Pacific Northwest NATIONAL LABORATORY

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U.S. DEPARTMENT OF ENERGY

1. Abstract

The behavior of melter feed has a significant impact on the rate of the high-level-waste vitrification. Simulated high-level waste feeds were studied to assess their behavior during a heat treatment similar to that which a melter feed experiences during processing. In particular, we examined the volume expansion (foaming) and the dissolution of quartz particles in feed samples heated at 5°C/min. Extensive foaming occurred in feeds with 5-µm quartz particles; these particles completely dissolved by 900°C. Quartz particles ≥ 150 µm formed clusters that slowed quartz dissolution. Moderate additions of sucrose had little effect on foaming or quartz dissolution.

2. Introduction

In the waste vitrification process, melter feed is converted to glass in a melter (Figure 1).

The waste-site cleanup lifecycle depends on the rate of melting that in turn is influenced by foaming and the dissolution of quartz particles and enhanced by the additions of sucrose.

3. Experimental

Table 1 shows constituents of the feeds; A0 is the baseline, A0-AN1 and A0-AN2 are high in nitrates, and A0-AC is high in carbonates. Quartz particle sizes varied from 5 to 195 µm in A0 and A0-AN1 (Figure 2). The atomic ratio of carbon to nitrogen (C/N) in A0-AN1 was 1 and in A0-AN2 varied from 0 to 1.25. A0-AC contained 75 µm quartz particles and no sucrose. All these feeds yield a glass of a composition shown in Table 2.

Feed slurries were mixed and dried for testing.

Dissolution of quartz particles was investigated by heating feed samples at 5°C/min and quenching at temperatures from 400 to 1200°C. X-ray diffraction patterns were evaluated using JADE 6 and RIQAS 4 (Figure 3)

To investigate foaming, feed pellets heated at 5°C/min were photographically monitored (Figure 4) and the images were evaluated with Adobe Photoshop PS3.

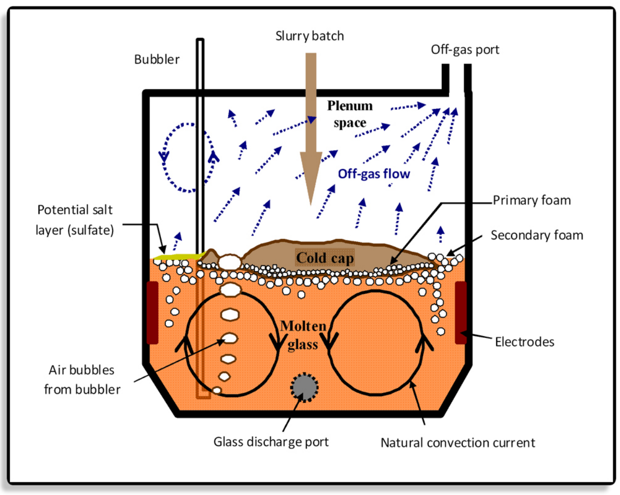

Figure 1. Schematic of high-level waste processing in a joule heated melter (courtesy of D. S. Kim)

Table 1. Feed Compositions in g/kg glass

	A0	A0-AN1	A0-AN2	A0-AC
$Al(OH)_3$	367.49	367.49	367.49	367.49
$Bi(OH)_3$	12.80	12.80	12.80	12.80
$Ca(NO_3)_2 \cdot 4H_2O$		210.56	210.56	
$CaCO_3$				108.49
CaO	60.79	10.79	10.79	
$Fe(H_2PO_2)_3$	12.42	12.42	12.42	12.42
$Fe(OH)_3$	73.82	73.82	73.82	73.82
H_3BO_3	269.83	269.83	269.83	269.83
K_2CO_3				2.08
KNO_3	3.04	3.04	3.04	
Li_2CO_3	88.30	4.22		88.30
$LiNO_3$		156.90	164.78	
$Mg(OH)_2$	1.69	1.69	1.69	1.69
$Na_2C_2O_4$		1.26	1.26	1.26
$Na_2C_2O_4 \cdot 3H_2O$	1.76			
Na_2CO_3				102.60
Na_2CrO_4	11.13	11.13	11.13	11.13
Na_2SO_4	3.55	3.55	3.55	3.55
NaF	14.78	14.78	14.78	14.78
$NaNO_2$	3.37	3.37	3.37	3.37
$NaNO_3$		112.97	112.97	12.34
NaOH	99.41	46.30	46.30	16.22
$Ni(NO_3)_2 \cdot 6H_2O$			15.58	
$NiCO_3$	6.36	6.36		6.36
$Pb(NO_3)_2$	6.08	6.08	6.08	
$PbCO_3$				4.91
SiO_2	305.05	305.05	305.05	305.05
$Zn(NO_3)_2 \cdot 4H_2O$	2.67	2.67	2.67	
ZnO				0.83
$Zr(OH)_4 \cdot xH_2O$ [(a)]	5.49	5.49	5.49	5.49
Total	**1350**	**1643**	**1655**	**1425**
[(a)] x = 0.65				

