Effect of Feeding Rate on the Cold Cap Configuration in a Laboratory-Scale Melter - 13362

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ABSTRACT

High-level-waste melter feed is converted into glass in a joule-heated melter, where it forms a floating layer of reacting feed, called the cold cap. After the glass-forming phase becomes connected, evolving gases produce bubbles that form a foam layer under the feed. The bubbles coalesce into cavities, from which most of the gases are released around the edges of the cold cap while gases also escape through small shafts in the reacting feed. The foam layer insulates the cold cap from the heat transferred from the molten glass below. The cold cap behavior was investigated in a laboratory-scale assembly with a fused silica crucible. A high-alumina waste simulant was fed into the crucible and the feed charging rate was varied from 3 to 7 mL min^{-1}. After a fixed amount of time (35 min), feed charging was stopped and the crucible was removed from the furnace and quenched on a copper block to preserve the structure of the cold cap during cooling. During the rapid quenching, thermal cracking of the glass and cold cap allowed it to be broken up into sections for analysis. The effect of the charging rate on the height, area and volume of the cold cap was determined. The size of the bubbles collected in the foam layer under the feed increased as the cold cap expanded and the relationship between these bubbles and temperature will be determined for input into a mathematical model.

INTRODUCTION

There are approximately 200,000 cubic meters (m^3) of radioactive waste located in the Hanford waste tanks in southeastern Washington State. The high-level-waste (HLW) portion of the tank waste will be vitrified at the Hanford Tank Waste Treatment and Immobilization Plant (WTP) [1]. The conversion of HLW to a durable glass occurs through the addition of glass-forming additives and heating to temperatures around 1150°C in a joule-heated melter.

The melter feed is charged into a joule-heated melter where it forms a floating layer of reacting feed, called the cold cap. Many processes take place in the cold cap, including water evaporation, melting of salts, evolution of gases, formation of borates and their reactions with salts, dissolution of quartz particles, and finally the formation of borosilicate glass melt [2]. After the glass-forming melt becomes connected, evolving gases produce bubbles that form a foam layer under the feed. The bubbles coalesce into cavities, from which a majority of the gases are released around the edges of the cold cap. However, small shafts through the reacting feed vent a portion of the gases. The foam layer insulates the cold cap from the heat transferred from the molten glass below. Two types of foam may appear: primary and secondary. Primary foam is generated from the evolved CO_2 and NO_x in the glass-forming reactions and secondary foam from O_2 in the oxidation-reduction reactions within the glass melt due to ferric oxide components [3]. Additionally, the temperature of the cold cap decreases vertically from the glass melt interface up to the gas plenum [2]. More information is desired about the formation and behavior of the foam layer since it is one of the factors affecting the rate of melting of HLW. A mathematical model is being developed to simulate the melting of HLW as well as other waste feeds and the relationship of bubble/cavity distribution relative to melt temperature and radial direction are desired for incorporating into the model [2].

To this end, a laboratory-scale melter (LSM) system was created at Pacific Northwest National Laboratory [4, 5]. A schematic of the LSM can be seen in Fig. 1. The LSM was designed to allow the cold cap formation to be visually observed during charging [5]. After quenching, the cold cap can be broken into sections and the size and distribution of the cold cap structure within the glass melt can be examined. The sections can be compared with previous tests to determine the temperature at various points within the cold cap and this information can be added to the mathematical model.

