Conversion degree and heat transfer in the cold cap and their effect on glass production rate in an electric melter

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Background

- The nuclear waste stored in underground tanks at Hanford site will by vitrified in electric melters and stored in steel canisters.
- One of the potential bottlenecks for processing rate of WTP is the feed-to-glass conversion rate.

Hanford

Electric melters

Waste Treatment and Immobilization Plant (WTP)

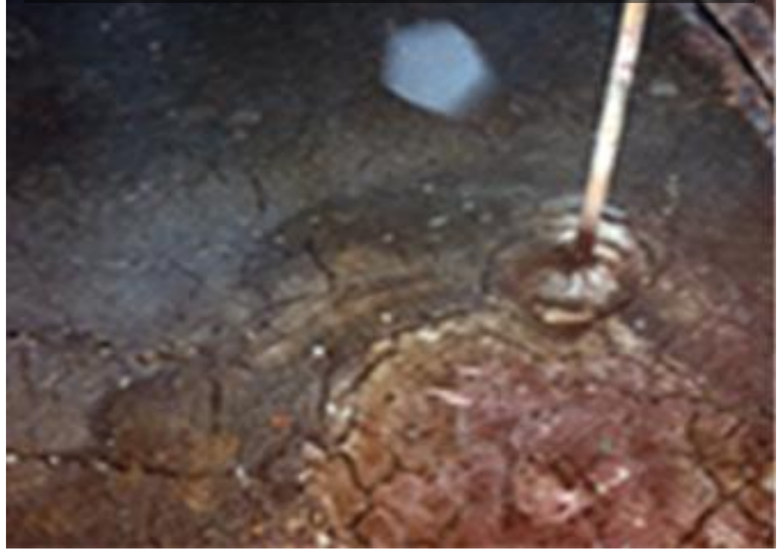
hanford.gov

Nuclear Waste Feeds

- Nuclear waste was created as a byproduct of plutonium production
- Contains about 60 chemical elements
- Mixed with glass formers, other additives
- Converted to glass in vitrification melters
- Waste composition in tanks is greatly variable
- Thousands of glass compositions will be produced
- Impossible to test every composition
- Laboratory tests are mostly performed on non-radioactive simulants
- Composition-property models were developed to ensure that glass is processable, chemically durable, and contains as much waste as possible to minimize the product volume

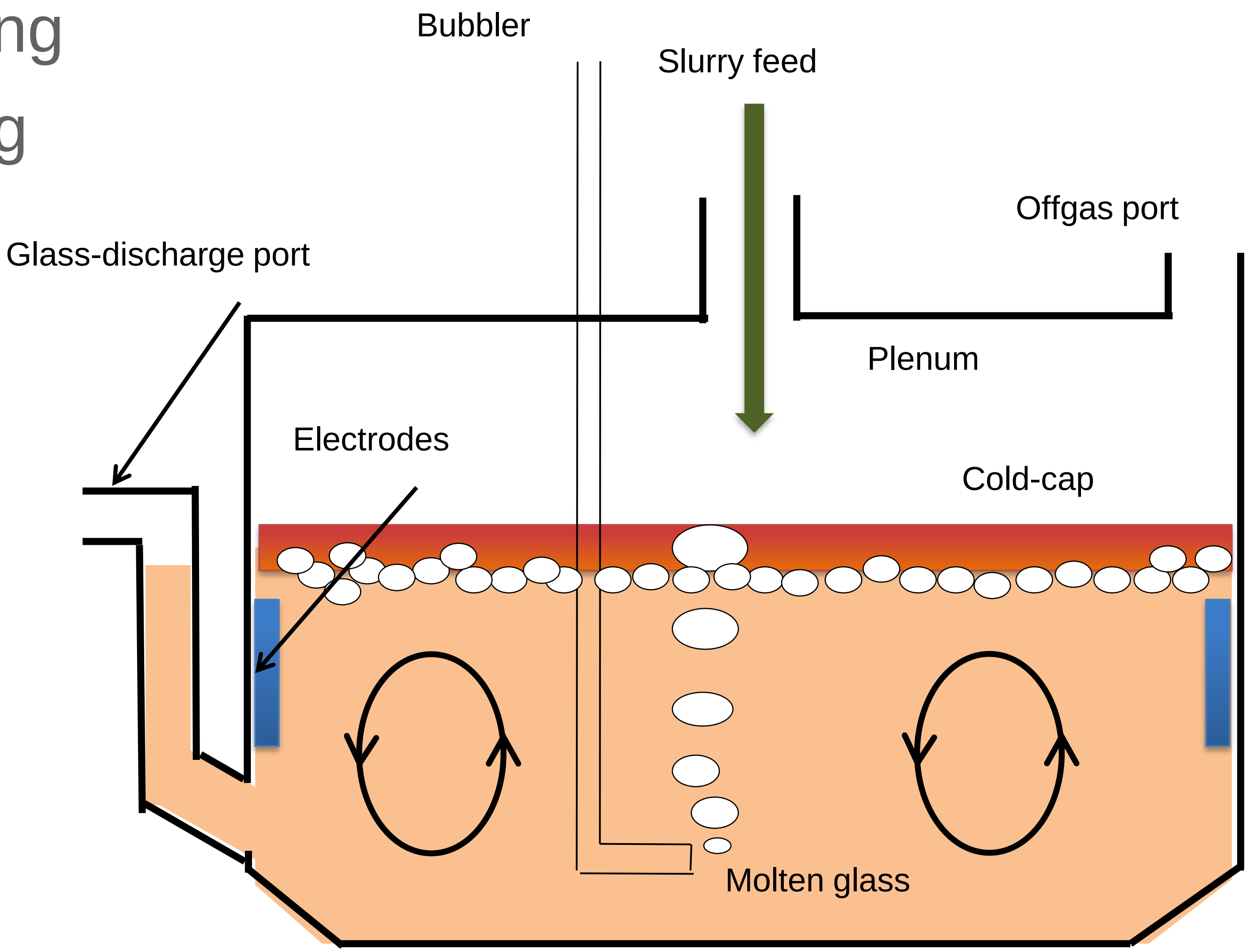
Crystallized saltcake in single-shell tank 105-B

