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Effects of Quartz Particle Size and Sucrose Addition on Melting Behavior of a Melter Feed for High-Level Waste Glass

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Office of River Protection

P.O. Box 450
Richland, Washington 99352

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Effects of Quartz Particle Size and Sucrose Addition on Melting Behavior of a Melter Feed for High-Level Waste Glass

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Abstract

The behavior of melter feed (a mixture of nuclear waste and glass-forming additives) during waste-glass processing has a significant impact on the rate of the vitrification process. We studied the effects of silica particle size and sucrose addition on the volumetric expansion (foaming) of a high-alumina feed and the rate of dissolution of silica particles in feed samples heated at 5°C/min up to 1200°C. The initial size of quartz particles in feed ranged from 5 to 195 µm. The fraction of the sucrose added ranged from 0 to 0.20 g per g glass. Extensive foaming occurred only in feeds with 5-µm quartz particles; particles ≥150 µm formed clusters. Particles of 5 µm completely dissolved by 900°C whereas particles ≥150 µm did not fully dissolve even when the temperature reached 1200°C. Sucrose addition had virtually zero impact on both foaming and the dissolution of silica particles.

Introduction

Over 100 sites in the United States are currently tasked with the storage of nuclear waste. The largest is the Hanford Site located in southeastern Washington State with 177 subterranean tanks containing over fifty-million gallons of nuclear waste from plutonium production from 1944 through 1987 [1]. This waste will be vitrified at the Hanford Tank Waste Treatment and Immobilization Plant. In the vitrification process, feed is charged into a melter and converted into glass to be ultimately stored in a permanent repository. The duration of waste-site cleanups by the vitrification process depends on the rate of melting, i.e., on the rate of the feed-to-glass conversion. Foaming associated with the melting process and the rate of dissolution of quartz particles (silica being the major glass-forming additive) are assumed to be important factors that influence the rate of melting.

Previous studies on foaming of high-alumina feed demonstrated that varying the makeup of a melter feed has a significant impact on foaming [2]. The volume of feeds that contained 5-µm quartz particles substantially increased because of foaming. The extent of foaming decreased as the particle size of quartz increased [2]. Moreover, samples containing quartz particles 195 µm formed agglomerates at temperatures above 900°C that only slowly dissolved in the melt [3].

This study continues previous work on the feed-melting process [3], specifically on the effects of the size of silica particles on the formation of nuclear-waste glasses to determine a suitable range of silica particle sizes that causes neither excessive foaming nor undesirable agglomeration. Apart from varying the silica-particle size, carbon was added in the form of sucrose. Sucrose has been used to accelerate the rate of melting [4]. In this study, we have observed its impact on feed foaming and quartz dissolution.

Experimental

Table 1 lists the compositions of the three feeds tested. The baseline feed, A0, was formulated for high-alumina waste [2]. It contains hydroxides, nitrates, and carbonates. The other two feeds were modified by using glass-forming additives in the form of nitrate salts. In the A0-AN1 feed, the content of carbonates is limited to that coming from the waste. No carbonate is present in the A0-AN2 feed.