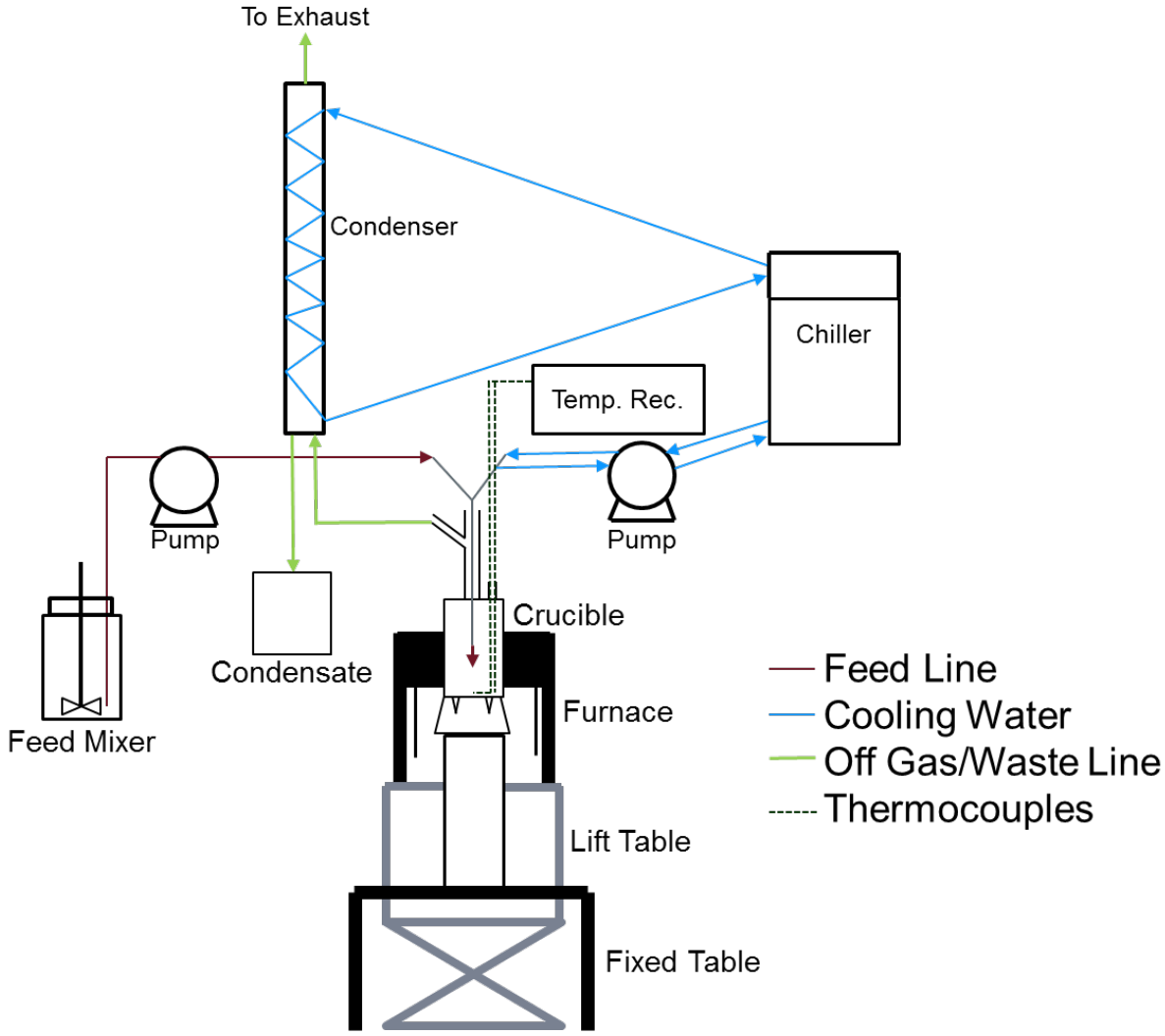

Fig. 1. Schematic of the LSM assembly

EXPERIMENTAL

Batch Composition

The simulated HLW feed used in these experiments was a high-alumina feed called A0 [3], the composition of which is shown in Table I. The feed was prepared in a batch to make 400 g of glass. The feed slurry contained 400 g L^{-1} glass components (oxides and halides).