Water insoluble sludge

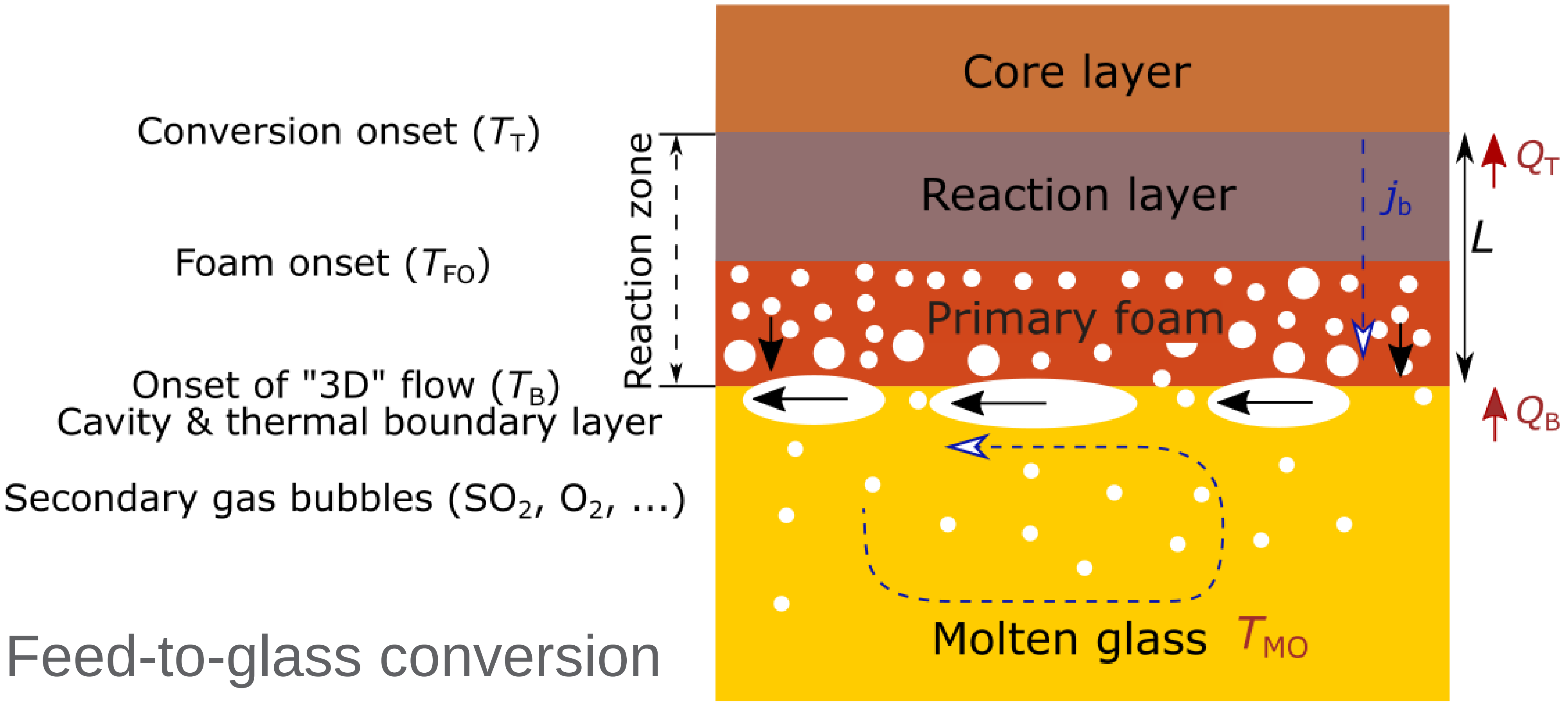


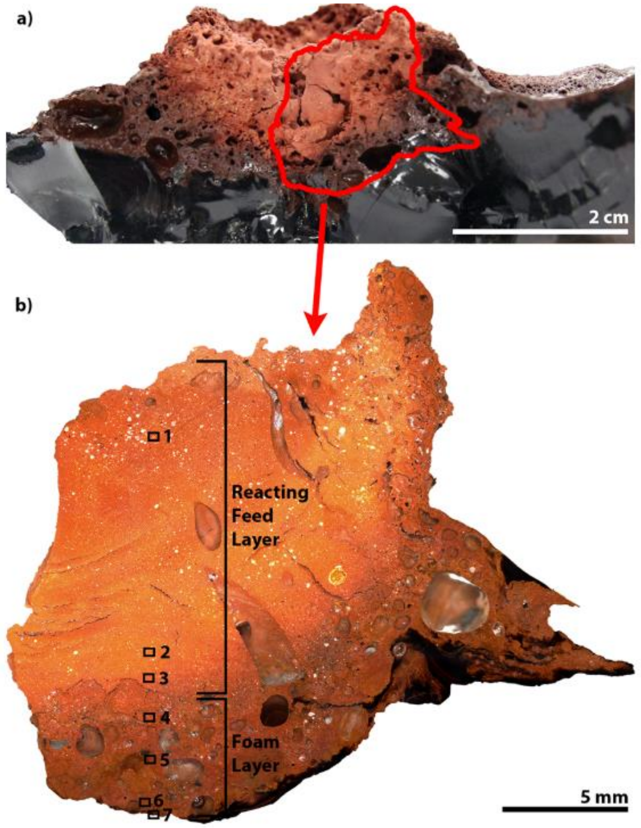
Slurry-fed Joule-heated Melter

- Glass melt is stirred by air bubbling
- Heat is delivered by Joule heating
- Aqueous slurry is poured from the top
- Dried slurry creates a layer of reacting materials (cold cap) that floats on the melt
- Typical computational fluid dynamics (CFD) models do not predict the rate of melting
- Cold-cap model is the missing link of the puzzle



Cold-cap Structure





- Feed-to-glass conversion
  - Water evaporates
  - Salts melt
  - Gases evolve
  - Silica dissolves
  - Foam collapses

