

Comparison of High Level Waste Glass Feeds Containing Frit and Glass Forming Chemicals-16154

Brad VanderVeer, Pavel Hrma, Zach Hilliard, David Peeler, Mike Schweiger

Pacific Northwest National Laboratory, Richland, WA 99352, USA

ABSTRACT

This study compares the impact of frit and glass forming-chemicals on high level waste feed melting behavior. Feeds formulated to yield high-boron (lower waste loading) and low-boron (higher waste loading) glass compositions were prepared by blending a simulated high-level waste with glass-forming additives either in the form of chemicals or pre-melted as glass frit. The feeds were pressed into cylindrical disc-shaped pellets using a die tool and a hydraulic press. Each pellet was heat-treated in a high-temperature furnace equipped with a window to view the pellet's response to increasing temperature, usually up to 1100°C, until the pellet turned into a molten glass droplet. A camera mounted in front of the viewing window was used to take high-quality pictures at predetermined intervals. Images were analyzed using a program that calculated the pellet profile area and volume as functions of temperature. The analyses are used to determine characteristic temperatures and associated volume expansions including foam onset and collapse.

INTRODUCTION

At the Hanford Site, 55-million gallons of nuclear waste are being stored in 177 underground tanks, waiting to be treated and vitrified in the Waste Immobilization and Treatment Plant (WTP) [1], which is currently under construction [2]. Effective melter feed preparation will help optimize the glass production efficiency.

The conversion of melter feed into molten glass occurs in the cold cap, where the feed components react and produce glass-forming melt that may expand to transient foam as a result of evolution of residual batch gases, release of dissolved gases such as H₂O, and evolution of oxygen from redox reactions [3-5]. Foam acts as an insulating layer and reduces the heat transfer from molten glass to the reacting feed, influencing the rate of melting [5]. The amount of foaming can be controlled by the feed formulation, such as the selection of the chemical form of glass forming and modifying additives (GFMA). For example, if one of the additives is alumina, it can be added in the form of corundum, gibbsite, or boehmite [3]. The GFMA can be premelted into frit [6].

Savannah River National Laboratory (SRNL) developed a method for evaluating feeds using x-ray computed tomography (XRCT). The feeds are added into a steel beaker and placed in a box furnace in which the beaker is heated from the bottom

with the sides insulated. After a fixed time, the beaker is allowed to cool and its content is analyzed with XRCT to determine the fraction of glass [6].

The aim of this study was to characterize four different high level waste feeds with respect to characteristic temperatures and associated volume expansions including foam onset and collapse. The four melter feeds were based on a fixed simulated high-level waste (HLW) composition with primary differences being the use of GFMA's added as either individual chemicals or in the form of premelted frit and the use of a high boron (original formulation; low waste loading) versus low boron (advanced formulation; high waste loading) additive. The feeds were prepared at SRNL and were also tested by XRCT [6].

As described below, the melter feeds were pressed into a pellet and the change of its shape and volume during heating at a constant rate were observed until the pellet turned into a droplet of molten glass. This method monitors the onset, growth, and collapse of transient foam that evolves during feed-to-melt conversion and was designed for the measurement of bulk density. Therefore, it provides information relevant for feed behavior in the cold cap.

EXPERIMENTAL PROCEDURE

Melter Feed Formulation and Fabrication

All four feeds were fabricated at SRNL. Table I lists compositions of frits from pre-melted GFMA's. Table II shows the compositions of waste simulant. The waste loadings are 35.09% for the original and 39.22% for the advanced formulation [6]. The frit was prepared using GFMA chemicals H_3BO_3 , SiO_2 , Na_2CO_3 and Li_2CO_3 , and melted at $1150^\circ C$ for 30 min. The frit was ground and sieved to 74-177- μm particle size. The waste simulant (Table II) was mixed with GFMA's as chemicals (H_3BO_3 , SiO_2 , Na_2CO_3 and Li_2CO_3) or frit to yield the melter feeds. Feeds were mixed and poured into stainless steel pans and dried in an oven at $100^\circ C$ overnight, crushed and passed through a 10 mesh screen.