Table 1. Feed compositions in g per 1 kg of glass

	A0	A0-AN 1	A0-AN 2
$Al(OH)_3$	367.49	367.49	367.49
$Bi(OH)_3$	12.80	12.80	12.80
$Ca(NO_3)_2 \cdot 4H_2O$	0.00	210.56	210.56
CaO	60.79	10.79	10.79
$Fe(H_2PO_2)_3$	12.42	12.42	12.42
$Fe(OH)_3$	73.82	73.82	73.82
H_3BO_3	269.83	269.83	269.83
KNO_3	3.04	3.04	3.04
Li_2CO_3	88.30	4.22	0.00
$LiNO_3$	0.00	156.90	164.78
$Mg(OH)_2$	1.69	1.69	1.69
$Na_2C_2O_4$	0.00	1.26	1.26
$Na_2C_2O_4 \cdot 3H_2O$	1.76	0.00	0.00
Na_2CrO_4	11.13	11.13	11.13
Na_2SO_4	3.55	3.55	3.55
NaF	14.78	14.78	14.78
$NaNO_2$	3.37	3.37	3.37
$NaNO_3$	0.00	112.97	112.97
$NaOH$	99.41	46.30	46.30
$Ni(NO_3)_2 \cdot 6H_2O$	0.00	0.00	15.58
$NiCO_3$	6.36	6.36	0.00
$Pb(NO_3)_2$	6.08	6.08	6.08
SiO_2	305.05	305.05	305.05
$Zn(NO_3)_2 \cdot 4H_2O$	2.67	2.67	2.67
$Zr(OH)_4 \cdot xH_2O$	5.49	5.49	5.49
Total	1349.82	1642.55	1655.43

Quartz was crushed and sieved to obtain various particle sizes. Figure 1 presents four quartz particle sizes used for testing. The A0 feeds were tested with 5-, 75-, and 195-µm particles of quartz. The A0-AN1 feeds were tested with silica particles of 5-, 45-, 75-, 150-, and 195-µm and with an addition of 0.16 g of sucrose per 1 g of glass. All A0-AN2 feeds contained 75-µm quartz and had varying sucrose additions of 0.08, 0.12, 0.16, and 0.20 g per g of glass. The particle sizes and the sucrose masses are listed in Table 2. Feeds containing sucrose are labeled by the carbon-nitrogen atomic ratio in the feed. Feed slurries were wet-mixed in 5-l beakers, stirred with heat until solid, and dried in an oven set to 105°C overnight.

Table 2. Feed variables

Feed ID[(a)]	Sucrose per 1 kg glass, g	Quartz particle size, µm
A0-5	0.00	5
A0-75	0.00	75
A0-195	0.00	195
A0 AN1-5 (1.00)	157.58	5
A0 AN1-45 (1.00)	157.58	45
A0 AN1-75 (1.00)	157.58	75
A0 AN1-150 (1.00)	157.58	150
A0 AN1-195 (1.00)	157.58	195
A0 AN2-75 (0.00)	0.00	75
A0 AN2-75 (0.50)	81.41	75
A0 AN2-75 (0.75)	122.39	75
A0 AN2-75 (1.00)	163.36	75
A0 AN2-75 (1.25)	204.33	75

(a) Feed type-Particle size in µm (carbon-to-nitrogen molar ratio)

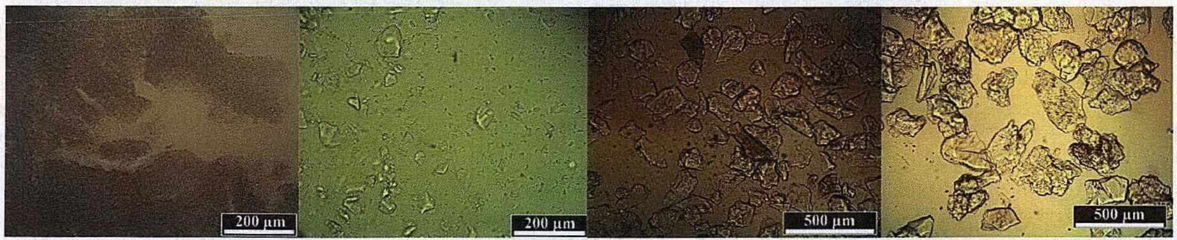

Figure 1. Microscopic images of quartz particles from left to right: 5, 75, 150, and 195 µm

Cylindrical pellets 1.25 cm wide and 0.5 cm tall prepared from 1.50-g feed samples were pressed at ~7 MPa and ramp heated at 5°C/min from room temperature to 1000°C. Images of the pellet profile were captured through a window in the furnace wall. These images were analyzed on Adobe Photoshop PS3© to obtain the pellet profile as a function of temperature.