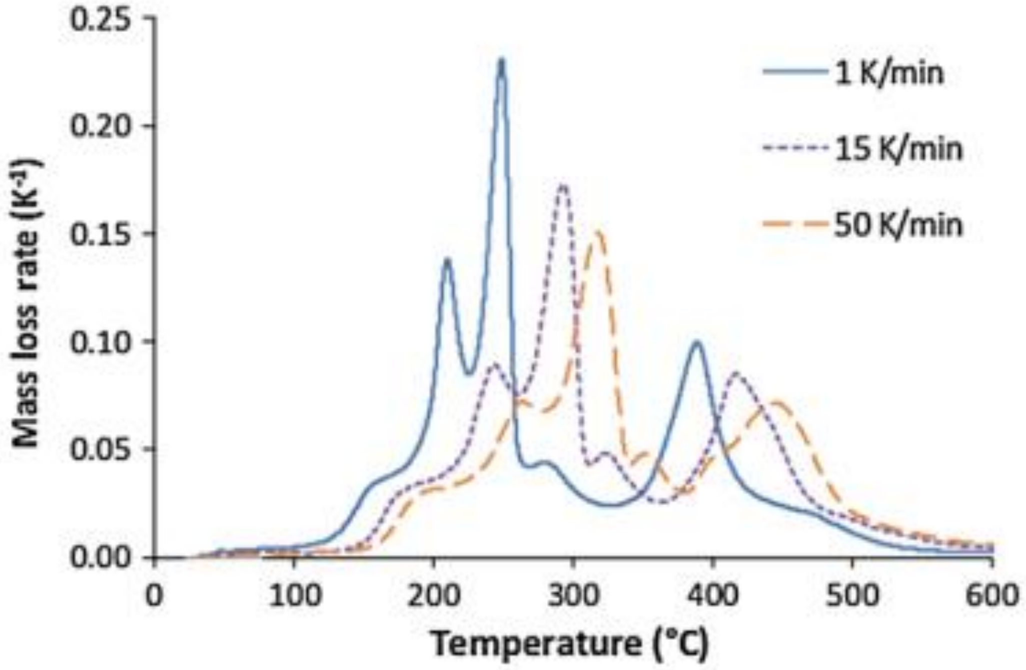
- Condensed materials move down
- Most of the heat is delivered through the bottom
- Gas from collapsing foam escapes sideways

D.R. Dixon, et al., Temperature Distribution within a Cold Cap during Nuclear Waste Vitrification, Environmental Science & Technology, 49 (2015) 8856-8863.

Conversion Degree

Thermogravimetric analysis

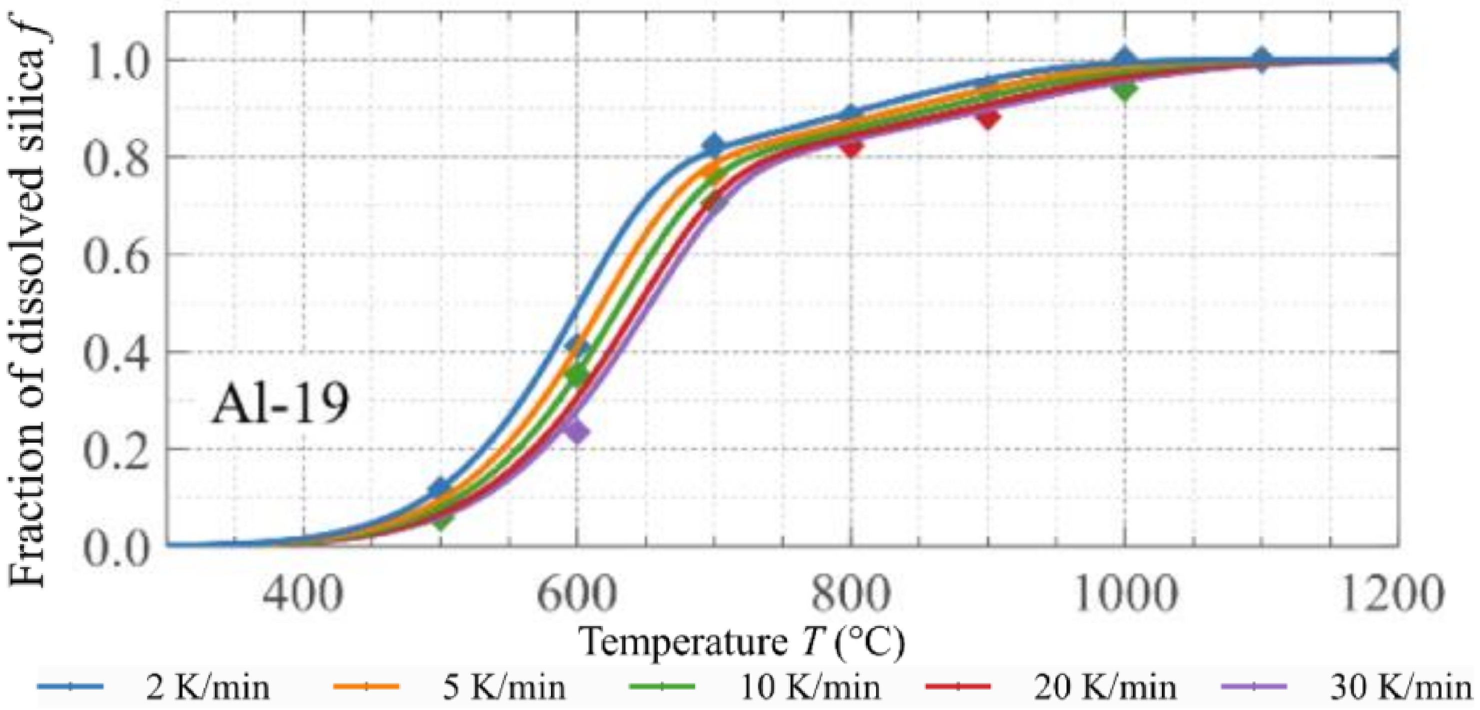
- Can be combined with evolved gas analysis and differential scanning calorimetry to identify reactions and reaction heat.
- Reliable data only below foaming onset



Pokorny, R. and P. Hrma (2012). "Mathematical modeling of cold cap." Journal of Nuclear Materials 429: 245-256.