Table I. Target Compositions of Frits and Glasses.

| Component | Original Formulation | | Advanced Formulation | |
|-----------------------------------|----------------------|--------------|----------------------|--------------|
| | 35.09% Waste Loading | | 39.22% Waste Loading | |
| | Frit | Glass | Frit | Glass |
| Al ₂ O ₃ | | 8.95 | | 10.00 |
| B₂O₃ | 30.81 | 20.00 | 14.18 | 8.62 |
| BaO | | 0.05 | | 0.06 |
| CaO | | 0.55 | | 0.61 |
| Cr ₂ O ₃ | | 0.09 | | 0.10 |
| CuO | | 0.05 | | 0.06 |
| Fe ₂ O ₃ | | 10.69 | | 11.94 |
| K ₂ O | | 0.13 | | 0.15 |
| Li₂O | 0.48 | 0.31 | 0.00 | 0.00 |
| MgO | | 0.50 | | 0.55 |
| MnO | | 3.09 | | 3.46 |
| Na₂O | 11.25 | 13.83 | 25.25 | 22.64 |
| NiO | | 1.32 | | 1.47 |
| P ₂ O ₅ | | <0.08 | | <0.09 |
| SO ₃ | | 0.31 | | 0.35 |
| SiO₂ | 57.46 | 38.36 | 60.57 | 38.01 |
| SnO ₂ | | 0.03 | | 0.03 |
| TiO ₂ | | 0.03 | | 0.03 |
| ZnO | | 0.05 | | 0.05 |
| ZrO ₂ | | <0.05 | | <0.05 |

Table II. High Level Waste Simulant Composition.

| Waste Simulant (wt%) | | | |
|---|-------|---------------------|-------|
| Mg(NO ₃) ₂ | 8.00 | NaPO ₄ | 0.531 |
| KMnO ₄ | 2.29 | NaF | 0.027 |
| Fe(NO ₃) ₃ | 45.67 | NaCl | 0.097 |
| Ni(NO ₃) ₂ (H ₂ O) ₆ | 4.32 | NaNO ₂ | 3.04 |
| NaOH | 14.38 | NaNO ₃ | 2.78 |
| Al(OH) ₃ | 11.75 | PbO | 0.007 |
| BaO | 0.049 | SiO ₂ | 0.84 |
| CaO | 0.566 | NaOH | 1.92 |
| Cr ₂ O ₃ | 0.083 | ZnO | 0.039 |
| CuO | 0.040 | ZrO ₂ | 0.120 |
| NaAlO ₂ | 0.750 | Ce(OH) ₃ | 0.090 |
| Na ₂ C ₂ O ₄ | 0.222 | Mg(OH) ₂ | 0.400 |
| Na ₂ CO ₃ | 1.29 | TiO ₂ | 0.017 |
| Na ₂ SO ₄ | 0.429 | CaCO ₃ | 0.192 |
| KNO ₃ | 0.057 | | |

Pellet Formation and Heating

Using a die tool and a hydraulic press, dried melter feeds were pressed at 168 MPa into disc shaped pellets of approximately 13-mm diameter and 6-mm height. A pellet was placed on an alumina plate and set on a stand inside of a high-temperature furnace. With a camera mounted in front of a viewing window on the furnace, the pellet was melted at $10^{\circ}\text{C min}^{-1}$ from room temperature to 1100°C . Photographs were taken at pre-determined intervals as the pellet expanded and contracted while melting. Fig. 1 shows the contraction, expansion, and collapse of a pellet formulated from the advanced melter feed with GFMA chemicals. Each photograph was evaluated in Photoshop^{®1} to determine the pellet profile area and then the volume using a program created in MATLAB^{®2}.

