

Aspects of Cold Cap Melting

12th ESG 2014

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23 September 2014

Hanford Tank Waste Treatment and Immobilization Plant



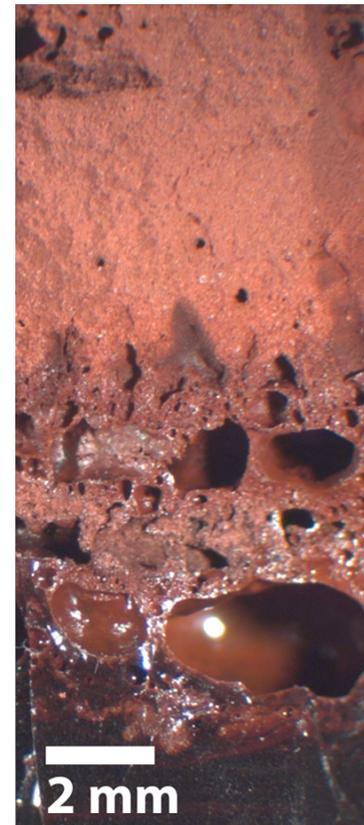
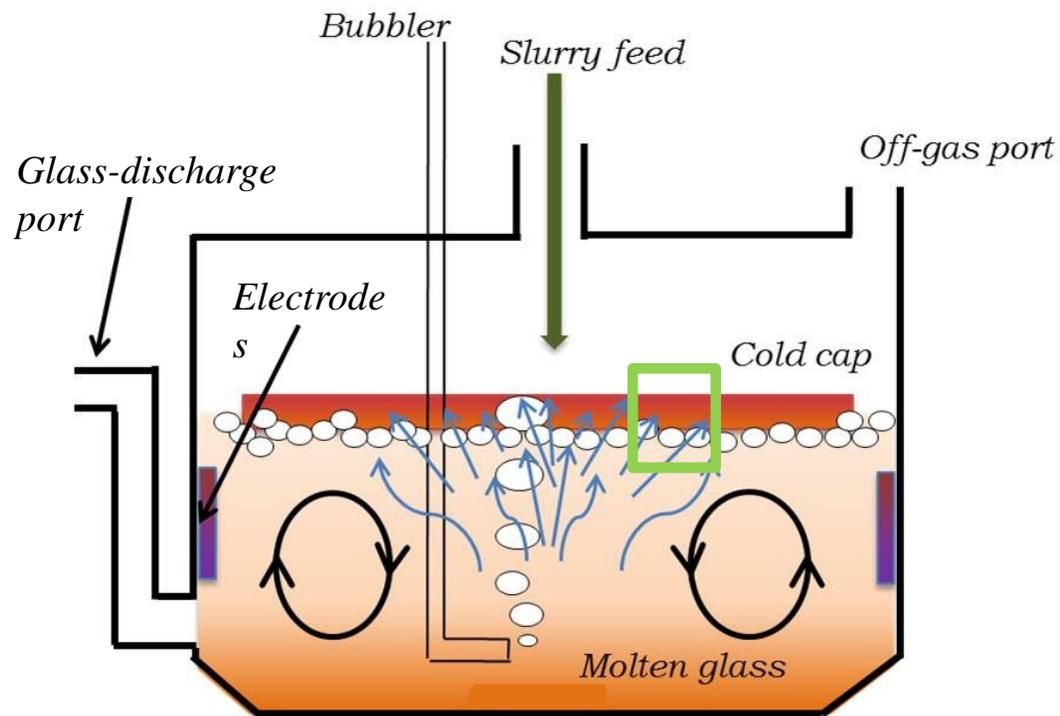
200,000 m³ of radioactive waste from plutonium production: 1943 – 1987

Outline

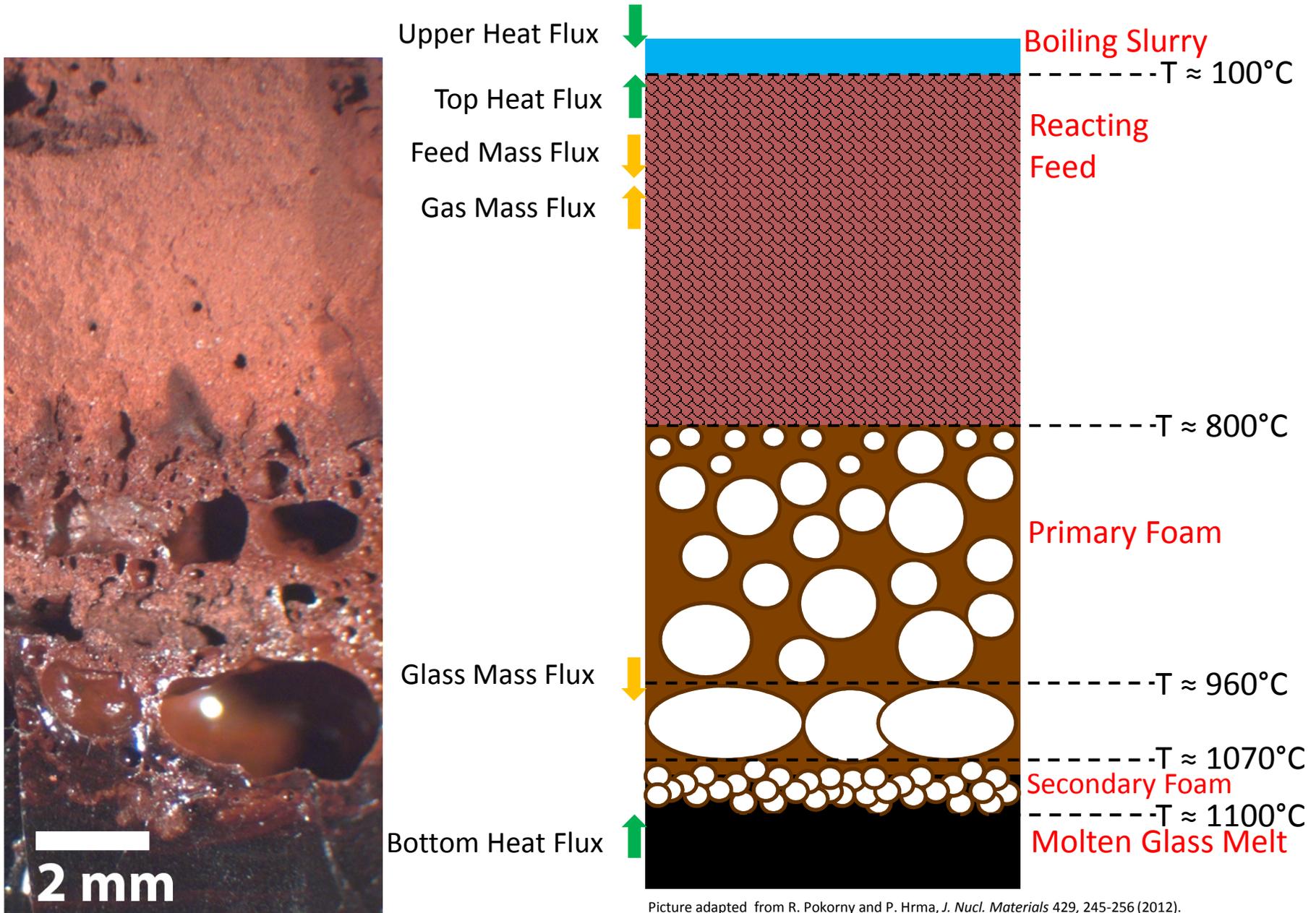
- Glass-melting furnace (melter) and cold cap (batch blanket)
- Melter feed conversion to molten glass
- Mathematical modelling
- Data for modelling:
 - Gas generation kinetics: thermal and evolved gas analyses
 - Effective heat capacity: differential scanning calorimetry
 - Density and porosity
 - Heat conductivity
 - Viscosity
 - Crystalline phases: XRD and SEM-EDS
- Model results: Cold cap temperature profile, glass production rate
- Cold cap produced in laboratory
- Bubbling