X-ray diffraction

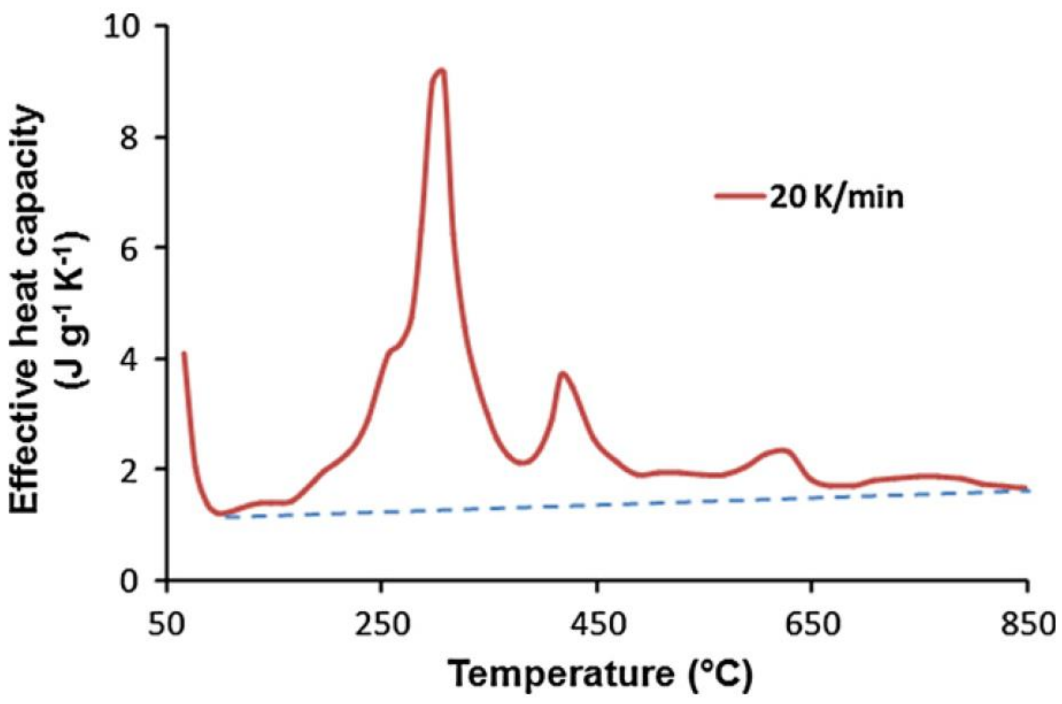
- Silica dissolves in broad temperature range, it can be used to measure conversion degree
- Need to combine with feed expansion test and evolved gas analysis to identify T_B.



P. Ferkl, et al., Conversion degree and heat transfer in the cold cap and their effect on glass production rate in an electric melter, International Journal of Applied Glass Science. (2022).

Heat Transfer in Cold Cap

- Both heat and mass transfer are essentially one-dimensional
- Feed composition affects reaction heat (endothermic or exothermic)
- Feed undergoes morphological changes, leading to dramatic variations of density and effective thermal conductivity



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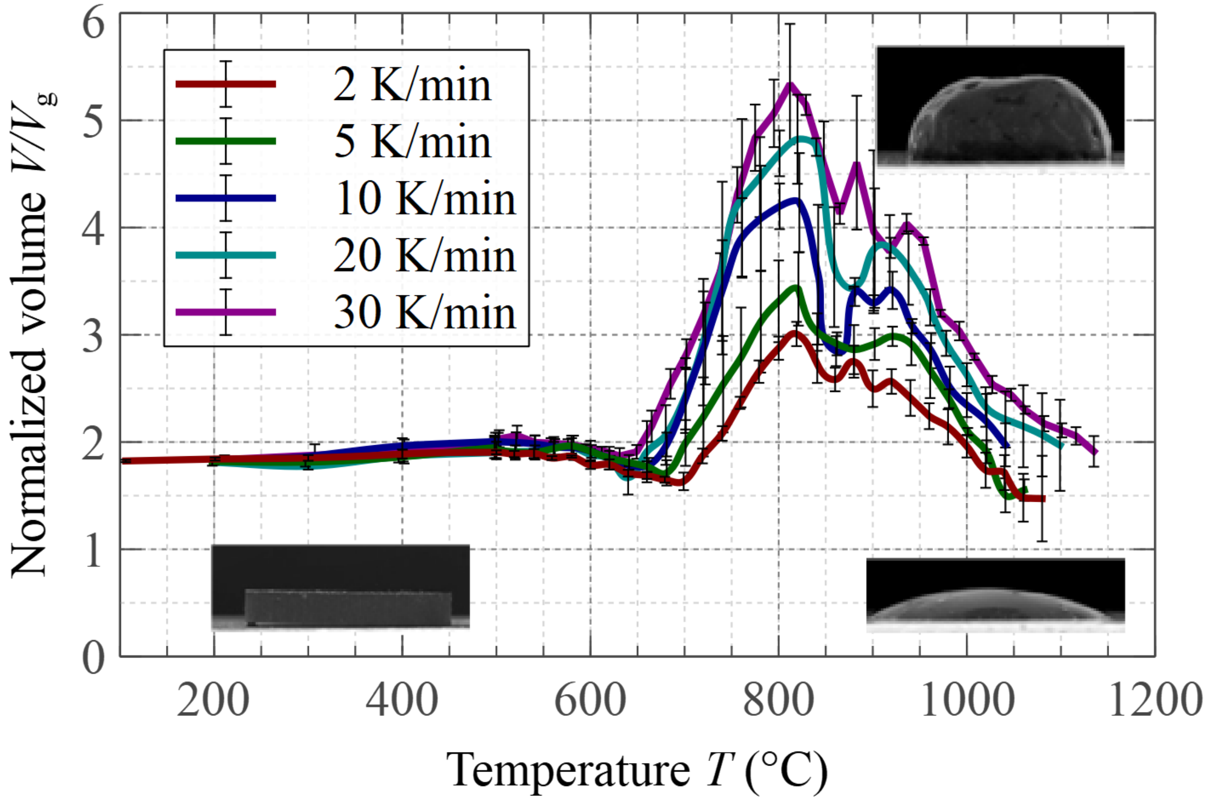
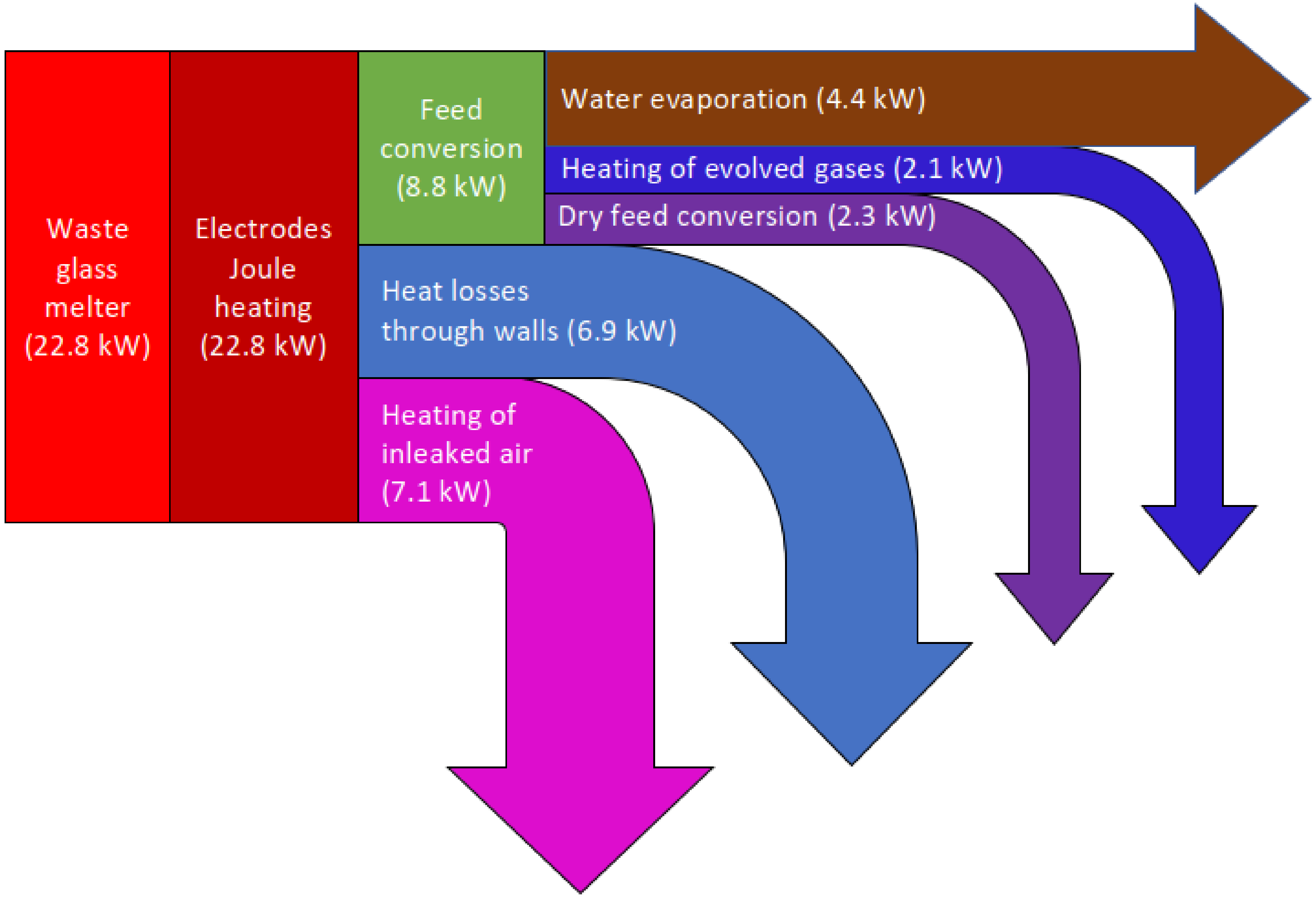