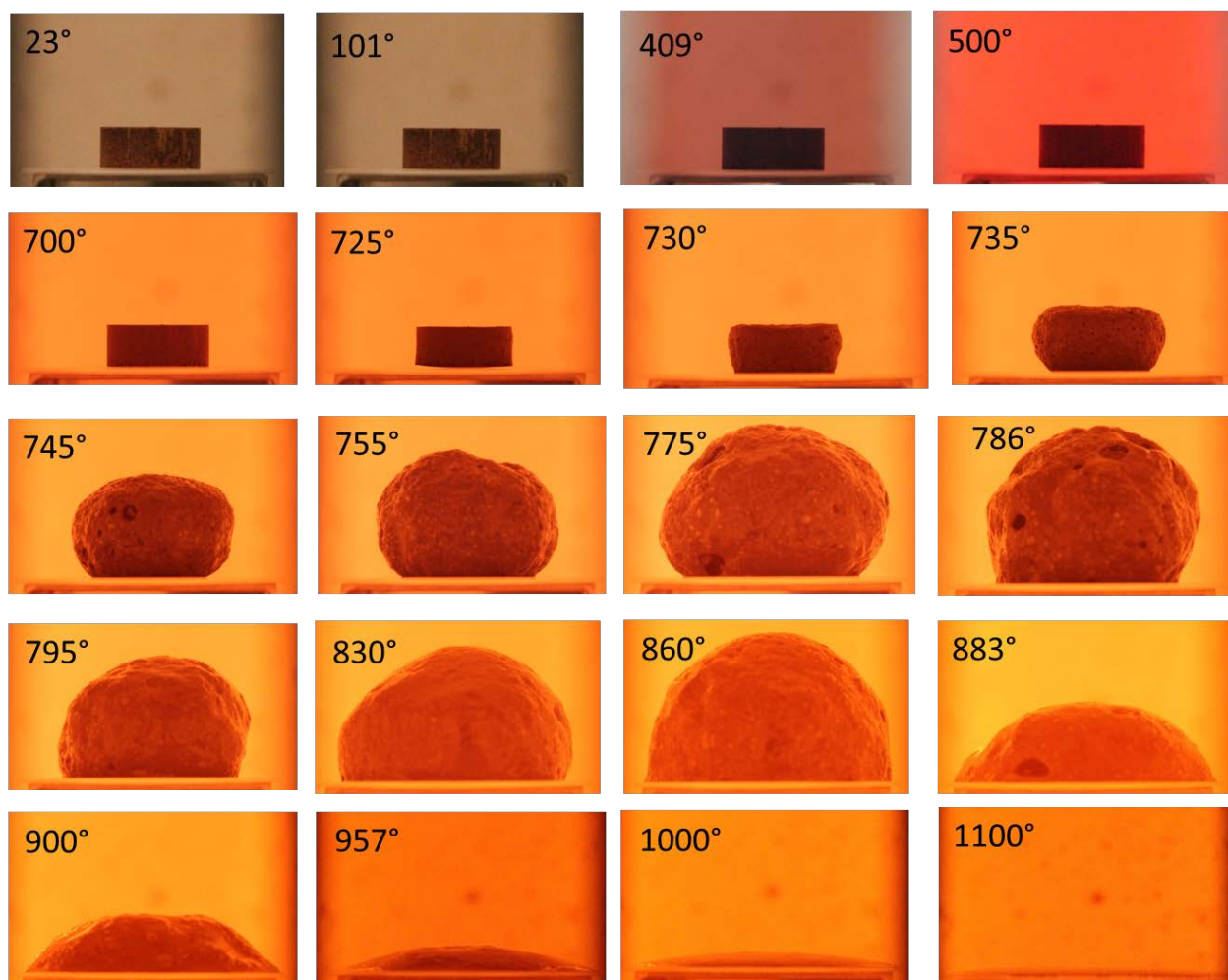


Fig. 1. Advanced Melter Feed Pellet with GMFA Chemicals Heated at $10^{\circ}\text{C min}^{-1}$.