Table I. A0 Feed Composition and Component Mixing Order for 400g of Glass

Compound	Amount (g)	Order Added
$Al(OH)_3$	146.99	7
$B(OH)_3$	107.93	5
$Bi(OH)_3$	5.12	4
CaO	24.31	4
$Fe(H_2PO_2)_3$	4.97	4
$Fe(OH)_3$	29.53	8
KNO_3	1.22	2
Li_2CO_3	35.32	6
$Mg(OH)_2$	0.68	4
$Na_2C_2O_4$	0.50	1
Na_2CrO_4	4.46	2
Na_2SO_4	1.42	1
NaF	5.91	4
$NaNO_2$	1.35	1
NaOH	39.77	3
$NiCO_3$	2.54	4
$Pb(NO_3)_2$	2.43	2
SiO_2	122.02	9
$Zn(NO_3)_2 \cdot 4H_2O$	1.06	1
$Zr(OH)_4 \cdot 0.65H_2O$	2.19	2
Total	539.74	-

Batch Preparation

The A0 feed slurry preparation began in a 1000 mL beaker with 500 mL deionized water (DIW) stirred with a Yamato Labo-Stirrer (Model LR-41C). The components were added in several groups in the order listed in Table I. Iron hydroxide was added in the form of 13 wt% slurry. After all of the components had been added and mixed, the feed slurry was transferred into a graduated cylinder and filled to 1000 mL with DIW.

LSM Preparation and Setup

The fused-silica crucible used in the LSM run is shown in Fig. 2. One hundred grams of previously melted A0 glass were crushed and placed in the crucible. Two thermocouples were inserted into the side port of the crucible; one was positioned by the wall near the bottom of the crucible and the second was bent into an ‘L’ shape so that the tip was located at the center ~3 mm above the crucible bottom; both were submerged just below the molten glass surface. The LSM crucible was placed into a modified Deltech furnace through a top opening of 10.2 cm in diameter.

The crucible rested on a four-point platinum base and was insulated around the sides so that heat could flow into the bottom of the melt but not through the sides of the plenum.

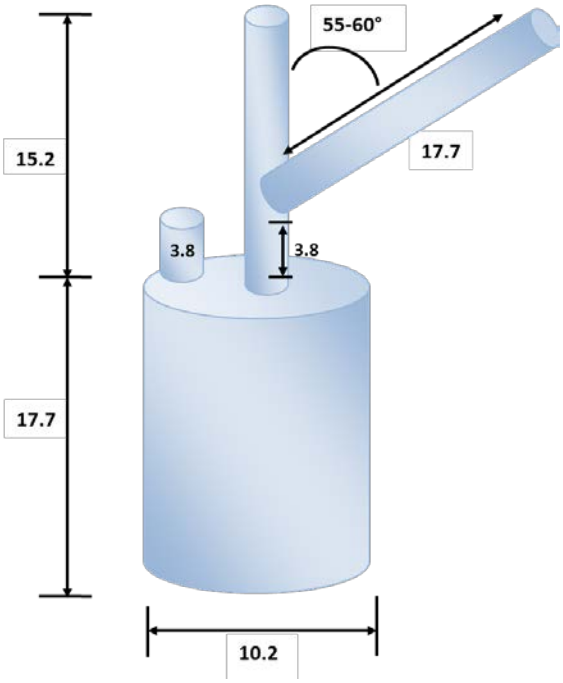

Fig. 2. Silica glass crucible used in the LSM runs.
All units are given in cm unless marked otherwise.

LSM Operation

To begin the LSM runs, the furnace was heated to 1200°C as monitored by an internal thermocouple. Water for the off-gas condensation column was cooled to 10°C in the Neslab RTE-211 Chiller. The thermocouples in the crucible were attached to a Fluke Hydra Data Bucket and set to record the temperature of the crucible at 20 s intervals. The angled off-gas port on the crucible was attached to the off-gas condensation column from which the off-gas lead to the exhaust port in a fume hood. The feed slurry was continuously stirred and pumped to fill the feed line with a Masterflex®[1] L/S Precision Pump attached to an injection nozzle that was cooled by the 10°C chiller water through an external Chrom Tech®[2] Flash pump.

After the base glass in the crucible melted and reached a plateau temperature between 1100°C and 1200°C as recorded by the melt-edge thermocouple, the feed pump was started at the appropriate charging rate and the nozzle was placed in the crucible. The run time began when the first drop of feed slurry hit the molten glass.