Glass melting

- Nuclear waste will be vitrified in all-electric (Joule-heated) melters.
- Glass-formers are mixed with the waste and charged into melters operating at 1150°C.
- Melter feed (the slurry batch) forms a **cold cap** floating on molten glass.



Melter feed conversion to molten glass



Picture adapted from R. Pokorny and P. Hrma, *J. Nucl. Materials* 429, 245-256 (2012).

Mathematical model: Mass and energy balance

$$\frac{d\rho_b}{dt} + \frac{d(\rho_b v_b)}{dx} = r_b \quad r_g + r_b = 0$$

$$\rho_b c_b \frac{dT}{dt} = (j_b c_b^{Eff} - j_g c_g) \frac{dT}{dx} - \lambda^{Eff} \frac{d^2 T}{dx^2}$$

ρ is the spatial density

v is the velocity

r is the mass change rate (via chemical reactions)

c is the heat capacity

cb^{Eff} is the effective heat capacity (includes reaction heat)

x is the spatial coordinate (vertical position)

t is the time

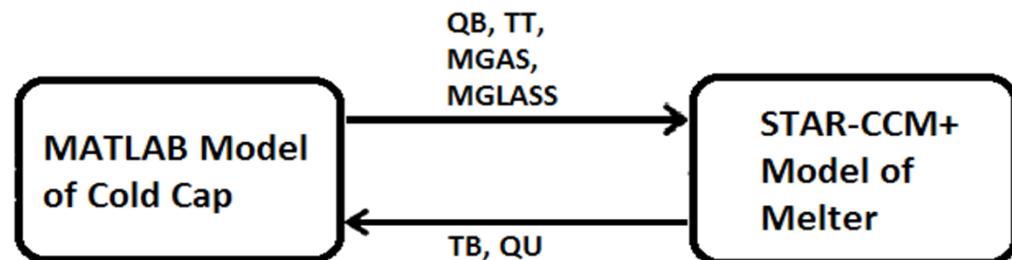
j is the mass flux

subscripts

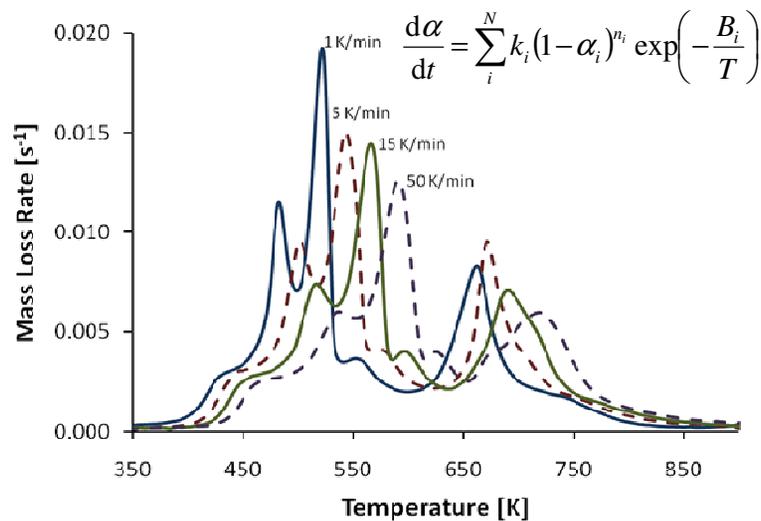
b and g denote the condensed phase and the gas phase

1. Cold cap gas phase and condensed phases (solids, molten salts, glass-forming melt) move vertically (1D model).
2. Condensed phases (solids, molten salts, glass-forming melt) move with the same velocity.
3. Finite volume method is simple, efficient and adequate to problem

Coupling cold cap model with melter model

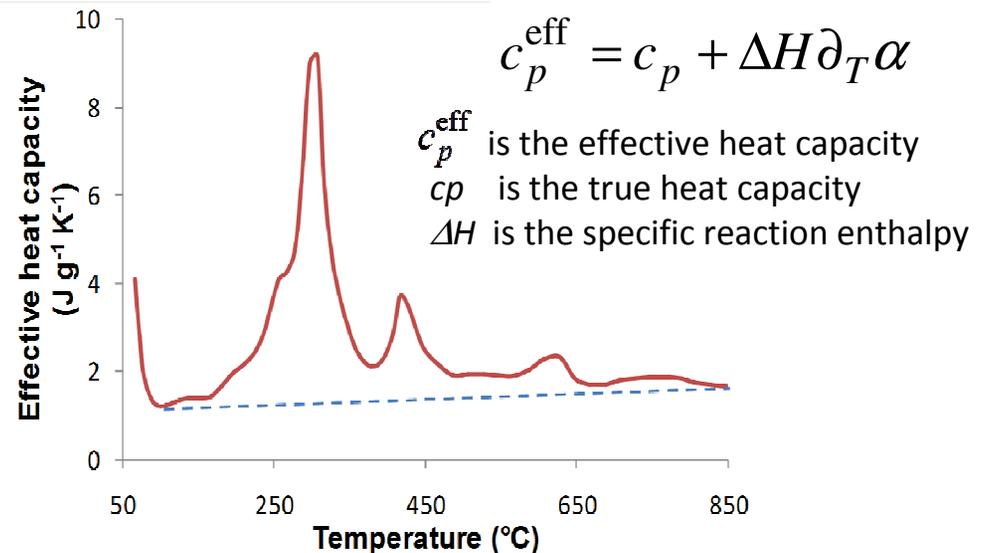
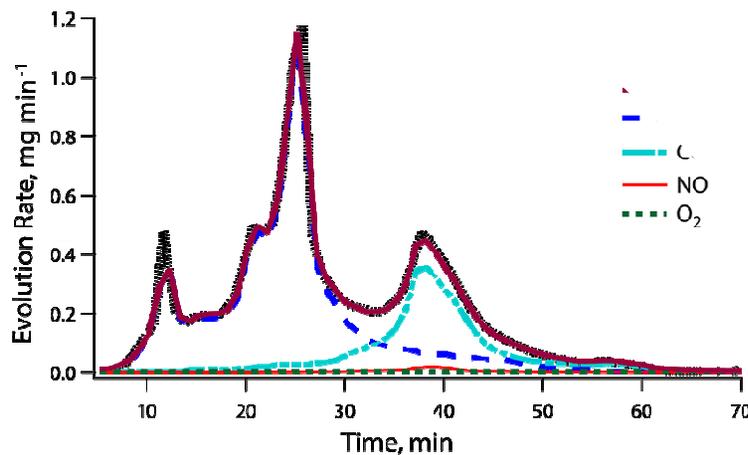