P. Ferkl, et al., Conversion degree and heat transfer in the cold cap and their effect on glass production rate in an electric melter, International Journal of Applied Glass Science. (2022).

Heat Transfer in Melter

- A significant amount of heat is consumed on slurry water evaporation and in-leaked air
- Heat losses through walls accounted for approximately 30% of delivered heat.
- Dry feed conversion required about 20% of input heat.



P. Ferkl, et al, Conversion degree and heat transfer in the cold cap and their effect on glass production rate in an electric melter, International Journal of Applied Glass Science. (2022).

Cold-cap Modeling

- Conversion reactions are studied at constant heating rates
- Reaction kinetics are represented by the rate equations:

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \sum_{i=1}^{n} c_i \frac{\mathrm{d}f_i}{\mathrm{d}t} \qquad \frac{\mathrm{d}f_i}{\mathrm{d}t} = A_i {f_i}^m (1 - f_i)^n \exp\left(-\frac{E_i}{RT}\right)$$

- The temperature distribution function is a solution of the heat transfer equation:

$$\left(j_\mathrm{b} c_{p,\mathrm{b}}^{\mathrm{eff}} - j_\mathrm{g} c_{p,\mathrm{g}}\right) \frac{\mathrm{d}T}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}\left(\lambda^{\mathrm{eff}} \frac{\mathrm{d}T}{\mathrm{d}x}\right)$$

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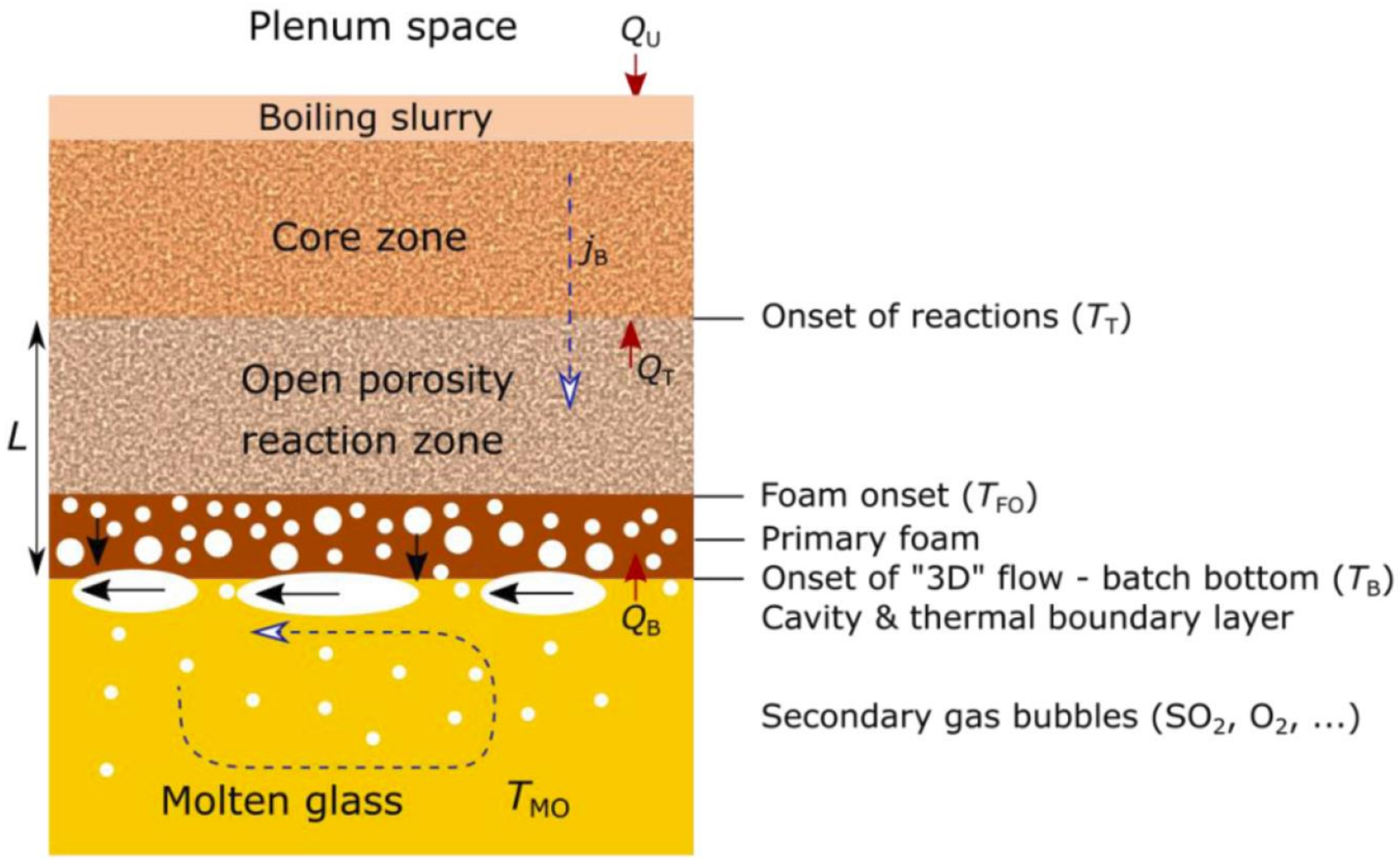
Boundary Conditions