Table 2. Glass Composition

Glass	Mass Fr	Glass	Mass Fr
Al_2O_3	0.2402	ZrO_2	0.0040
B_2O_3	0.1519	SO_3	0.0020
CaO	0.0608	Bi_2O_3	0.0115
Fe_2O_3	0.0591	Cr_2O_3	0.0052
Li_2O	0.0357	K_2O	0.0014
MgO	0.0012	NiO	0.0040
Na_2O	0.0959	PbO	0.0041
SiO_2	0.3051	P_2O_5	0.0105
ZnO	0.0008	F	0.0067

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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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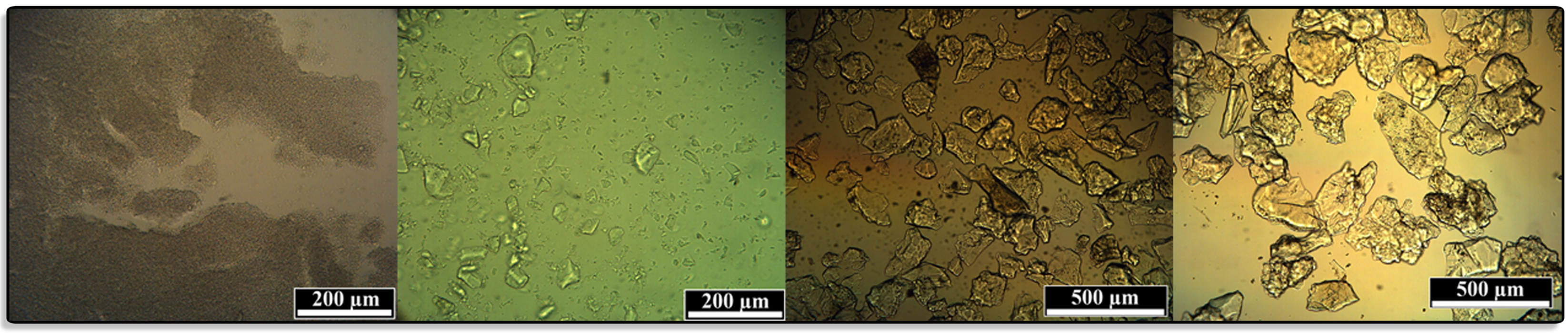

Figure 2. Optical micrographs of quartz particles (from left to right) 5, 75, 150, and 195 µm.

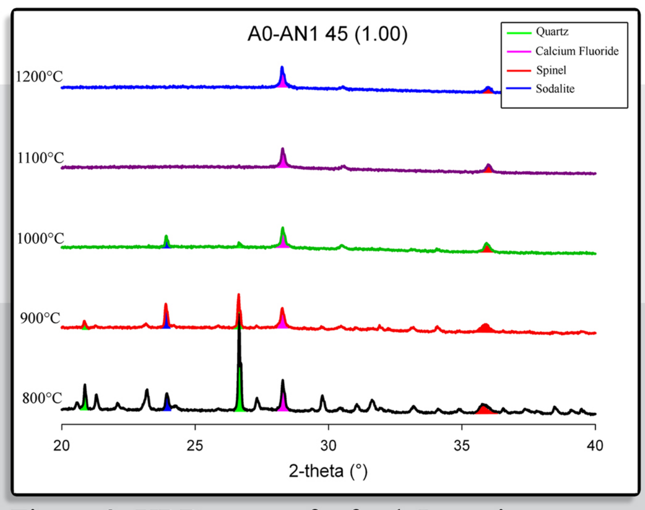

Figure 3. XRD scans of a feed. Intensity counts are scaled to keep CaF_2 peak intensities constant.