Reaction kinetics– TGA, EGA, and DSC

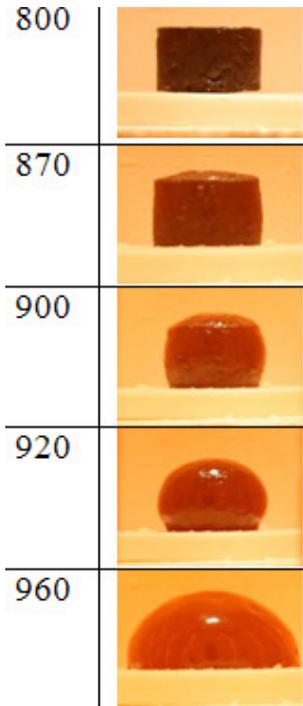


Reaction rates from thermogravimetric analysis (TGA), evolved gas analysis (EGA), and differential scanning calorimetry (DSC)

- The n^{th} -order reaction kinetics satisfactorily describes most of the melting reactions
- EGA can be calibrated for quantitative analysis

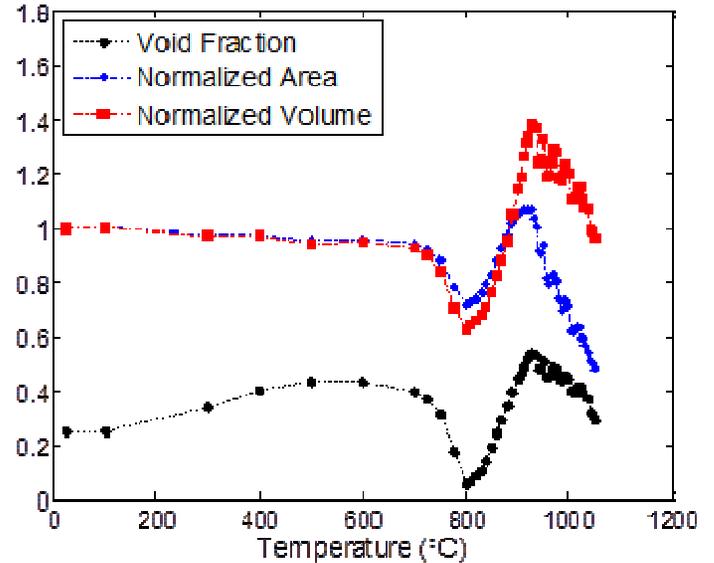


Feed density and foaming

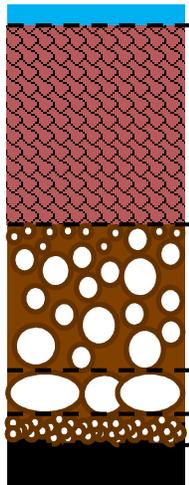
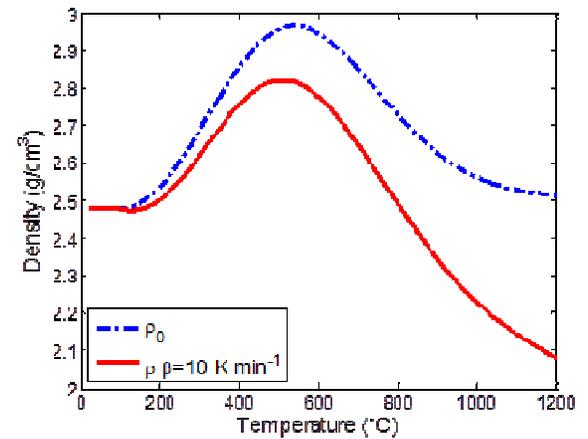


“Foaming curves” are obtained from feed expansion experiments. Feed pellets are photographed and their profile area is measured. Pellet volume, density, and void fraction (porosity, ρ) is then computed.

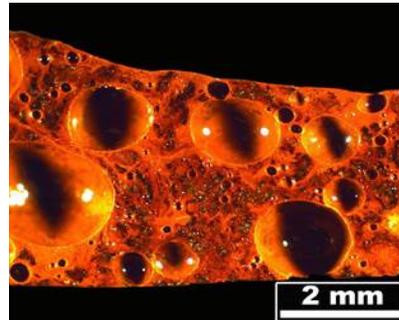
$$\rho = \frac{\rho_b}{\rho_m} \quad \begin{array}{l} \rho_b \text{ bulk density} \\ \rho_m \text{ material density} \end{array}$$



Below: Effect of heat-treatment temperature, T , on ρ_m : sample quenched from T to room-temperature and sample heated to T at 10 K min^{-1} (computed)



The rate of the feed-to-glass conversion (the rate of melting) is controlled by the heat delivered to the cold cap across the foam layer and from the plenum space.