While the cold feed slurry was being charged into the crucible on top of the hot molten glass, the cold cap began to form, and the water from the slurry evaporated and exited the crucible through the off-gas line. Some of the feed turned to droplets that fell on the sides and top of the crucible, making it difficult to

[1] Masterflex is a registered trademark of Cole-Parmer Instrument Company
[2] Chrom Tech is a registered trademark of Chrom Tech, Inc.

observe the melt surface; a point was eventually reached at which the melt could no longer be seen, thus limiting the duration of the test.

The feed was charged for a run time of 35 minutes, which was enough time for the cold cap to reach a steady state and prior to the melt surface becoming unobservable. At the end of the run time, the feed pump was turned off, the crucible off-gas port was disconnected from the condensation column, and the crucible was removed from the furnace and quenched on a 15.2 cm diameter, 4.4 cm thick copper block. The temperature was recorded until the thermocouples read below 100°C. Thermal cracking began to occur around 500°C. Once the crucible reached room temperature, the A0 glass and cold cap were separated from the top portion of the crucible and the thermocouples were broken out of the glass melt.

RESULTS

Temperature Profiles

The temperature profiles for each LSM run are shown in Fig. 3. One thermocouple recorded the temperature of the glass melt near the crucible wall (solid line) and the other that of the cold cap (dashed line). Arrows denote the moments when the feed charging began and when the crucible was removed from the furnace.