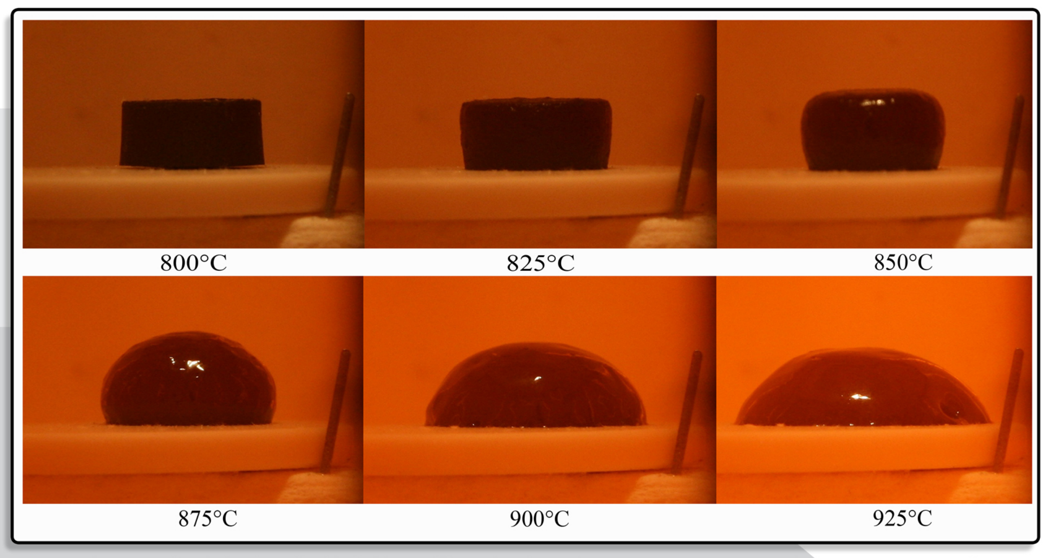

Figure 4. A0-AN2 (1.00) pellet during heat treatment. The segment of Pt wire is 10 mm tall

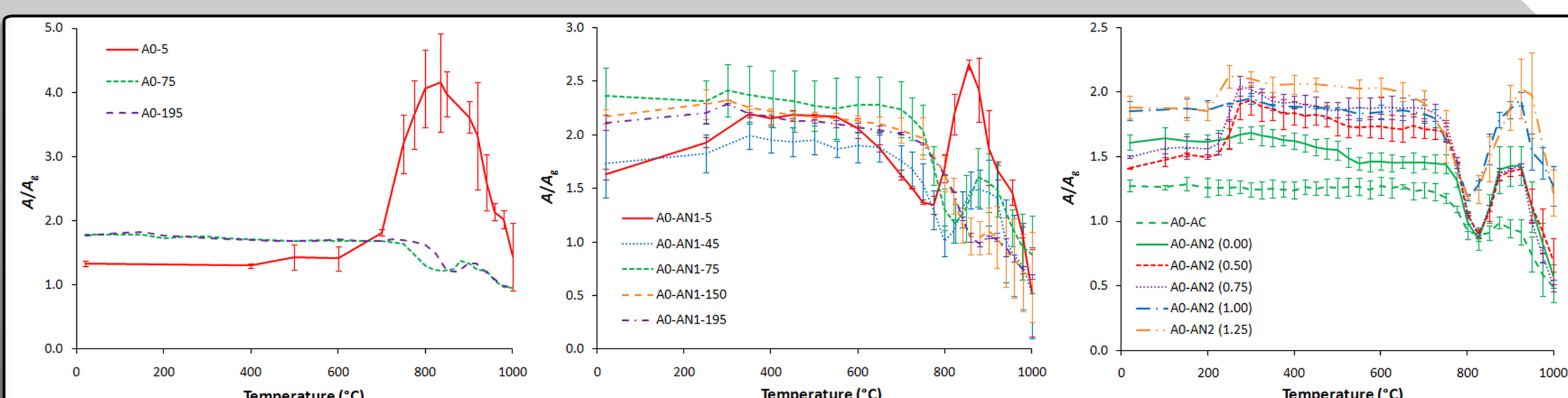

Figure 5. Cross-sectional normalized pellet area for three feed chemistries (left to right) A0, A0-AN1, and A0-AN2