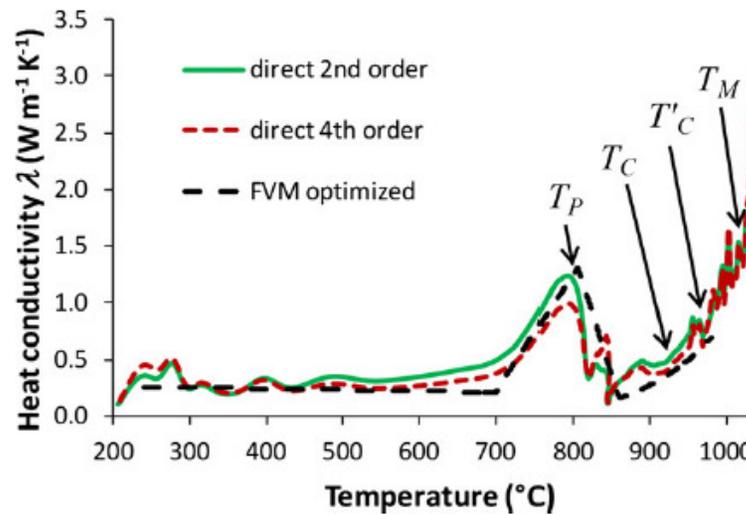
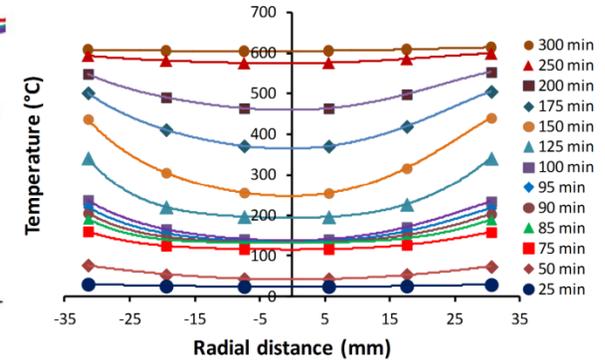
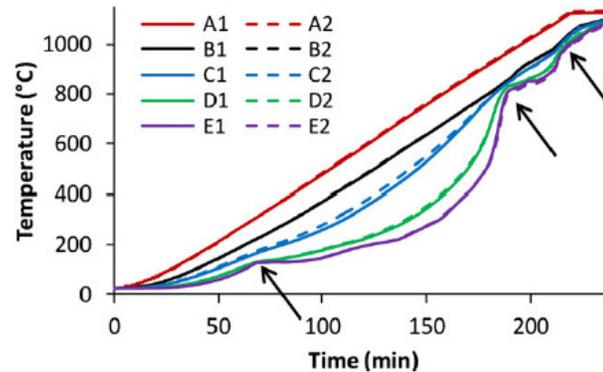
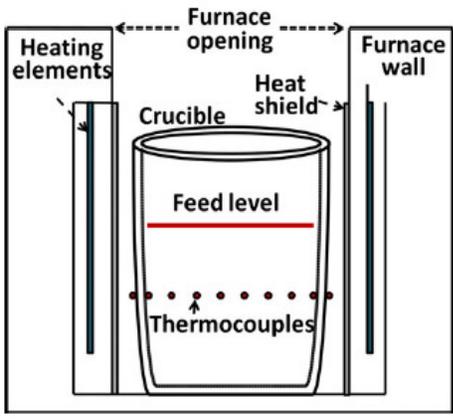


Triple foam layer occurs under the cold cap:

- primary foam (from trapped batch gases)
- gas cavities (moving sideways)
- secondary foam (from rising bubbles)

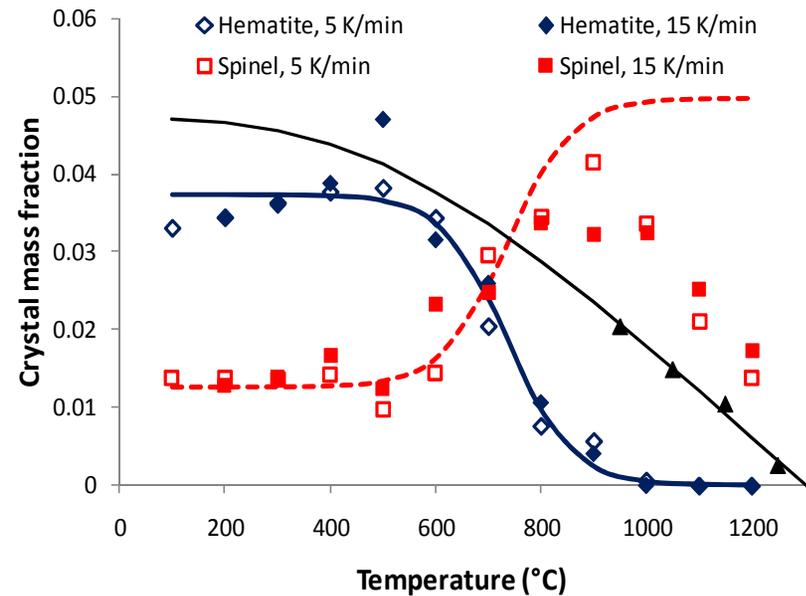
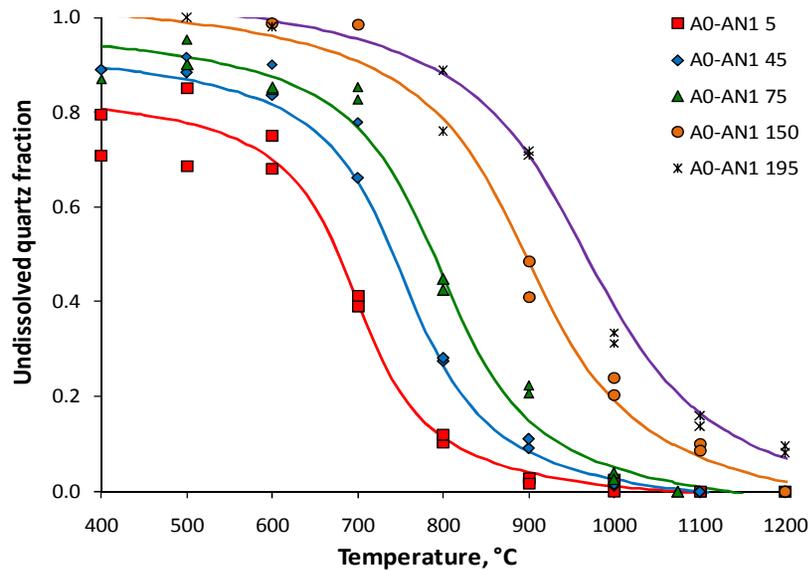
Heat conductivity

- Heat conductivity, λ^{Eff} , estimated from crucible experiments



The glass-forming melt became connected at T_P . Foam evolved between T_P and T_C and collapsed at $T > T_C$.