- Only the reaction layer (open porosity reaction zone and primary foam layer) are modeled.
- Thickness of core zone varies in location and time as slurry spreads and dries on top
- Main conversion reactions start around 200 °C
- Heat flux continuity between cold cap, melt, and plenum
- Temperature or silica fraction at cold cap bottom



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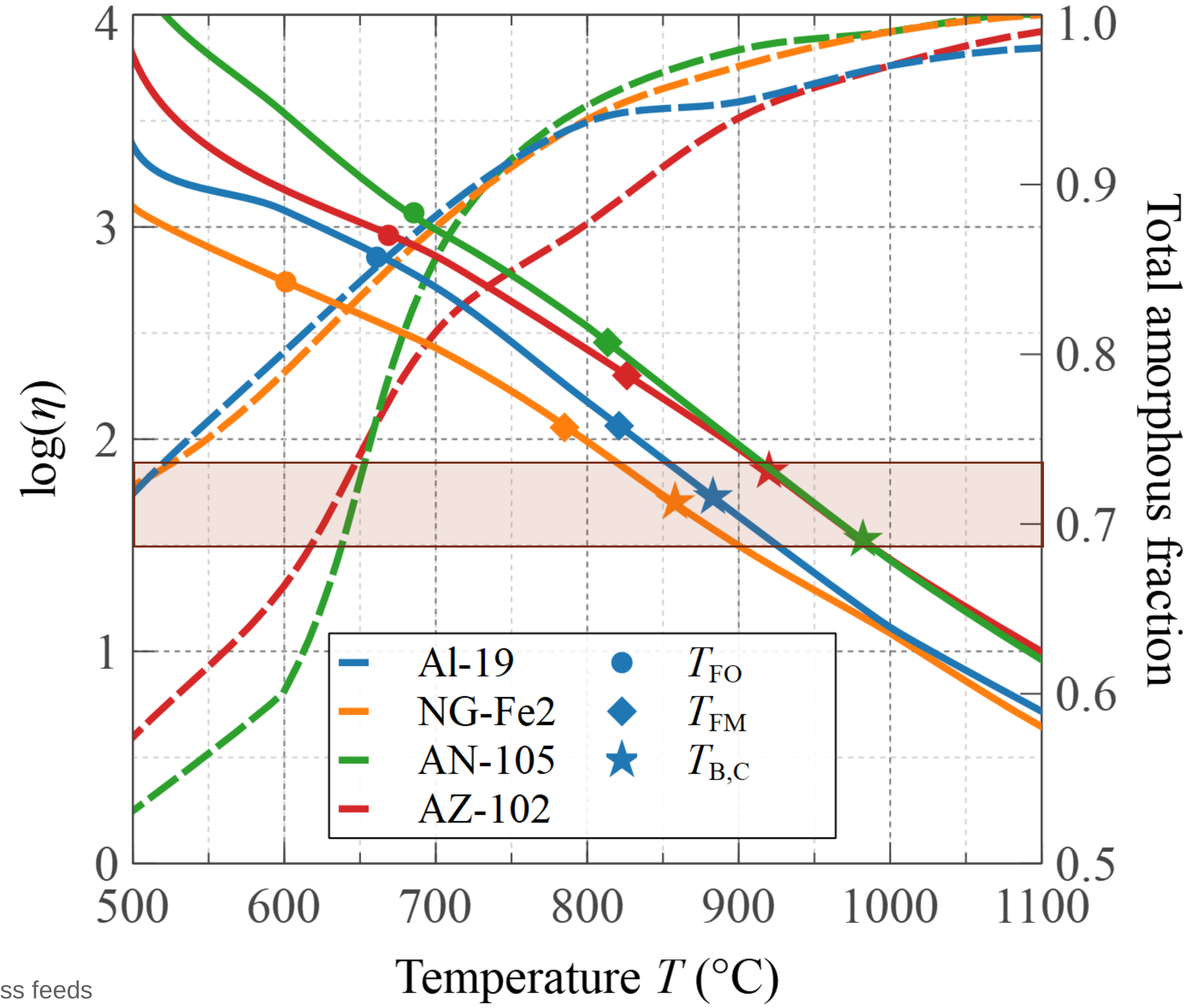
Amorphous Phase Viscosity

- Viscosity of amorphous phase estimated by Arrhenius model with temperature-dependent composition, accounting for gradual dissolution of crystalline phases
- Values of estimated cold-cap bottom temperature (T_B) lie in relatively narrow range of viscosity