¹ Photoshop[®] is a registered trademark of Adobe Systems Incorporated in the United States and/or other countries.

² MATLAB[®] is a registered trademark of The MathWorks, Inc. in the United States and/or other countries.

RESULTS

For clarity, Fig. 2 shows the normalized volume of feeds plotted against the temperature and Fig. 3 compares the four feeds in one plot. In general, for all four feeds, the pellet volume remained nearly constant up to approximately 600 or 700°C. Then, after a shallow minimum, once enough glass-forming melt was produced to seal the open pores, the pellet turned to a sessile drop, in which gas began to build up, leading to foam formation. The volume increased, reaching a maximum that typically consisted of several peaks caused by bursting of large bubbles. The last peak was followed by a gradual volume reduction that continued until the droplet turned into a nearly bubble-free melt.

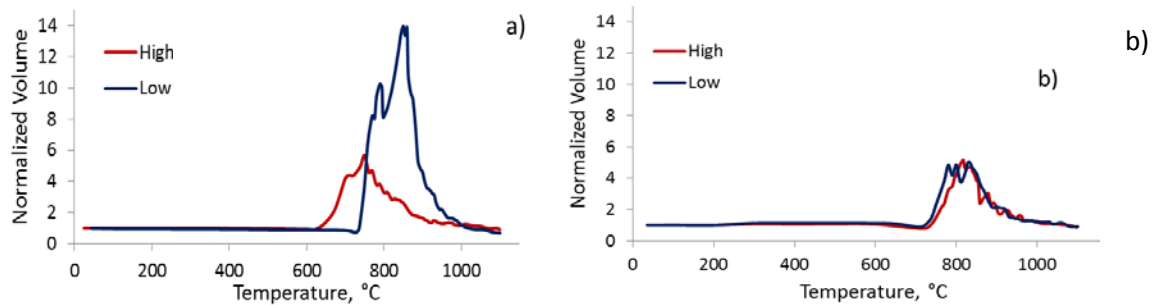


Fig. 2. Normalized Pellet Volume: Original (blue) and Advanced (red) Formulation with Chemicals (a) and with Frit (b).

Foaming began between 710 and 725°C except for the original feed with chemicals, which started to foam at 625°C. The normalized volume peaked at 5 to 6, with the exception of the advanced feed with chemicals. The advanced feed with chemicals foamed extensively to about 14 times the volume of the original pellet. Foams completely collapsed at approximately 990°C except for the advanced feed with chemicals that foamed until 1010°C.

Foaming occurred until the temperature reached ~1000°C. Feeds with frit foamed over a temperature interval of ~275°C, while feeds with chemicals foamed over an interval of at least 300°C. The foaming intervals (peak onset to complete collapse) of the feeds with chemicals was wider than those with frit by ~60°C for the original feeds and by ~20°C for the advanced feeds. These differences can be attributed to the larger volume of gas released from chemicals (~110 and ~220 ml CO₂ per gram of glass for the original and the advanced feed, respectively; the gas volume was normalized to 800°C).

