Enhancement of DWPF Melt Rate Model (WP 4.2.3)

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Objective: **Develop a predictive tool for the impact of feed chemistry on relative melt rate of HLW glasses.**

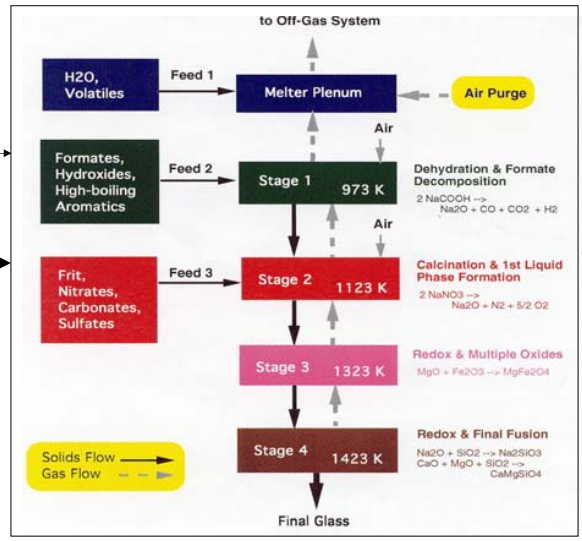
Methodology:

Premise:
The more negative the total free energies of melt and/or calcine gases are, the higher the melt rate is.

4-Stage DWPF Cold Cap Model

Feed Chemistry → **Input**

NIST Free Energy Database for Complex Liquids



Output → Phase Equilibria & Speciation of Melt, Intermediate Condensed Phases, Calcine Gases and Their Free Energies

→ Free energy output is re-arranged into various functional groups based on literature data on aluminoborosilicate glass structural units

Melt Rate Furnace (MRF) Experiments

→ Visual Reading of Relative Melt Rates (Old)

→ X-Ray Imaging & Computed Tomography (CT) Analysis (New)

→ Derive an empirical correlation of relative melt rates using free energy functional groups.

$$MRI = \left(\frac{R'}{K}\right)_{frit} \frac{\Delta G_{f,m}(sludge\ Na-Al-B)^{0.9} \cdot \Delta G_{f,m}(frit\ Na-Al-B)^{0.1} \cdot \Delta G_{f,m}(S)^{0.2}}{\Delta G_{f,m}(Al+B) \cdot \Delta G_{f,cg}}$$

$$where\ R' = ([Na_2O] + 0.7[Li_2O] - [Al_2O_3])/[B_2O_3]$$

$$K = [SiO_2]/[B_2O_3]$$

→ Existing **Melt Rate Indicator (MRI)**

* Calibrated using visual melt rate data only within limited compositional ranges.

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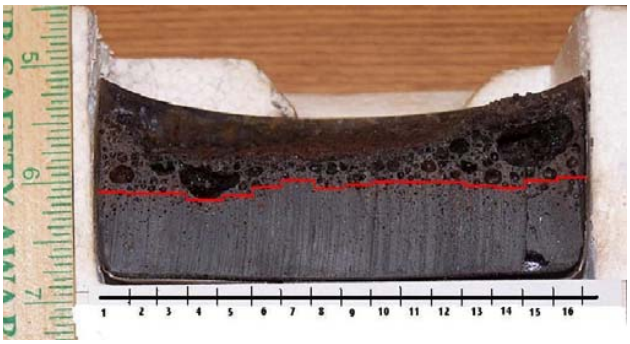
FY10 Scope:
- Generate CT melt rate data by conducting MRF tests over wider compositional ranges.
- Partition ΔG_f of total boron into 3- and 4-coordinated boron terms – spectroscopic studies.
- Improve thermodynamic database – import Associated Species data for borates.
- Re-calibrate MRI using both visual and CT melt rate data.

Visual Determination of Melt Rate:

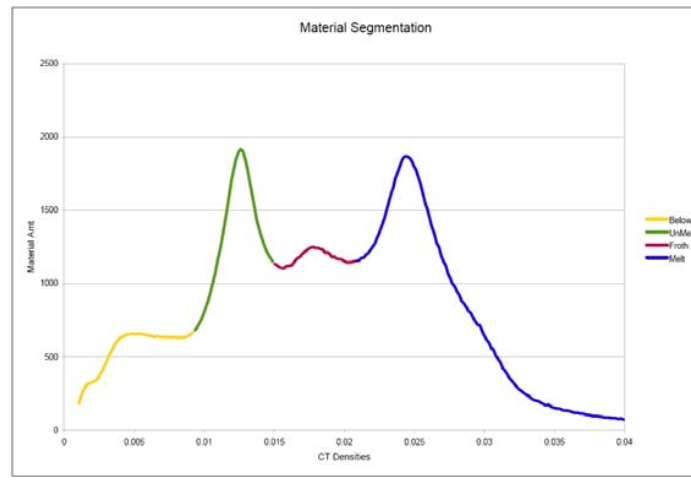


Methodology: The SS beaker is sectioned along its diameter and the glass height is measured for each of the 16 vertical segments up to the red lines where relatively large-sized bubbles begin to appear. Melt rate is determined as the average of all 16 glass height readings (in/hr).