For heat treatments, 10-g samples were added to platinum-rhodium boxes, weighed, and ramp heated at 5°C/min in a furnace. Samples were removed at 100-degree intervals from 400°C to 1200°C. After cooling, heat-treated samples were removed from the crucibles and divided for optical micrographs and X-ray diffractometry (XRD). Thin sections for optical microscopy could only be prepared with fused samples, which typically formed at temperatures exceeding 700°C. For examination by XRD, samples were mixed with 5 mass% of CaF_2 as an internal standard and crushed in a tungsten-carbide mill. Figure 2 shows a series of XRD scans from the 45-μm A0-AN1 feed to demonstrate the changes taking place in samples as a function of temperature. XRD scans were analyzed for content of crystalline phases by the programs JADE 6© and RIQAS 7©. The pink peaks (A) belong to the internal standard. The content of quartz (the green peaks, B) decreases rapidly after 800°C. Spinel (the red peaks, C) is present even at 1200°C. Sodalite (the blue peaks, D) dissolved at <1100°C.

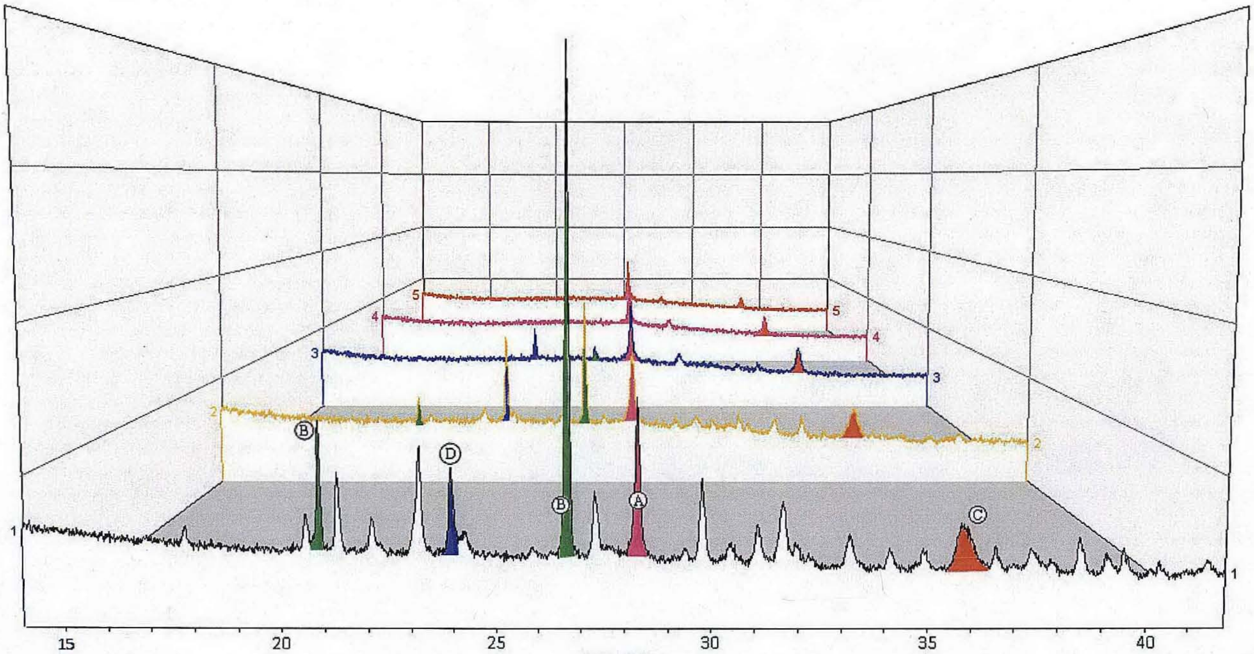

Figure 2. X-ray diffraction patterns of A0-AN1 45 (1.00) from 800°C (1) to 1200°C (5)

The relative fraction of undissolved quartz, *s*, determined from XRD analysis was calculated as $s = x_s/x_{s0}$, where x_s is the fraction of solid silica per mass of glass, and x_{s0} is the total silica fraction. The *ad hoc* arctangent function,

$$s = \frac{s_{-\infty}+s_{+\infty}}{2} - \frac{s_{-\infty}-s_{+\infty}}{\pi} arctan\frac{T-T_0}{T_1} \qquad (1)$$

was fitted to data to guide the eye [3], where $s_{-\infty}$, $s_{+\infty}$, T_1, and T_0 are constant parameters.

