batch Vitrification Process Description

The batch vitrification process includes the three distinct steps of drying, calcination and vitrification prior to draining the glass into a storage canister.

The drying step removes the free aqueous fraction required to transfer the precipitated feed slurry to the melter and the 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 the volume of flush water used. Water is the main constituent in the off-gas during the drying step. Nitrous oxides and a small quantity of carbon monoxide and carbon dioxide also are 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. Typical heating rates are in the range of 4-10°C/min. At a nominal rate of ~8°C/min calcination requires approximately one hour to complete. During the calcination step, carbon monoxide (CO) and carbon dioxide (CO_2) are evolved from oxalate decomposition.

Vitrification occurs as the oxides resulting from the calcination step begin to react with the 25SrABS glass-forming composition. The softening point of the 25SrABS composition (which produces a high viscosity initial liquid phase) is around 1100°C. Additionally, it is known that cerium oxide (CeO_2) will reduce at high temperatures in lanthanide borosilicate glass.[3] However, the cerium is only partially reduced ($Ce^{+4} \Rightarrow Ce^{+3}$) at about 1150°C and is completely reduced at 1300°C.[3] The overlap of the 25SrABS softening point (high viscosity initial liquid phase) with the liberation of oxygen due to cerium reduction results in a 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. Bubbles in the final product would not affect the product performance criteria of recoverability.

Table 1. Surrogate feed and 25SrABS glass former compositions

Early testing of the integrated batch process (i.e., 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 inch high, open top cylindrical melter is constructed of 90% platinum and 10% rhodium alloy with an inside diameter of 2.5 inches. 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 processing 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 identified with two semi-related 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 (oxygen evolution). 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 (74-177µm). 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 volume of the batch 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 of a cold cap sample showed that the material was primarily unreacted frit (25SrABS frit rich), with just a small amount of oxides from the surrogate 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 (glass produced by reprocessing the 25SrABS frit and pouring into a water batch to produce a larger particle size and particle size distribution). A batch was prepared as described above with a 25SrABS cullet composition added in place of the frit. No sintered frit surface increase was noted in this run, nor in over 20 additional runs using cullet. However, solving this problem revealed the second processing issue. 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 also was 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 to produce a highly viscous initial liquid phase trapping the evolving gas in small bubbles. The layer of bubbles insulated the melt pool below it which resulted in an extremely rapid increase in the bed/glass temperature (60C+ per minute), perpetuating the problem through 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 increased the melted glass volume by two to three times. A review of the literature revealed that cerium is completely reduced from a +4 valence state to a+3 at temperatures in the 1120°C to 1300°C range. [3] 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 content in the nominal 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 to sample the off-gas with a gas chromatograph. The results of the gas chromatography during the inert test show a substantial increase in the volume of oxygen present in the melter vapor space. Shown in Figure 2, the increased volume of oxygen is evidenced as an increase in volumetric ratio to nitrogen (O_2/N_2). This test qualitatively validated the hypothesis that the gas evolved at high temperature was oxygen.

These three tests, combined with laboratory tests [3], confirmed that the high temperature gas generation was oxygen resulting from cerium reduction. 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]

Figure 2. Volumetric Ratio of O2 to N2 during Inert Run

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 (minimizing the overlap of cerium reduction and the formation of a high viscosity liquid phase). 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 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/min and 10°C/min 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 melt temperatures of approximately 1370°C as well as higher temperatures can be utilized to fine the bubbles from the melt, although bubbles in the poured glass would not affect the product performance criteria of recoverability. 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 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 1450°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.

Acknowledgments

This paper was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U.S. Department of Energy.

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. J.D. Vienna, D.K. Peeler, J.G. Darab, J.R. Zamecnik, H. Li, and J.E. Marra, "Chemistry of Rare Earth Oxalate Vitrification," in *this volume*, Materials Research Society, 1999.