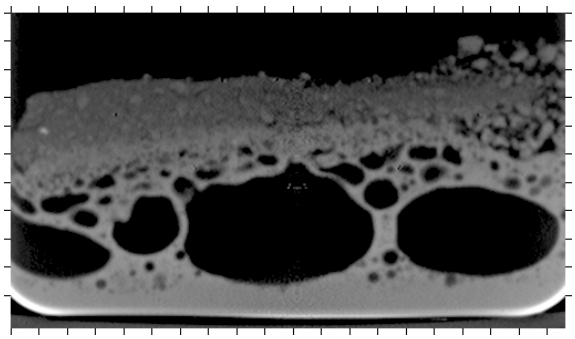
Issues:
- Glassy material interspersed among the bubbles above the red lines is excluded.
- Varying degrees of softening occurs even in the "seemingly-unmelted" layer at the top.
- There is no guarantee that a particular sectioned plane is representative of the entire sample volume (see orthogonal RGB plots below).
- The resolution of resulting data is not high enough to discern relatively small compositional effects.
- The subjectivity in drawing the red lines influences results.

Computed Tomography (CT) Analysis of Melt Rate:

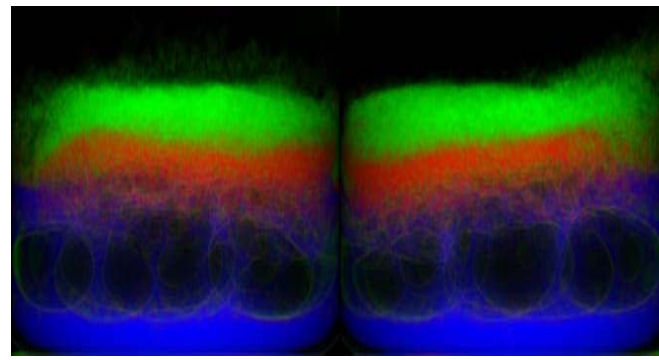
- The entire sample in a 2" diameter beaker is partitioned into ~200 horizontal slices; each slice 0.15 mm thick is scanned 360º with X-ray and voids larger than 0.15 mm is excluded.
- Radiographic attenuation is proportional to material density; the higher density → the greater CT intensity.
- There are four regions from the most to least dense:
  - **Melt**: Fully melted glass with little or no gas bubbles
  - **Froth**: Melted material interspersed among bubbles
  - **Unmelt**: Feed material which has softened somewhat or not melted at all.
  - **Below**: Material of very low but non-zero density arising from voids of gas or artifacts of radiography (x-ray beam-hardening, shadowing, etc).
- The histogram of material vs. CT intensity is integrated over a given intensity interval to determine the amount of material in each layer.
- The ratio of total material in the melt, froth and unmelt layers to the sum of their volumes is called the overall densification factor, which is a measure of the degree of compaction.



Melt, Froth, Unmelt, and Below Regions Based on CT Histogram



X-ray image of Sample SB6-CEF5 at 36% WL



Orthogonal RGB Plots of SB6-CEF5; Melt (Blue), Froth (Red), Unmelt (Green)

Note:
- RGB plots show that the **melt** layer extends above large voids
- The interface between the **melt** and **froth** layers is diffusive; they overlap.
- CT histogram shows that the **unmelt** layer covers a range of CT intensities.

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An Example of Melt Rate Comparisons: SB6 simulant coupled with 12 different frits at 36% WL