Results

Figure 3 shows photographs of expanding pellets of A0-AN1 and A0-AN2 feeds. Note the 1-cm segment of Pt wire used as a size gauge.

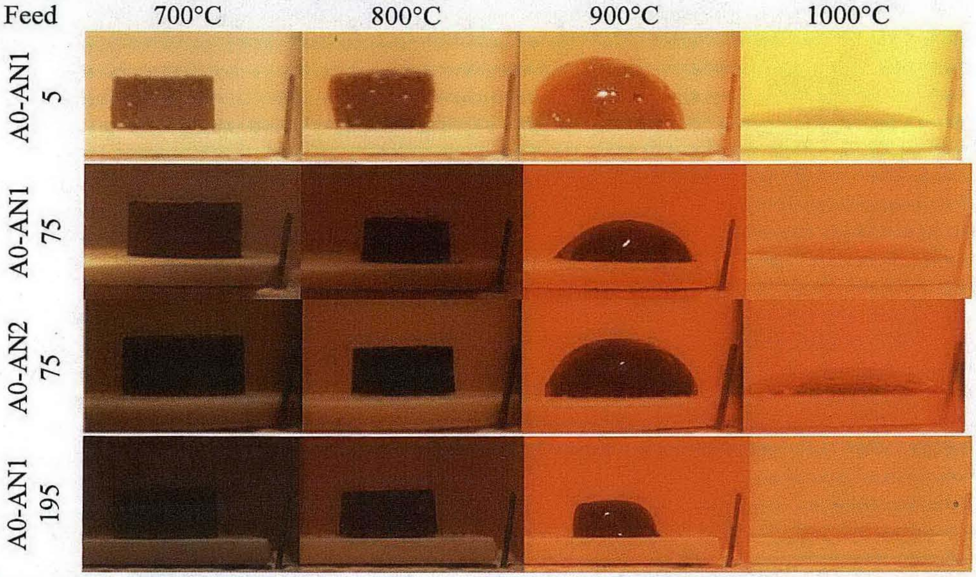

Figure 3. Photographic images of A0-AN1 feeds with 5-, 75-, and 195-µm quartz particles and A0-AN2 feed with 75-µm quartz particles

Figure 4A displays foaming curves for feeds with varying quartz particle sizes (as obtained from averaging two trials with A0-AN1 pellets). Solid lines represent A0 feeds and broken lines the A0-AN1 feeds. Feeds with 5-µm quartz continuously expanded to foam, the A0 feed from 700°C to 900°C and the A0-AN1 feed from 800°C to 850°C. The foam collapsed as the temperature increased. Both A0 and A0-AN1 feeds with 75-µm quartz initially shrank from 700 to 800°C, then expanded to approximately the initial profile area at 900°C, and finally collapsed by 1000°C. The A0 feed with 195-µm quartz shrank rapidly after 800°C, reaching a minimum profile area at 850°C. In A0-AN1, the use of 195-µm quartz particles resulted in gradual pellet shrinking from 700 to 800°C followed by rapid shrinking until a minimum was reached at 875°C.

Expansion resulting from trapped gases as a result of feed reactions is often referred to as primary foaming, whereas secondary foaming is caused by gases from redox reactions [5]. Unlike feeds with 5-µm quartz, feeds with larger quartz particles did not exhibit primary foaming because a high-viscosity melt formed only after reaction gases evolved. Secondary foaming occurred at temperatures >800°C. Figure 4B shows that foaming in A0-AN2 feeds was not significantly affected by the carbon content.