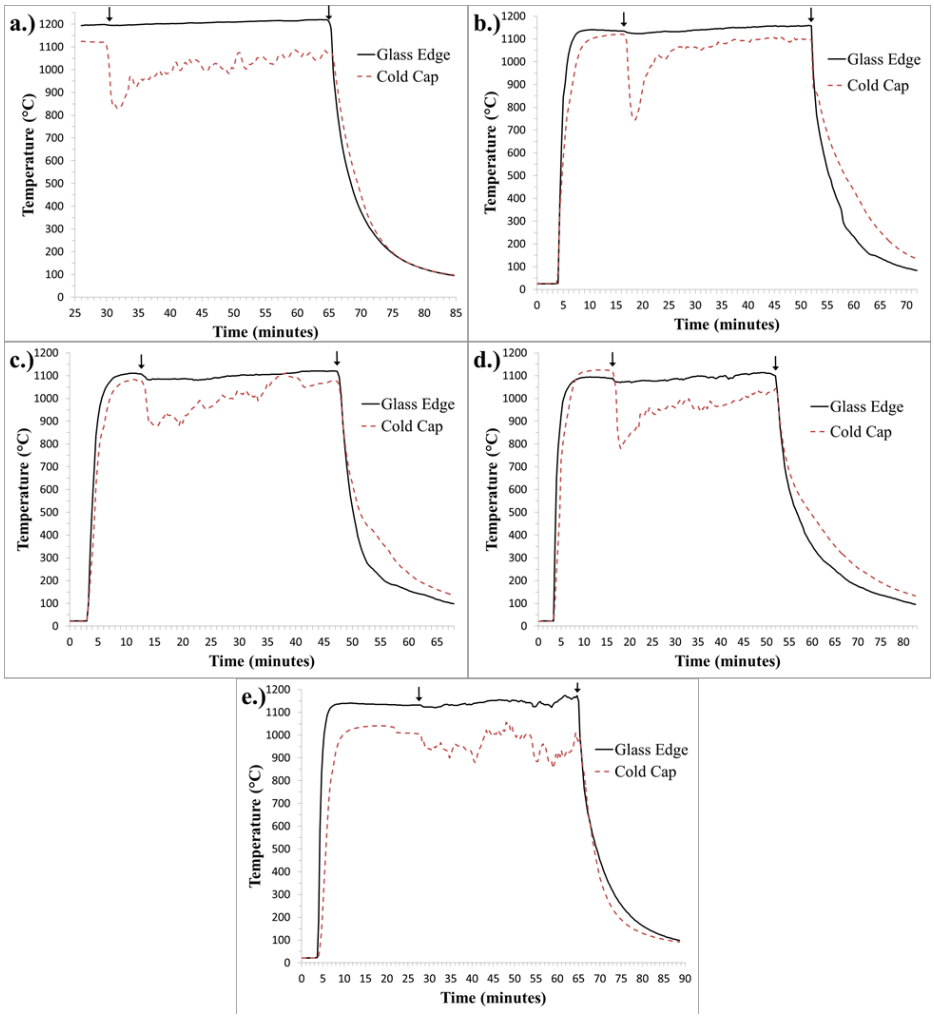

Fig. 3. Temperature Profiles for the runs at charging rates
a) 2.99, b) 4.03, c) 5.03, d) 6.03, e) 7.03 mL min^{-1}

Cold Cap Images

Photographs were taken with a Canon Rebel T1i camera of the side and top profiles of the glass and cold cap after quenching. The top profiles at each charging rate can be seen in Fig. 4 and the side profiles in Fig. 5. The 2.99, 5.03, and 6.03 mL min^{-1} melts broke into pieces upon being separated from the crucible and were fitted back together for the profile images. A small amount of unreacted feed was released onto the glass melt surface of the 4.03 mL min^{-1} run after charging had ended and the crucible had been removed from the furnace.