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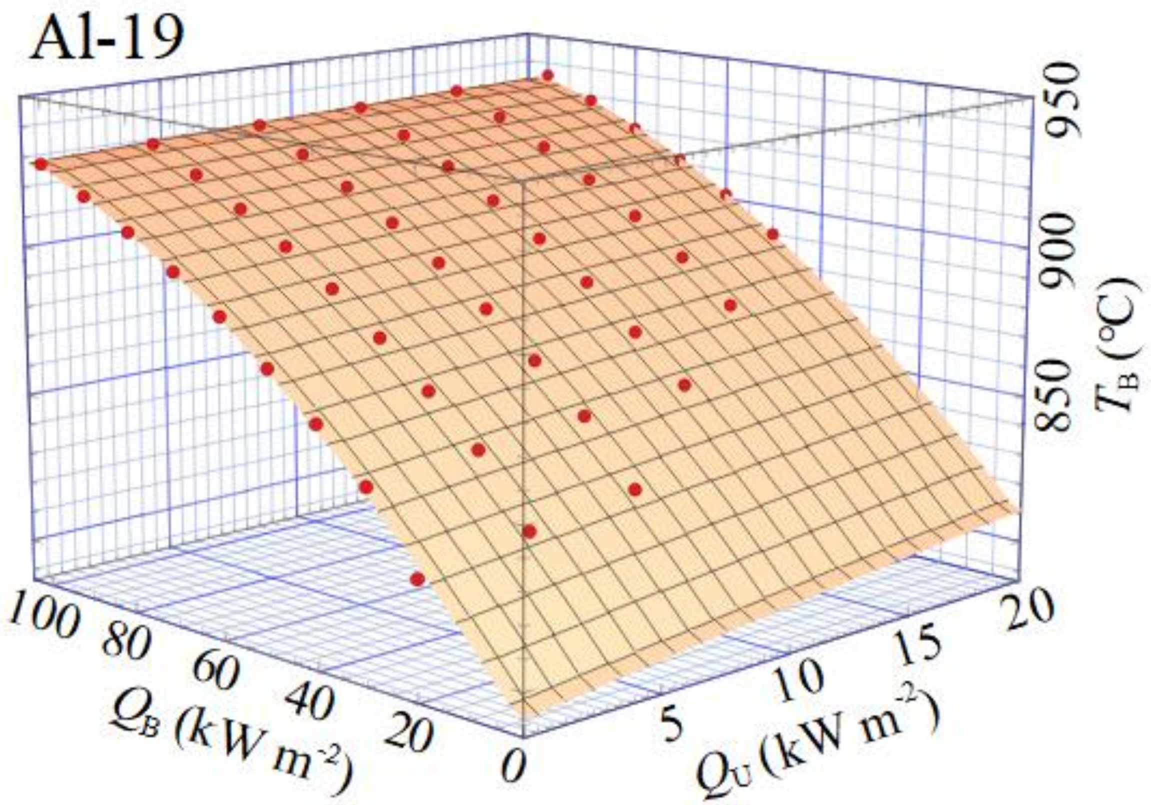
Cold-cap Model in the CFD Model

- Reduced model developed to simplify computation:
  - Cold-cap bottom temperature as a function of heat fluxes from top, Q_{U}, and bottom, Q_{B}



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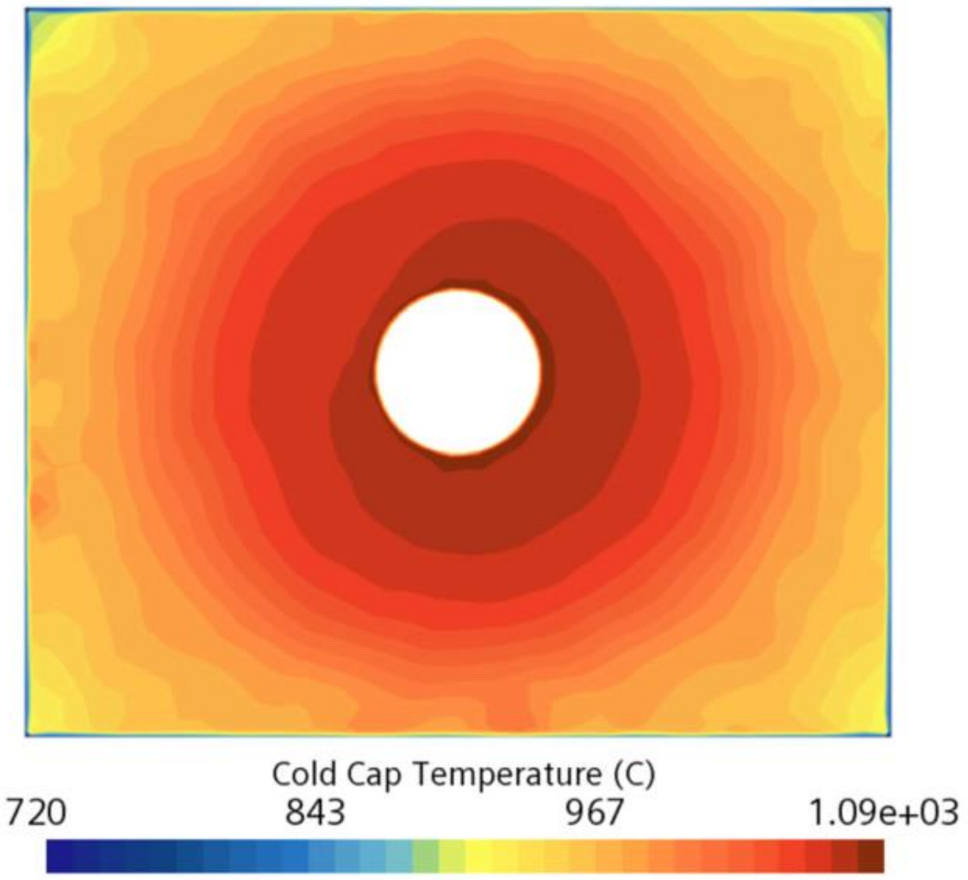
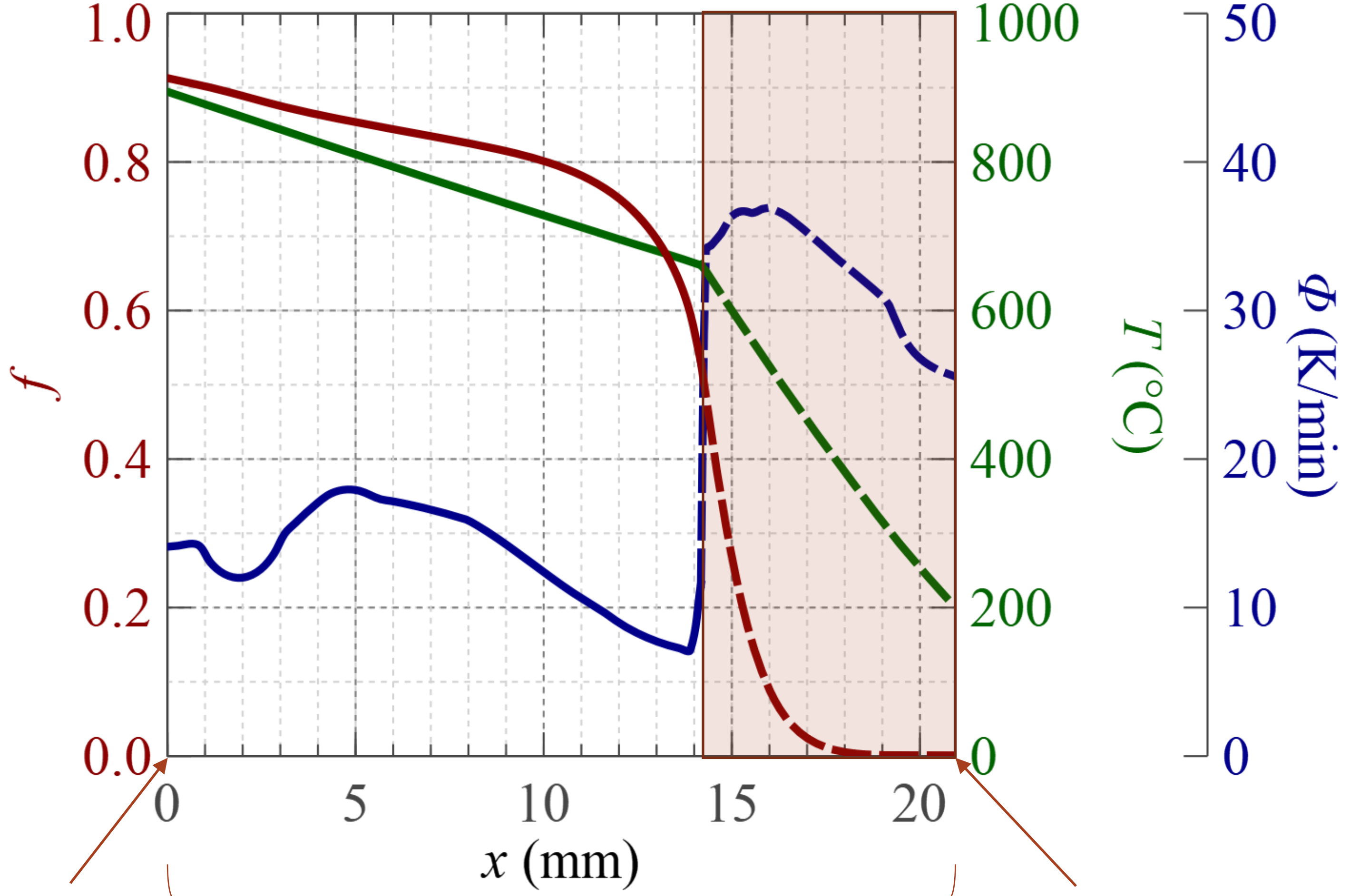
Temperature distribution at bottom of the cold cap