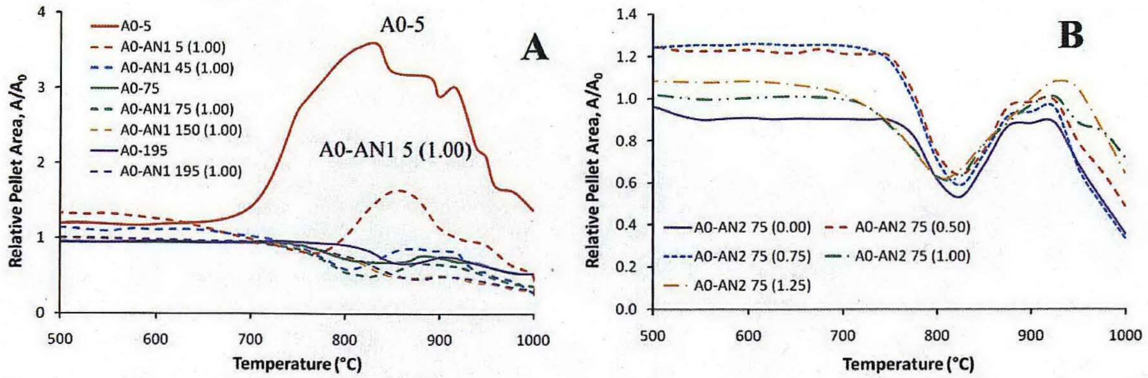

Figure 4. The effect of quartz-particle size on pellet expansion in A0 and A0-AN1 feeds (A) and the effect of sucrose addition on pellet expansion in A0-AN2 (B)

Figure 5A presents the dissolution of silica in A0 feed (solid points and lines) and A0-AN1 feeds (open points and dashed lines). The lines were fitted using Equation (1). Quartz particles in A0-AN1 feeds reached the same extent of dissolution as A0 feeds at temperatures up to 100°C higher. The quartz particles ≤75 μm fully dissolved below 1100°C. The fraction of dissolving quartz particles in A0-AN2 feeds is shown in Figure 5B. The sucrose addition was the only variable and had no noticeable effect on the dissolution of quartz. Therefore, a single line was fitted to data. Table 3 lists the dissolution coefficients defined by Equation (1).

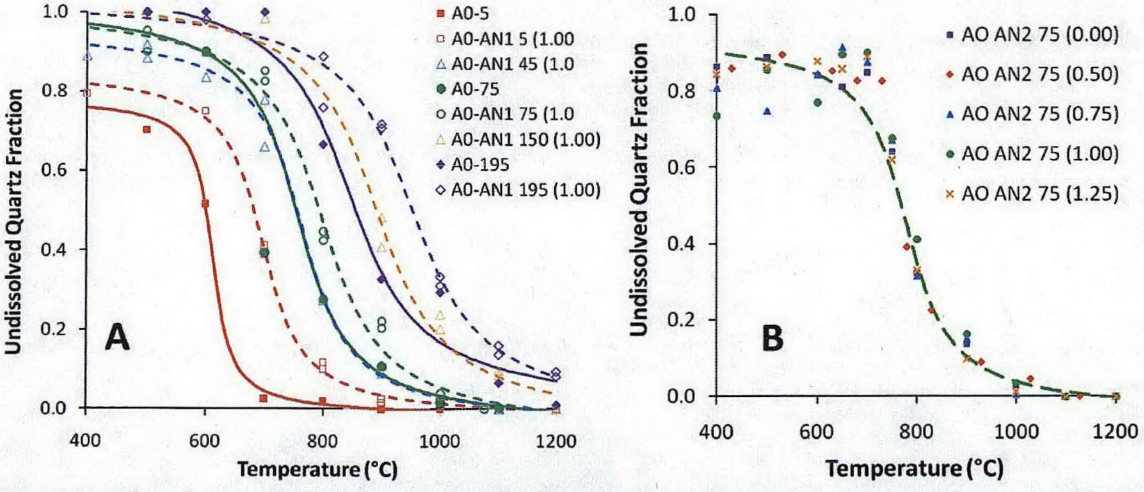

Figure 5. The effect of particle size on the dissolution of quartz in A0 and A0-AN1 feeds (A) and the effect of sucrose addition on the dissolution of quartz in A0-AN2 (B).