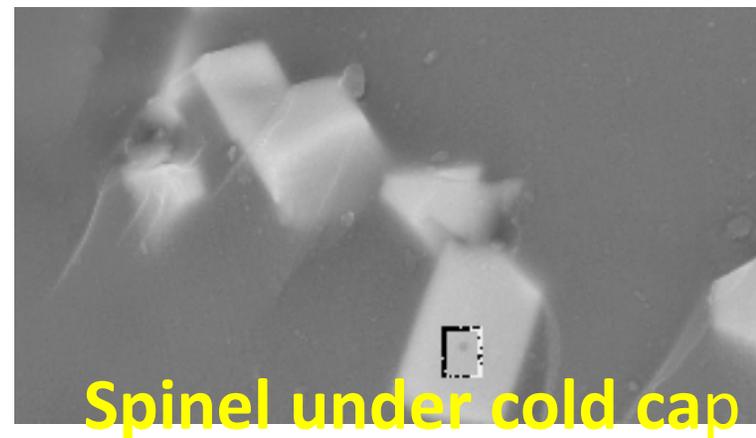
Quartz dissolution and spinel formation



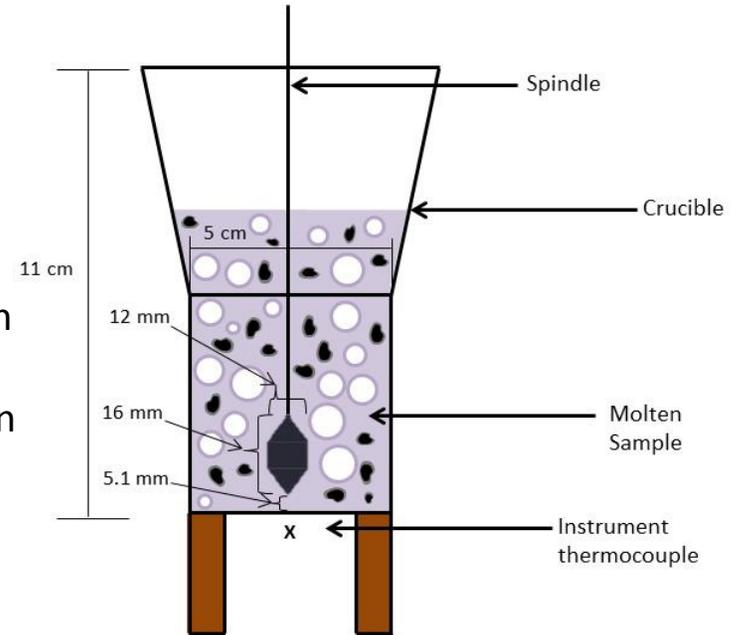
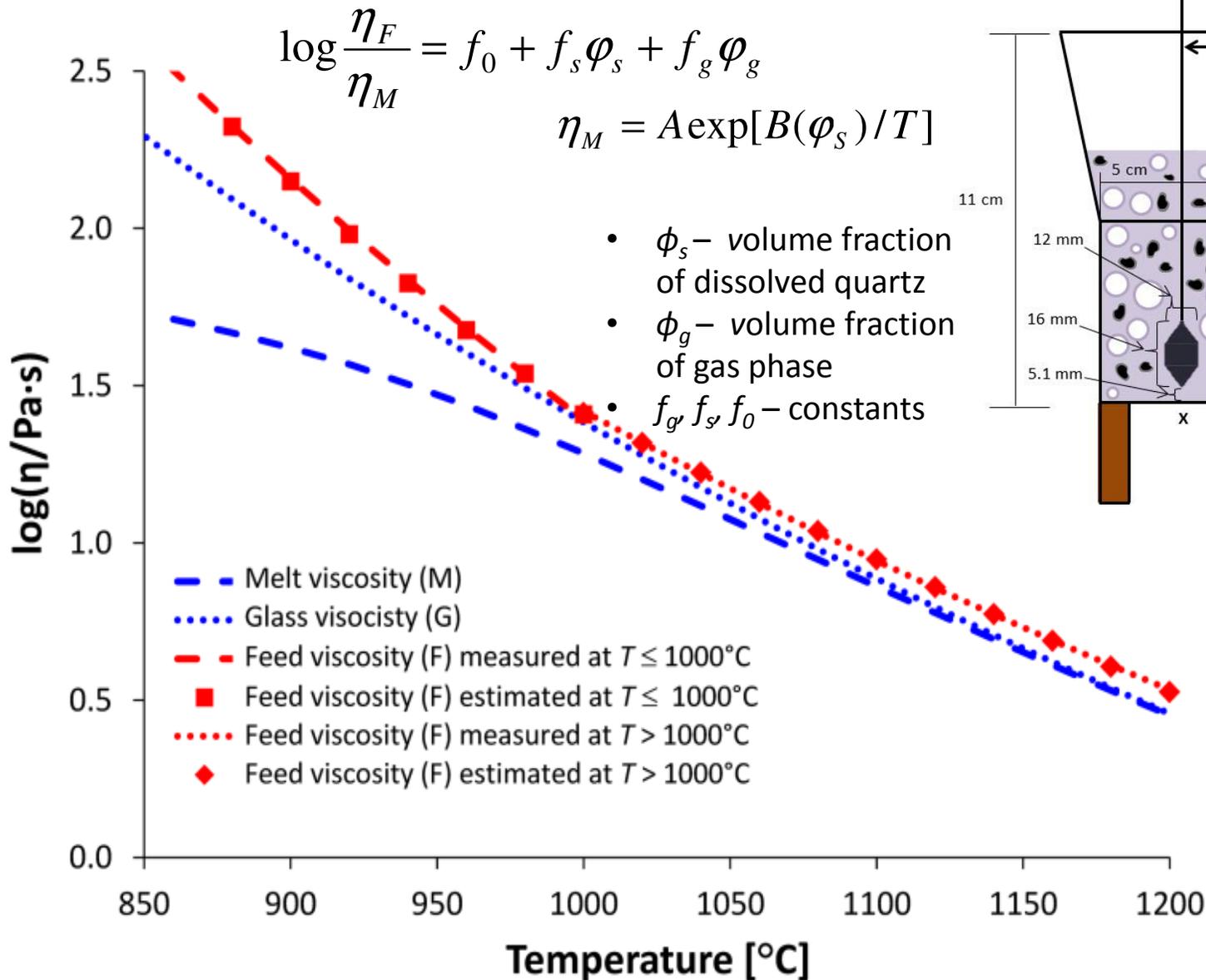
The legend indicates that the average particle sizes

Quartz dissolution can be represented as n^{th} -order process:

$$\frac{dx}{dt} = A(1-c)^n \exp\left(-\frac{B}{T}\right)$$

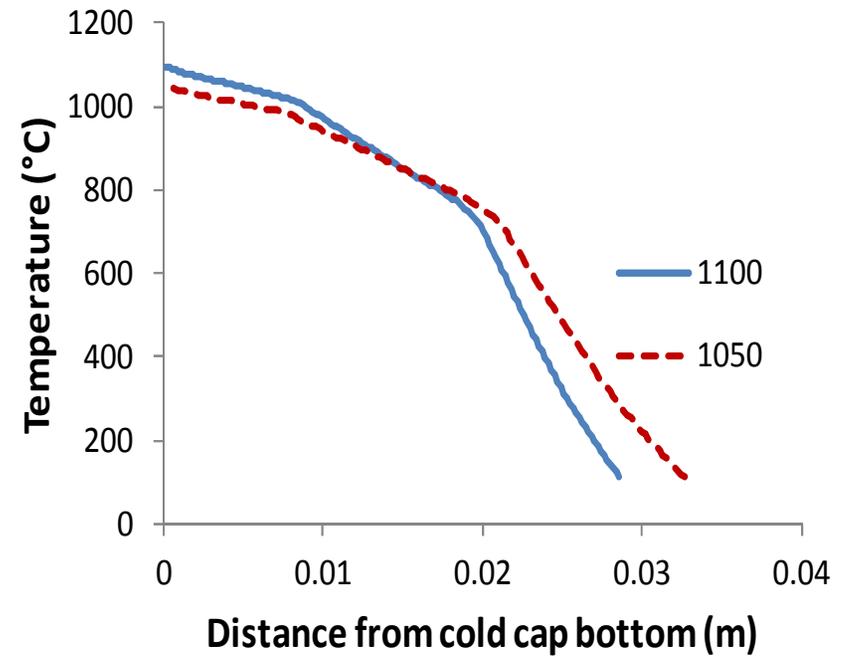
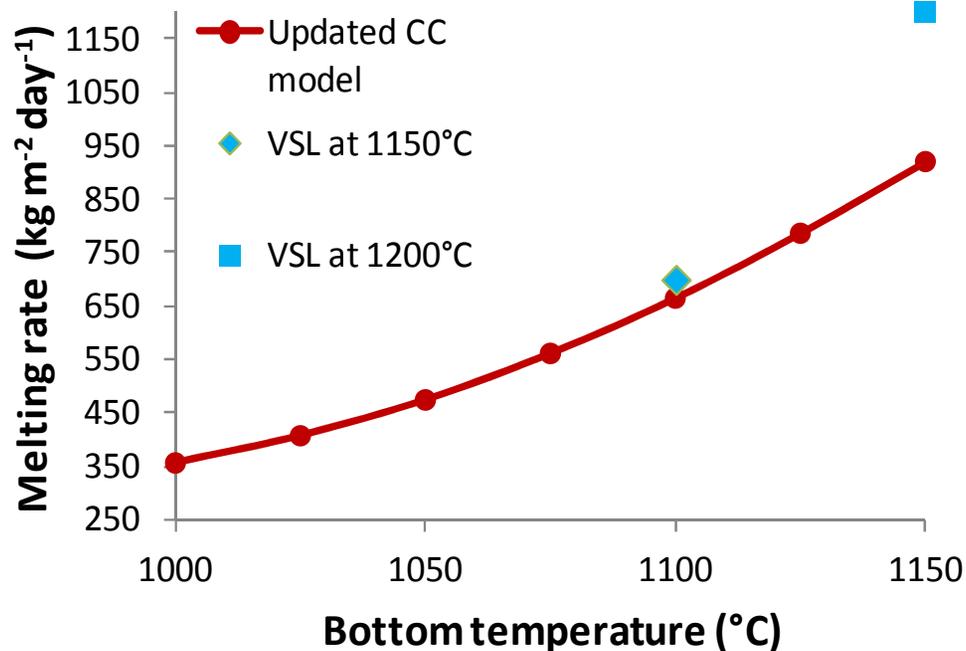


Transient glass-forming phase viscosity



Model results

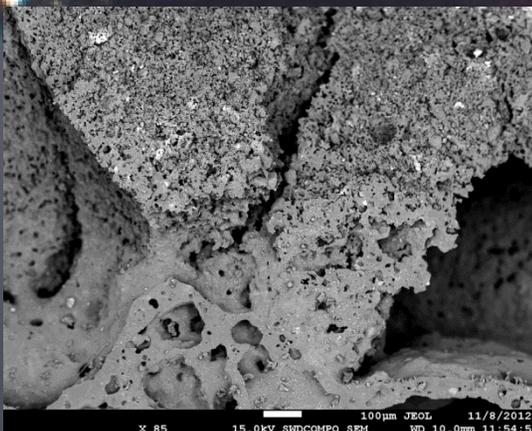
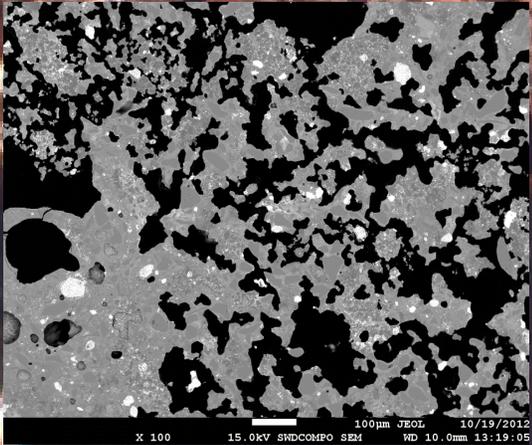
Melting rate versus cold cap bottom temperature
No fitting coefficients were used.
Blue points represent melter data reported by the Vitreous State Laboratory (VSL).



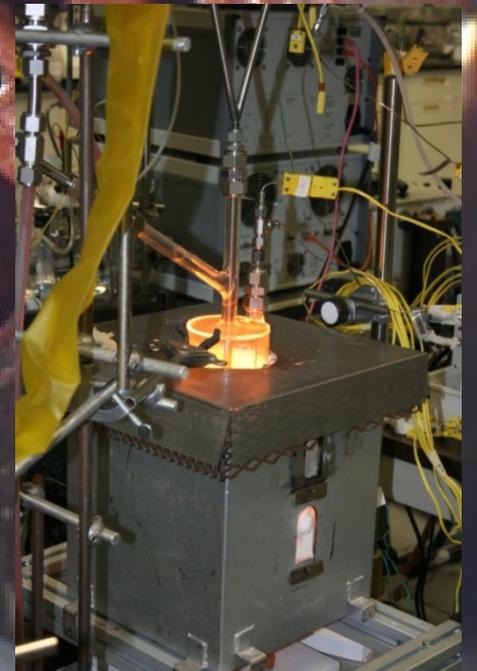
Cold cap temperature distribution for two bottom temperatures

Laboratory scale melter (LSM)