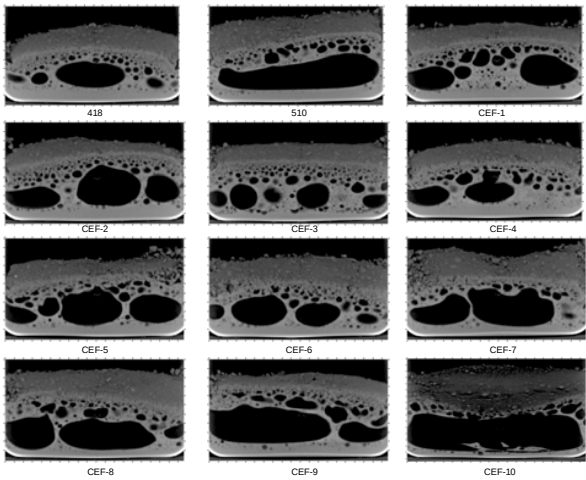
Frit	418	510	CEF-1	CEF-2	CEF-3	CEF-4	CEF-5	CEF-6	CEF-7	CEF-8	CEF-9	CEF-10
B_2O_3	8	14	11	11	11	8	8	8	8	8	8	16
CaO	0	0	0	0	0	0	0	0	2	2	2	0
Li_2O	8	8	8	8	9	8	8	8	8	8	8	8
MnO	0	0	0	2	4	1	2	4	1	2	4	0
Na_2O	8	8	8	6	5	8	7	6	7	6	6	4
SiO_2	76	70	73	73	71	75	75	74	74	74	72	72
Total	100	100	100	100	100	100	100	100	100	100	100	100

64%

36%

SB6 Oxides	measured (wt%)	normalized (wt%)
Fe2O3	27.0218	29.1825
Al2O3	29.9505	32.3454
MnO	7.6441	8.2553
CaO	1.3271	1.4332
MgO	0.7526	0.8128
P2O5	0	0
NiO	3.2318	3.4902
Cr2O3	0	0
CuO	0.2266	0.2447
TiO2	0.0234	0.0253
SiO2	0.3006	0.3246
Na2O	20.7589	22.4188
ZnO	0	0
K2O	0.0843	0.0910
Ce2O3		0
SrO	0.0579	0.0625
BaO	0	0
PbO	0	0
La2O3	0	0
ZrO2	0.2924	0.3158
SO3	0.924	0.9979
Total	92.5959	100.0001

Fusion

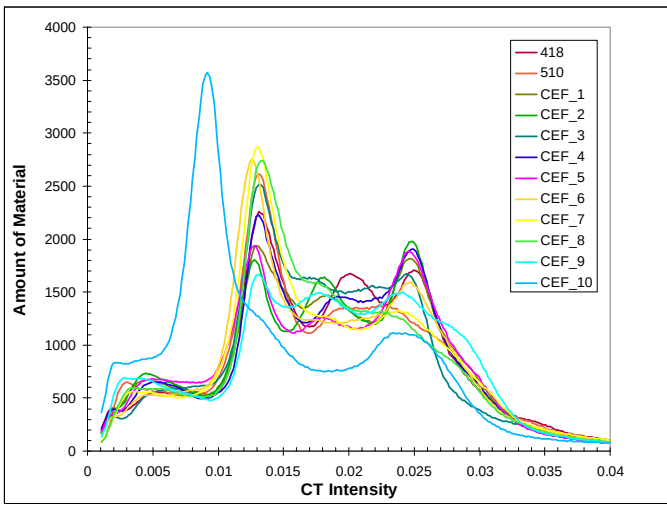


X-ray image of 12 SB6 Glass Samples at 36% WL

Visual

Ranking	Visual	CT
1	CEF-4	CEF-9
2	418	CEF-4
3	510	CEF-2
4	CEF-2	CEF-1
5	CEF-9	418
6	CEF-1	CEF-5
7	CEF-6	510
8	CEF-5	CEF-3
9	CEF-3	CEF-8
10	CEF-7	CEF-7
11	CEF-8	CEF-6
12	CEF-10	CEF-10

CT



Comparison of CT Results for 12 SB6 Glass Samples at 36% WL

Note:
- **CT method ranks CEF-9 glass first, which has the least unmelt material; Frit CEF-9 has 4% MnO and 2% CaO added at the expense of SiO_2 and Na_2O, respectively, compared to 418.**
- **Visual method ranks CEF-4 glass first, which has 1% MnO added at the expense of SiO_2; however, CEF-4 glass has more unmelt material than CEF-9.**
- **CT method ranks CEF-2 and CEF-1 higher than 418; both have 3% higher B_2O_3 than 418, while CEF-2 also has 2% MnO added at the expense of Na_2O.**

Path Forward:

1. **Expand the CT melt rate database by running additional MRF runs over wider compositional ranges of B, Al, alkali, and additives.**
2. **Repeat the Source-of-Alkali (SOA) MRF runs to confirm the bell-shaped melt rate vs. SOA profile obtained using the visual method.**
3. **Further expand the thermodynamic database to include additional melt and intermediate species, particularly the borates.**
4. **Reflect the boron partitioning between 3- and 4-coordinated states, as shown by the spectroscopy study, in defining functional groups.**
5. **Run 4-stage cold cap model using expanded database and re-compute functional groups.**
6. **Calibrate the MRI using CT database for quantitative relative melt rate rankings.**