Table 3. Dissolution coefficients$^{(a)}$

Composition	A0-AN1					A0-AN2	A0		
Quartz particle size, µm	5	45	75	150	195	75	5	75	195
Sucrose addition, g per 1 kg of glass	157					163	0.000		
$s_{+\infty}$	-0.033	-0.051	-0.071	-0.060	-0.037	-0.052	-0.020	-0.056	-0.015
$s_{-\infty}$	0.866	0.971	1.026	1.071	1.051	0.952	0.788	1.031	1.103
T_1	49	60	76	86	89	64	23	64	89
T_0	698	763	798	891	951	778	613	756	845

(a) Dissolution coefficients are defined by Equation (1).

Figure 6 shows optical micrographs of feeds. At 900°C, feeds with quartz ≤75 µm formed a connected glass melt that trapped gases and formed cavities as wide as 5 mm on the sample bottom. The motion of the bubbles as they escaped at high temperatures homogenized the melt. Feeds containing particles >75 µm appeared uniform at temperatures < 900°C with quartz evenly dispersed throughout the sample (particles appear as dark spots on samples in first row). At higher temperatures, the dissolution of these large particles formed dark regions of high-viscosity silica melt. Bubbles isolated in this region coalesced and eventually forced particles into large clusters. These clusters survived beyond 1200°C.

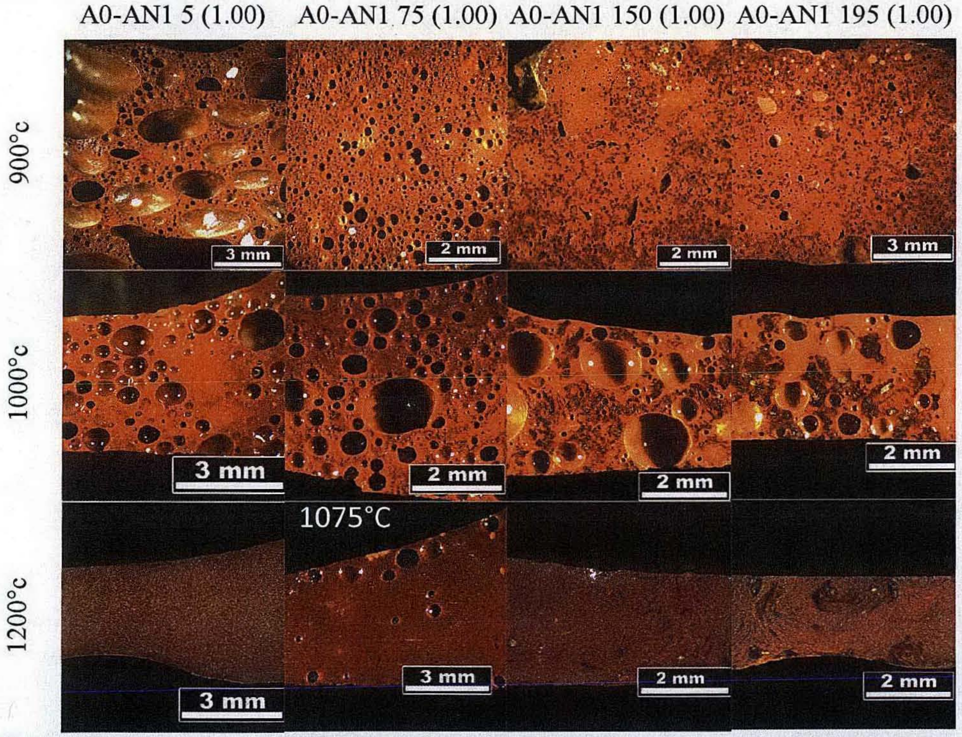

Figure 6. Optical microscopy of A0-AN1 feeds containing (from left to right) 5-, 75-, 150-, and 195-µm quartz particles

Discussion

Both primary and secondary foaming may insulate feed from external heat by reducing the rate of heat transfer and thus may reduce the rate of melting in a large-scale melter [2,5].