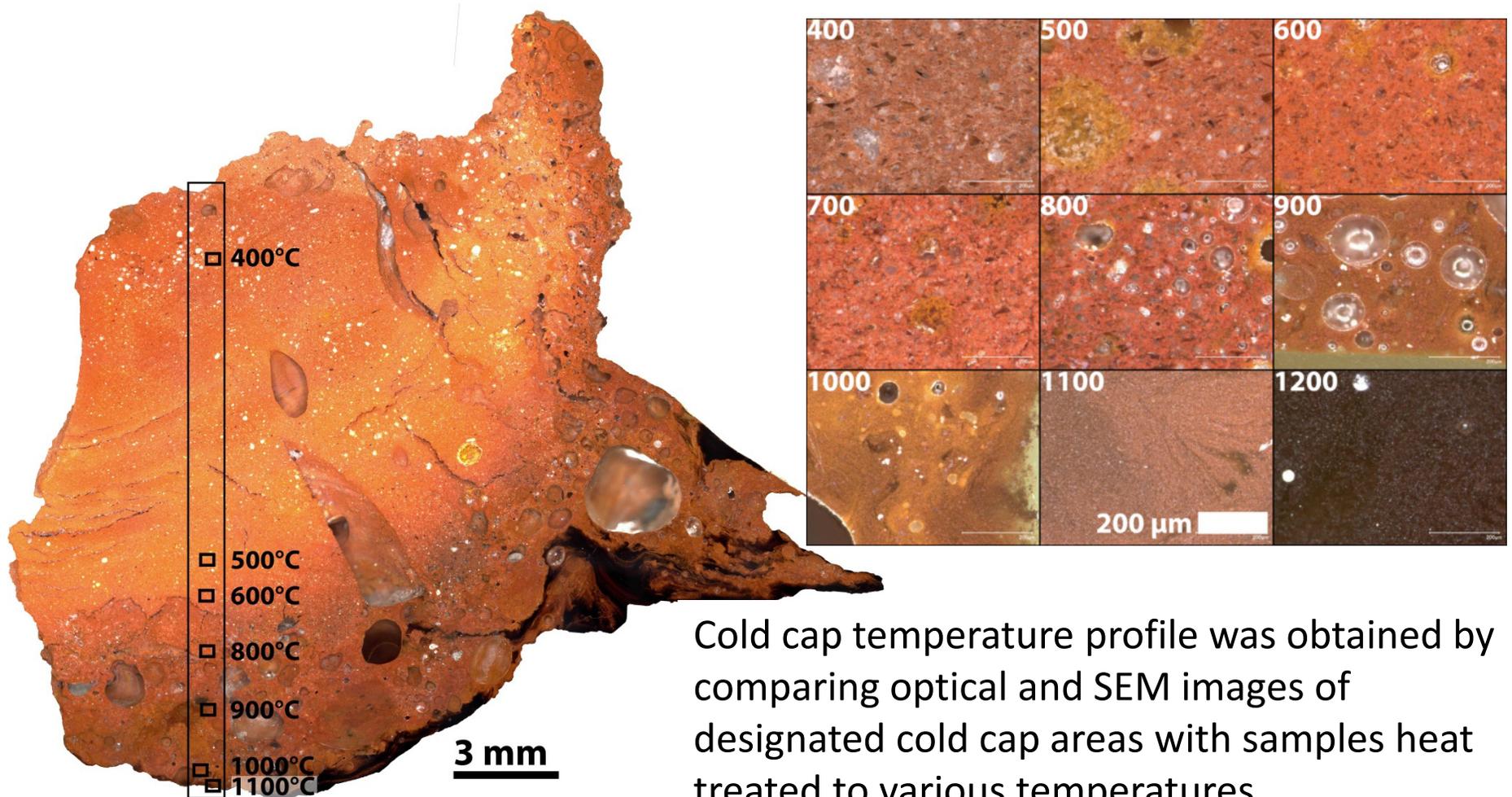
Fracture through cold cap



- Reacting feed with open pores
- Transition between reacting layer and foaming layer

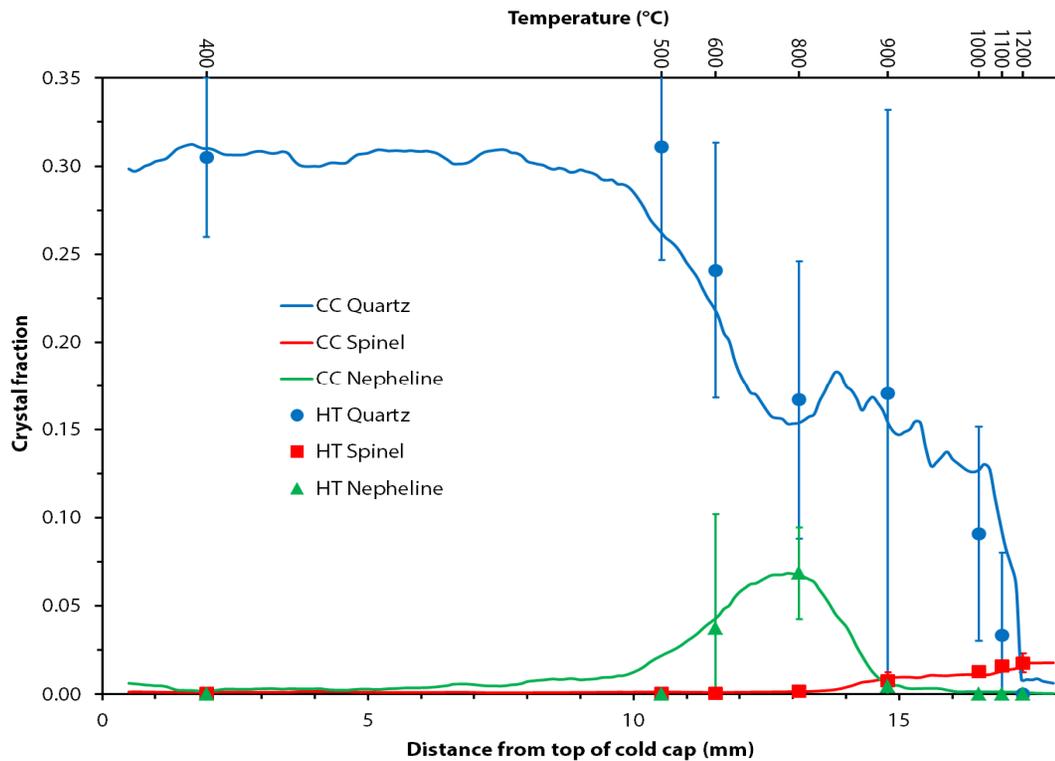


LSM cold cap temperature profile

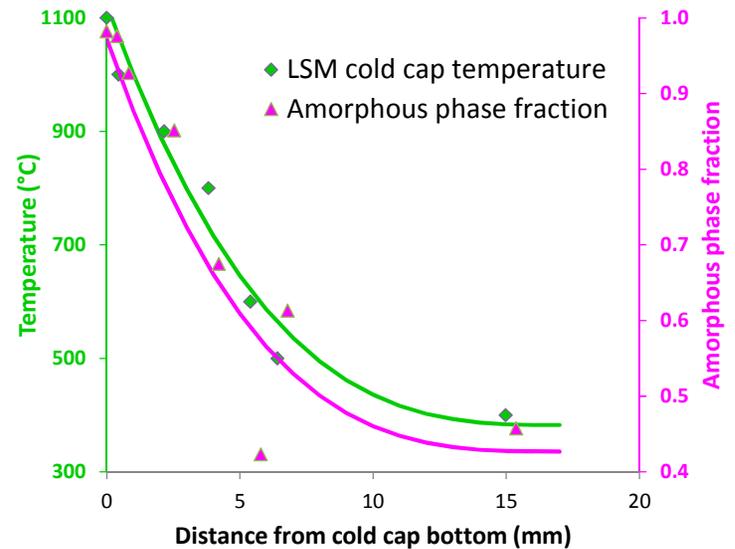


Cold cap temperature profile was obtained by comparing optical and SEM images of designated cold cap areas with samples heat treated to various temperatures. Additional check was performed by comparing micro-XRD data of the cold cap with XRD of heat-treated samples.