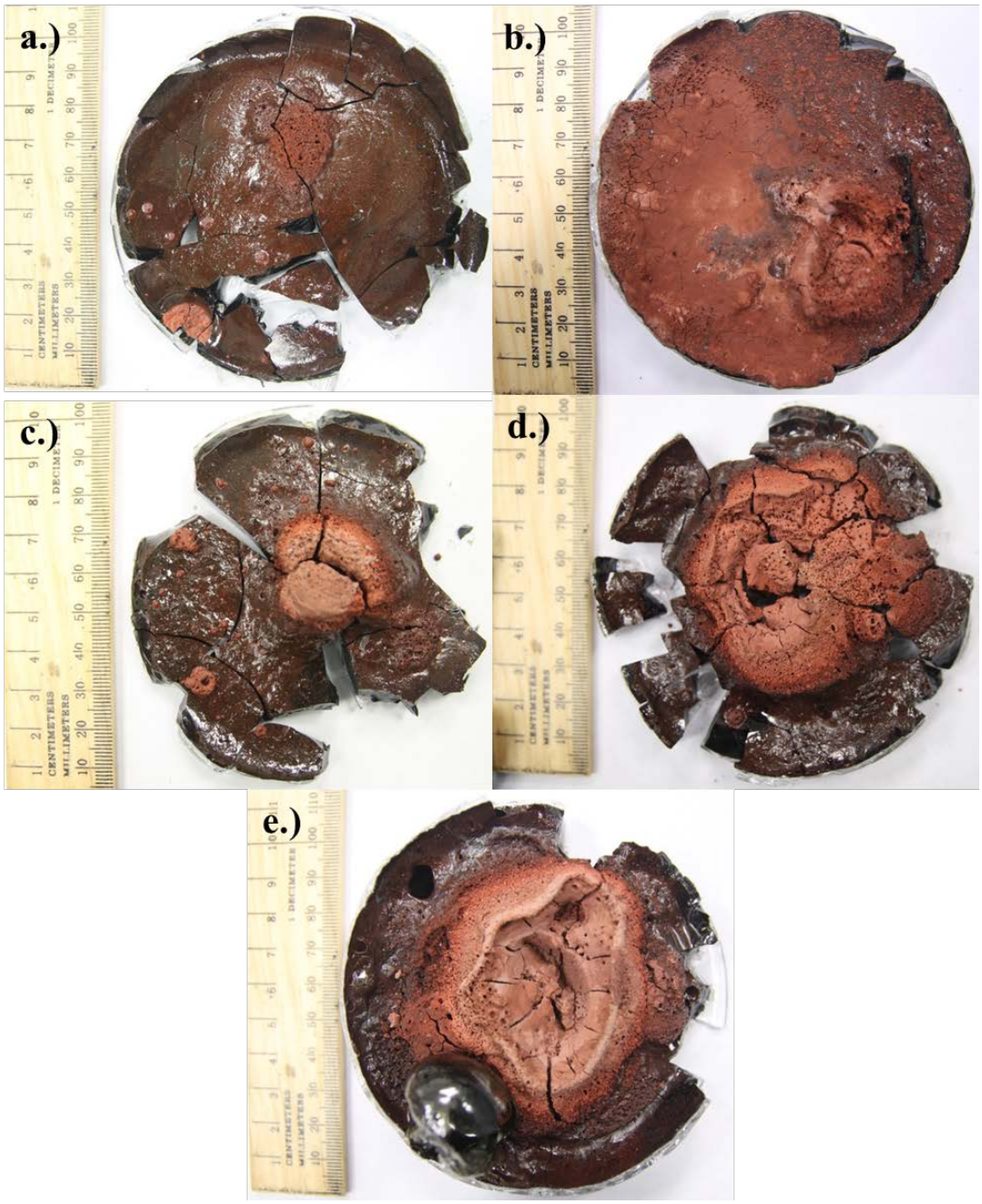

Fig. 4. Top view of the glass melts for the runs at charging rates
a) 2.99, b) 4.03, c) 5.03, d) 6.03, e) 7.03 mL min^{-1}

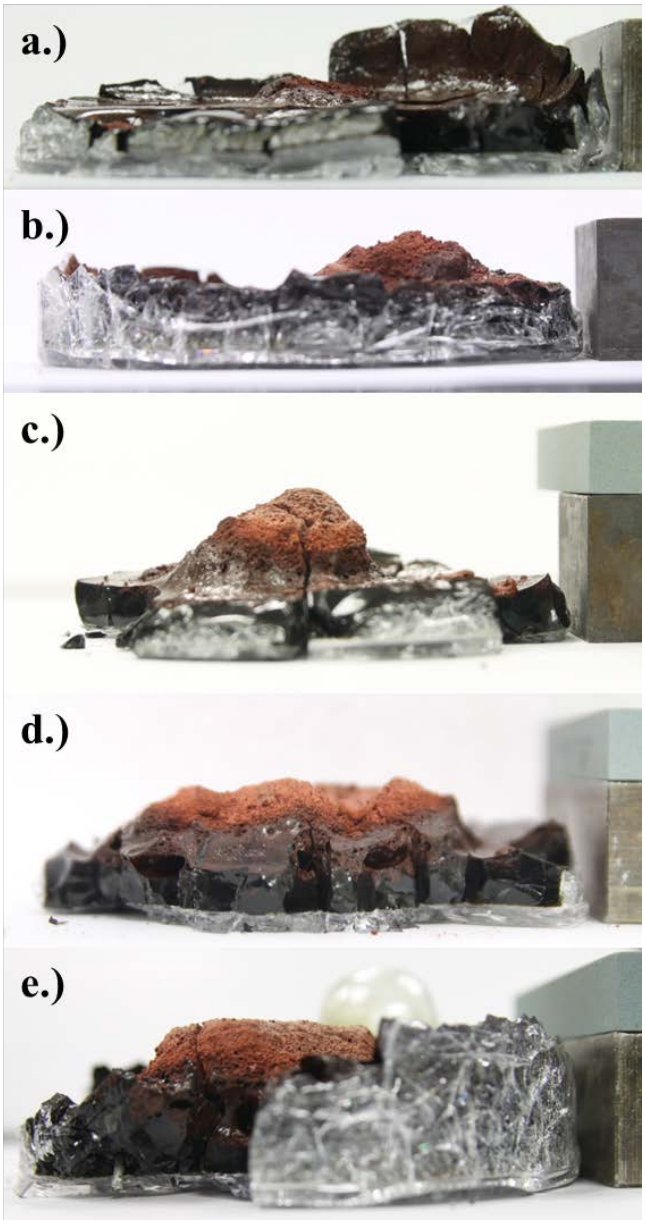

Fig. 5. Side view of the glass melts for the runs at charging rates a) 2.99, b) 4.03, c) 5.03, d) 6.03, e) 7.03 mL min^{-1}. The large measuring block was ~25 mm and the small measuring block ~12.5 mm in each of the profiles.