Volume expansion results and quartz dissolution data have demonstrated that foaming is primarily influenced by the fraction of silica dissolved. Noticeable foaming occurred when the fraction of solid quartz was reduced below 0.2 before 800°C (see Figures 4A and 5A). The use of fast-reacting 5-µm quartz particles, or "silica flour," resulted in a large volumetric expansion of samples at 900°C (Figures 3 and 4A). As Figure 5A illustrates, small particles completely dissolved by 1000°C and, as seen in Figure 6, the melt appears homogeneous at temperatures >1000°C.

Feeds with ≥75-µm quartz particles produce little primary foam and produced a limited amount of secondary foam (Figure 4). Silica particles remained still undissolved at 1000°C, and a high-viscosity melt surrounded the dissolving particles within the diffusion layers [3] while bubbles escaped through a low-viscosity bulk melt (Figure 6). However, inhomogeneities from the clustering of large particles may persist and, if not dispersed in the melter, may affect the glass corrosion resistance.

Since the sugar addition has little effect on both the dissolution of silica and foaming, no effects of sucrose addition on the rate of melting are expected beyond the melt-accelerating impact of the exothermic reaction of sucrose with nitrates.

Comparing the behavior of the baseline feed and the nitrate-modified feeds indicates that nitrate salts somewhat hinder the dissolution of quartz particles and reduce foaming. Further investigation is needed to ascertain the mechanism behind this trend.

Conclusions

Feeds with 5-µm quartz particles produced excessive foaming. Particles of ≥150 µm in size formed slowly dissolving clusters. Particle sizes of 45 to 75 µm appear to be optimum for processing. Adding sucrose to feeds containing nitrate (known to accelerate melting) has no adverse effect on foaming or quartz dissolution. Quartz dissolved somewhat faster in feeds containing both carbonates and nitrates than in fully nitrated feeds.

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References

1. http://www.hanford.gov/.
2. Hrma P., M. J. Schweiger, B. M. Arrigoni, C. J. Humrickhouse, V. V. Mantay, J. Marcial, J. A. Moody, T. T. Rainsdon, C. P. Rodriguez, R. M. Tate, N. E. TeGrotenhuis, and B. H. Tincher, Effect of Melter-Feed-Makeup on Vitrification Process, PNNL-18374, Pacific Northwest National Laboratory, 2009.
3. Schweiger M. J., P. Hrma, C. J. Humrickhouse, J. Marcial, B. J. Riley, and N. E. TeGrotenhuis, "Cluster formation of silica particles in glass batches during melting," Journal of Non-Crystalline Solids, accepted (2010).
4. Hrma P., M. J .Schweiger, C. J. Humrickhouse, J. A. Moody, R. M. Tate, N. E. TeGrotenhuis, B. M. Arrigoni, C. P. Rodriguez, "Effect of Melter-Feed-Makeup on Vitrification Process," 2009 ISRSM, Proceedings of International Symposium on Radiation Safety Management, Daejeon, Republic of Korea, 280-290 (2010).
5. Hrma P., M. J. Schweiger, C. J. Humrickhouse, J. A. Moody, R. M. Tate, T. T. Rainsdon, N. E. TeGrotenhuis, B. M. Arrigoni, J. Marcial, C. P. Rodriguez, B. H. Tincher, "Effect of glass-batch makeup on the melting process," Ceramics-Silikaty, accepted (2010).