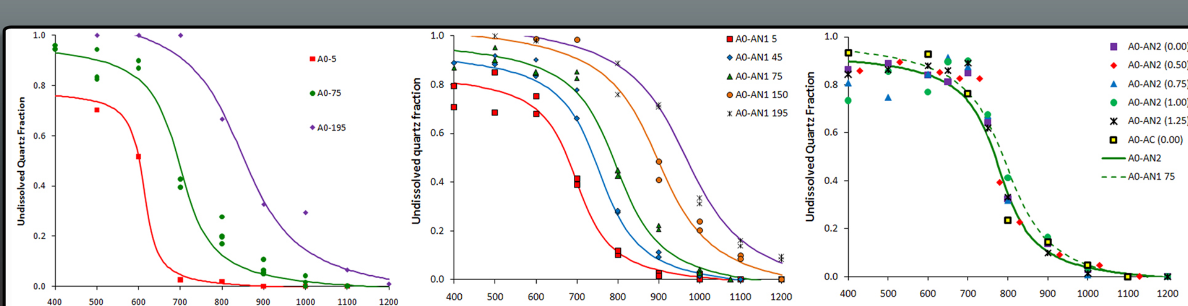

Fig ure 6. Quartz dissolution in three feed compositions (left to right) A0, A0-AN1, and A0-AN2

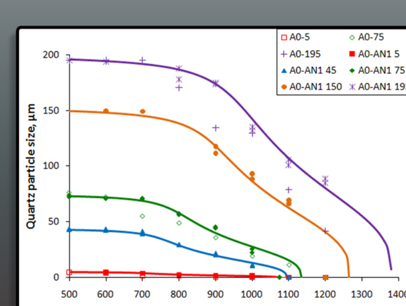

Figure 7. Quartz particle shrinking in A0 and A0-AN1

4. Results

Figure 5 displays the pellet area normalized to the area of a hemispherical drop of glass as a function of temperature. Pellets expanded as evolved gases became trapped in a high-viscosity melt, producing foam.

Figure 6 shows the fraction of solid quartz as a function of temperature and the initial size of quartz particles. Figure 7 shows the averaged quartz particle size as a function of temperature. Particles ≥ 150 µm formed clusters that slowed silica dissolution.

The use of carbonates in A0-AC resulted in less secondary foaming (Figure 5) while the rate of quartz dissolution was similar to the A0-AN2 feeds (Figure 6).

5. Discussion

Primary foaming is from feed reaction gases and secondary foaming is caused by gases evolving from redox reactions in the melt. Both primary and secondary foaming tend to insulate the cold cap (see Figure 1), probably reducing the rate of heat transfer from the melt below. As shown in Figures 5 and 6, foaming is largely influenced by the fraction of dissolved quartz. The use of fast-reacting 5-µm quartz particles resulted in a large volumetric expansion of samples because of primary foam. Feeds with quartz particles ≥ 75-µm produced only secondary foam (Figure 5).

The exothermal reaction of sucrose with nitrates accelerates melting. Although sucrose addition diminished the extent of primary foaming (Figure 5), it had little impact on secondary foaming unless an excessive amount (C/N ≥ 1.00) was used.

6. Conclusions

- Feeds with 5-µm quartz particles produced excessive foaming.
- Quartz particles of ≥ 150 µm formed slowly dissolving clusters.
- Quartz particles of 45 to 75 µm appear to be optimum for glass processing.
- Sucrose addition in C/N ratios ≤ 1.00 to feeds containing nitrates had no adverse effects on foaming or quartz dissolution.
- Excessive sucrose addition slightly increased secondary foaming.

7. Acknowledgements

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