Microscope Images

The melts were broken by hand into smaller sections and imaged, as seen in Fig. 6, with an Olympus SZH10®[3] Research Stereo optical microscope with a Jenoptik ProgRes®[4] SpeedXT Core 5 camera. Three distinct layers can be observed in the sections: glass melt, foam layer, and the reacting feed.

[3] Olympus SZ is a registered trademark of Olympus Corporation
[4] ProGres is a registered trademark of Jenoptik Optical Systems GMBH

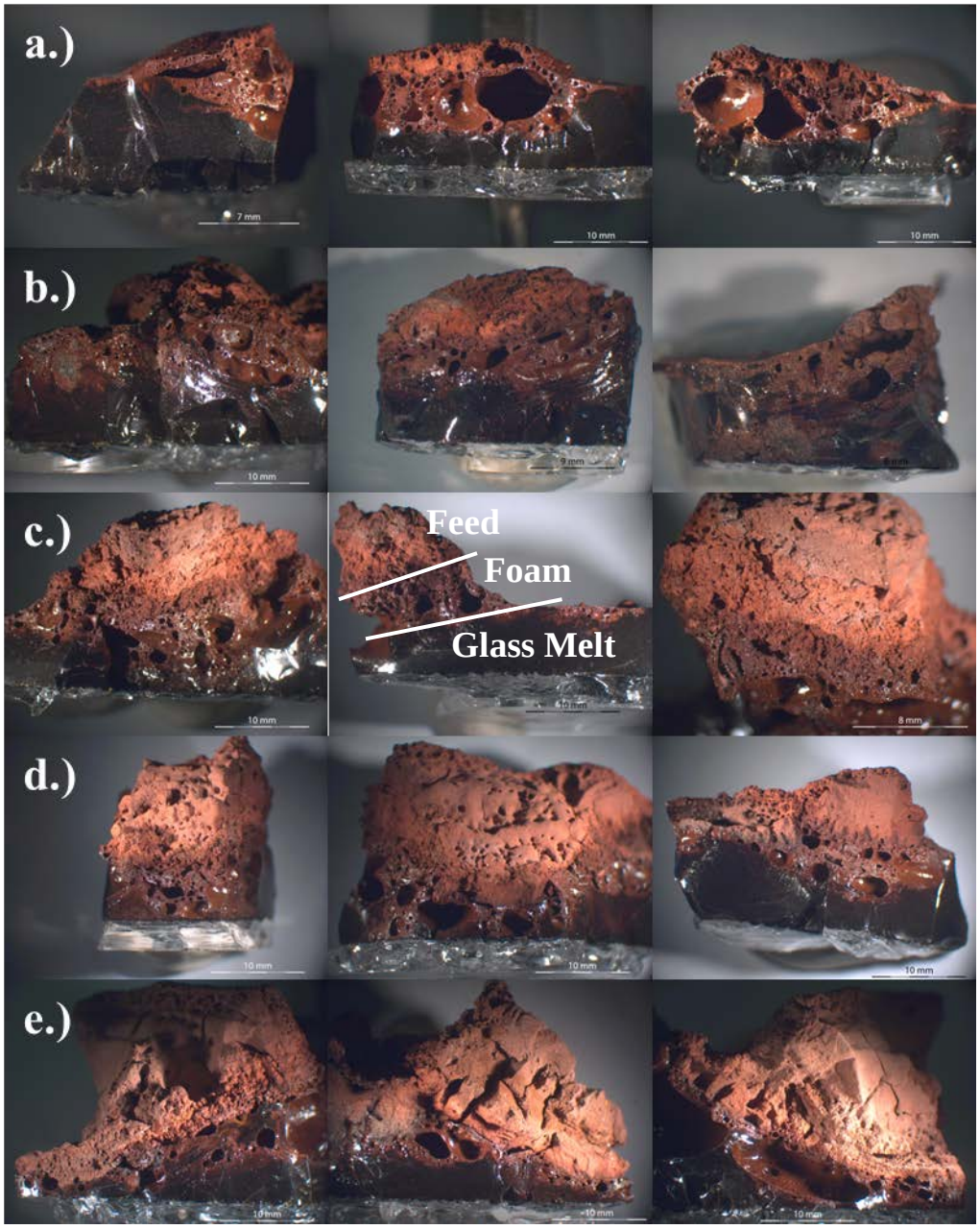

Fig. 6. Glass sections from tests at charging rates a) 2.99, b) 4.03, c) 5.03, d) 6.03, e) 7.03 mL min^{-1}. Each row contains images of three different fracture surfaces.

DISCUSSION

Table II shows the thickness of the melt/cold cap profiles measured with Adobe Photoshop[SM5] CS6 Extended software. Measurements of the cold caps were rough due to the irregularities in shape. The

[5] Photoshop is a registered service mark of Adobe Systems Incorporated.

height of the cold cap increased as the charging rate increased up to the 5.03 mL min^{-1} run and then decreased slightly. The area of the cold cap increased as the charging rate increased. Thus the total volume of the cold cap increased linearly with the increase in charging rate.

Table II. Cold Cap Dimensions

Charging Rate (mL min^{-1})	Cold Cap Height [a] (mm)	Area (mm^2)	Cold Cap Volume [a] (cm^3)
2.99	7.31	5.66×10^2	4.13
4.03	9.77	1.40×10^3	13.67
5.03	15.71	1.19×10^3	18.76
6.03	14.06	4.15×10^3	58.37
7.03	16.67	4.25×10^3	70.88

a) Measurement taken from top of unreacted feed to bottom of foam layer.

The time-temperature histories at the different charging rates (Fig. 3) show a large drop in the temperature at the center of the glass melt when feed charging began. The temperature at the center fluctuated as the feed was charged and gases evolved. At the edge of the glass melt, however, the temperature remained constant except for the run at 7.03 mL min^{-1} when the cold cap became large enough to approach the thermocouple.