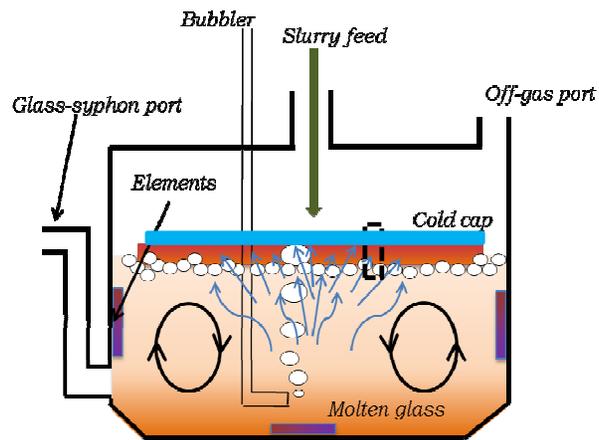
Temperature, crystallinity, and amorphous phase distribution in LSM cold cap



Left: micro-XRD of the LSM cold cap compared with XRD of heat-treated samples.
 Below: Temperature and amorphous phase distribution in the LSM cold cap.



Effect of bubbling on melting rate

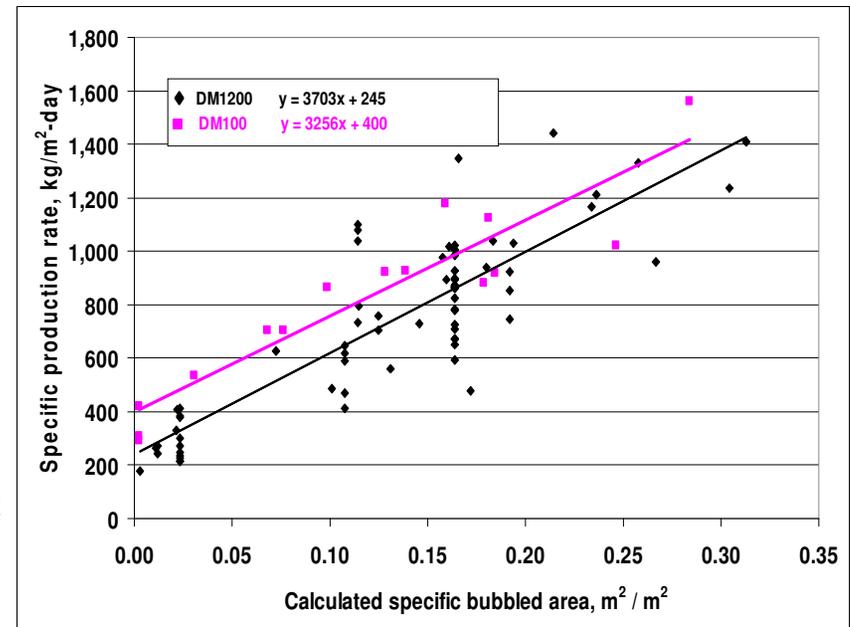


Bubbling outlets	Production rate kg/m ² /day
4	1060
5	1290
6	1400

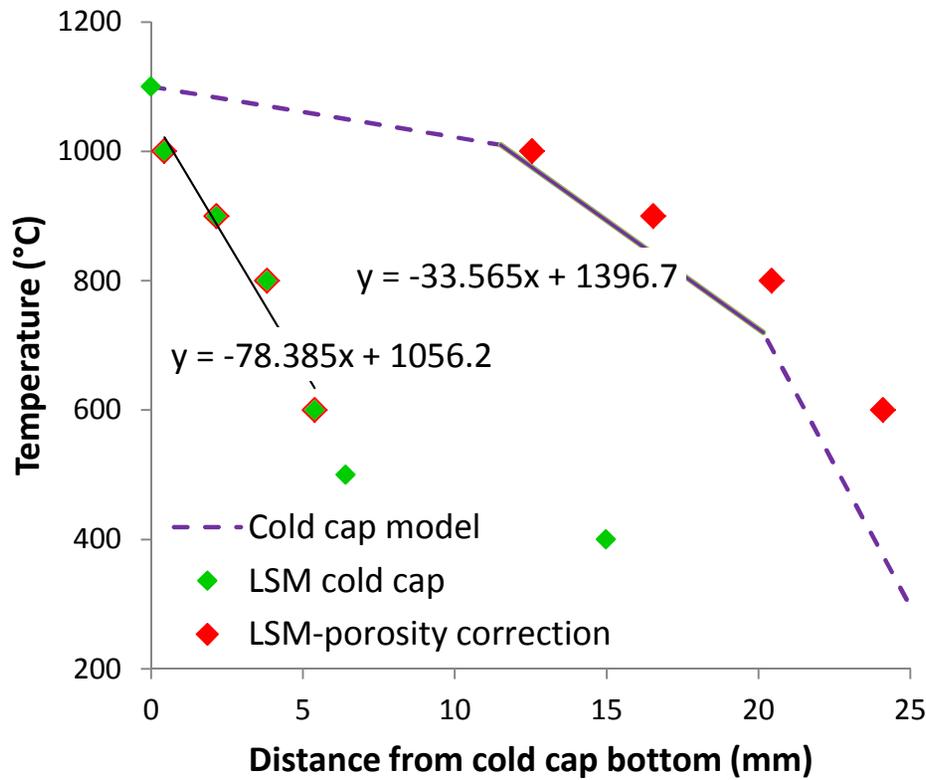
Energy Solution melter test data

No bubbling:
300-500 kg/m²/day

1. Bubbling generates forced convection in the molten glass
 - velocity gradients become steeper
 - thermal boundary layer is suppressed
 - cold cap bottom temperature rises
2. Bubbles from bubblers sweep the secondary foam formed under the cold cap into vent holes.
3. Feed is stirred into the melt at the edges of vent holes, exposing a fraction of the feed to high temperature.



LSM-model comparison of temperature profiles



Red points: LSM data shifted by secondary foam and cavity thickness; the slope was adjusted assuming that the unquenched sample had 57% porosity (primary foam).

Important difference: The top surface of the LSM cold cap was dry (400°C), whereas the model surface was wet (100°C).