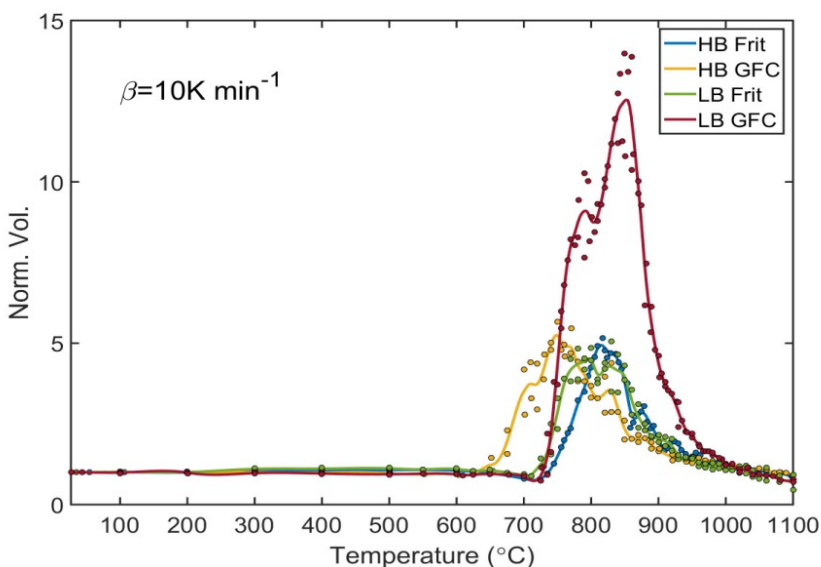


Fig. 3. Normalized Volume versus Temperature (red is advanced feed with chemicals, yellow is original feed with chemicals, green is advanced feed with frit, blue is original feed with frit and β is the heating rate).

DISCUSSION

The original feed (Table I) with chemicals began to foam $\sim 60^\circ\text{C}$ sooner than any other feed (Fig. 3). This could only happen if enough low-viscosity melt was produced to connect the glass-forming melt and trap evolving gases. The 1150°C viscosity was estimated as 5.0 Pa s for the original glass and 3.8 Pa s for the advanced glass. Provided that a similar difference exists from the foam onset, it could account for the lower extent of foaming and earlier collapsing of the original feed with chemicals. As stated above, the advanced feed with chemicals released about twice as much CO_2/g glass as the original feed with chemicals, which could account for the substantially higher extent of foaming of the advanced feed with chemicals.

Wider temperature intervals of foaming indicate a thicker foam layer under the cold cap, while larger foam volume suggests a higher porosity of the foam layer. Both thicker foam layer and higher foam porosity are likely to decrease the glass production rate. The narrower foaming interval and higher foam volume affected the advanced feed with chemicals in opposite direction with respect to the glass production rate. At this stage, it is impossible to determine which of these effects is more influential. Interestingly, the XRCT method employed at SRNL determined nearly identical fractions of melt formation in the two feeds with chemicals [6].

Feeds with frit evolve less gas, which is the likely reason that these feeds have significantly narrower temperature intervals of foaming. This result is consistent with the XRCT observation that melt fraction was significantly higher in the feed samples with frit [6]. Also, the advanced feed with frit produced more melt than the

original feed with frit. However, the foaming curves of original and advanced feeds with frit exhibit little difference.

Significant differences exist between the test methods used at SRNL and PNNL. In the feed sample heated from the bottom (SRNL method), the rate of heating that the feed experiences decreases from nearly instantaneous temperature increase at the bottom to an extremely slow heating rate at the top. On the other hand, the pellet melting method heats the sample at a rate deemed similar to that which the feed is subjected in the cold cap. The pellet method was designed for measuring (in conjunction with thermal gravimetry) the bulk density of feeds as a function of temperature. It remains to be established by future testing whether it can be employed for estimating, or at least ranking, the melting rates of melter feeds.

CONCLUSIONS

To compare the impact of frit and chemicals on feed melting behavior, simulated HLW feeds in the form of cylindrical disk-shaped pellets were heat treated at a constant rate of 10°C/min to 1100°C. The feeds were fabricated at SRNL and formulated to yield 35.09% and 39.22% WL glass compositions for simulated waste. Photographs were taken to monitor the pellet response to increasing temperature. The images were processed to determine volume versus temperature function for each feed.

Feeds composed with chemicals foamed considerably more than feeds composed with frit. The feed with chemicals and 35.09% WL foamed earlier than the other feeds. The melter feed with 39.22% WL and chemicals produced substantially more foam than the other feeds. The feeds containing frit had similar melting characteristics.

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