The images of cold cap sections (Fig. 6) show the reacting feed, foam, and glass melt layers in each run. Unreacted feed eventually reached near the bottom of the crucible regardless of the charging rate, though there was on average more unreacted feed present within the melt at the three higher rates. The foam layers consisted of small bubbles (0.1–0.5 mm) and larger cavities (3–8 mm). At the higher charging rates, however, the foam layer appeared to be thicker. Small shafts were also observed in the reacting feed for gases to vent through the cold cap. The temperature gradient within the cold cap was evident from the lighter red color at the top compared with the darker brown color near the glass melt. Given the temperature/color gradient, it was observed that the cold cap was present at higher temperatures for the two lower charging rates, indicating that the cold cap was more reacted in those cases. The cold cap sections will be compared with previous studies to quantitatively determine the temperature within the cold cap and the relationship between temperature and the bubble size distribution for inclusion in the mathematical model.

SUMMARY AND CONCLUSIONS

Cold cap and foam formation of HLW feed were investigated in the LSM with a silica glass crucible. The effect of the charging rate was determined at rates varying from ~3 to ~7 mL min^{-1}. The temperatures at the center and edge of the melt were recorded during the runs. Images of the side and top profiles were taken of the quenched cold caps. As the flow rate increased, the height of the cold cap increased up to a point when the area began to increase and the height changed little. The cold cap volume increased nearly linearly with the increase in charging rate, though the cold cap appeared to be further reacted and present at higher temperatures during the two lower rates. The melt temperature under the cold cap fluctuated during charging as large bubbles were passing by the thermocouple, while the melt temperature at the edge remained constant as long as the cold cap did not reach the thermocouple. The foam layer contained small bubbles and larger cavities regardless of the charging rate. Sections of the cold cap will be used for the analysis of bubble and cavity size distribution and then compared with previous studies to determine the effect of temperature on the foam and reacting feed.

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