Steady-state Profiles in Cold cap

- Laboratory tests are performed at constant heating rates
- Materials inside the cold-cap experience highly nonlinear temperature history
- Profiles are estimated by modeling one-dimensional flow of condensed materials through the cold-cap, accounting for its properties



closed porosity (foam)

open porosity (reaction layer)

Cold cap bottom

Reaction zone

Interface with core layer

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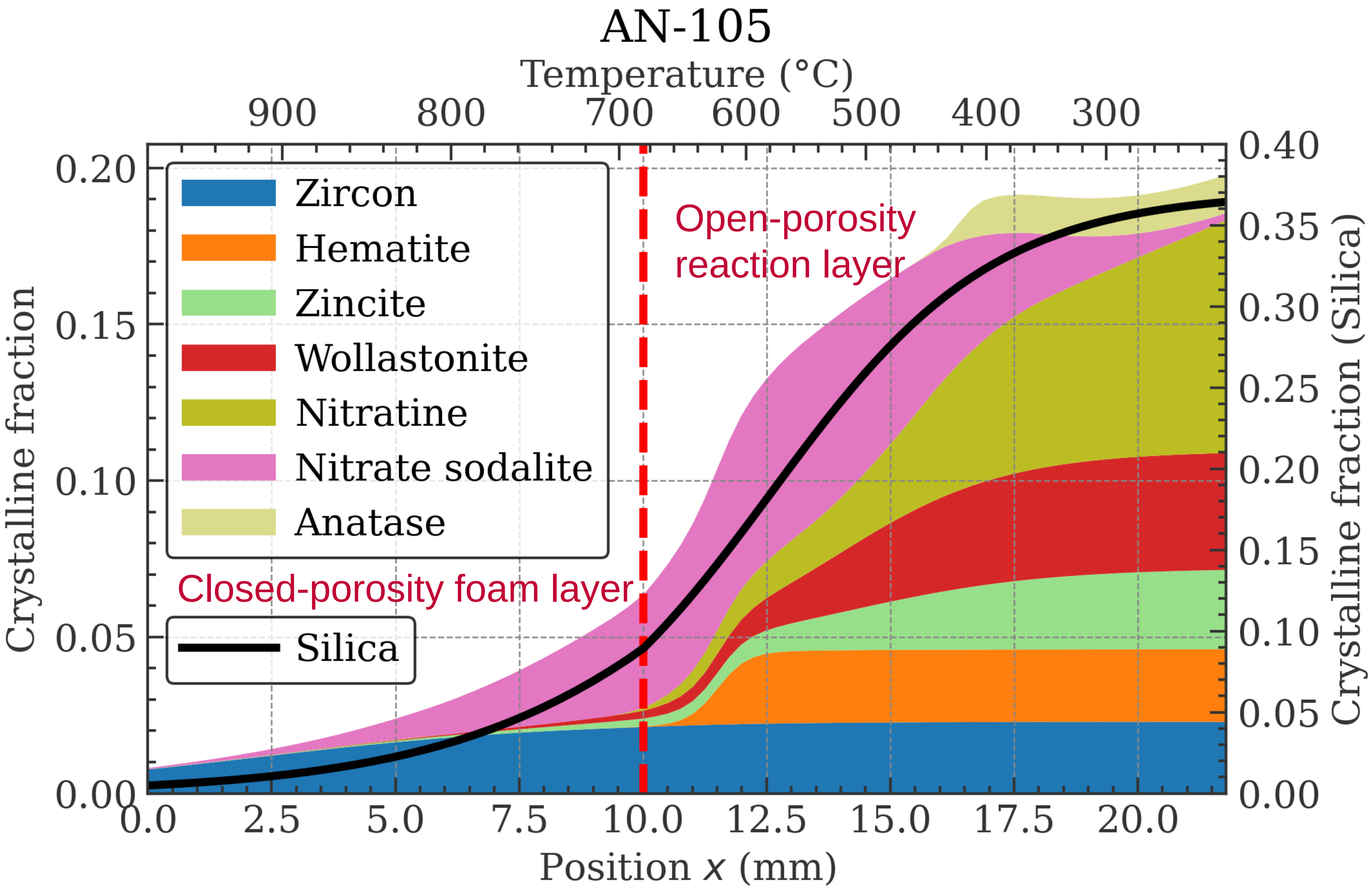
Crystalline Phases in Cold cap



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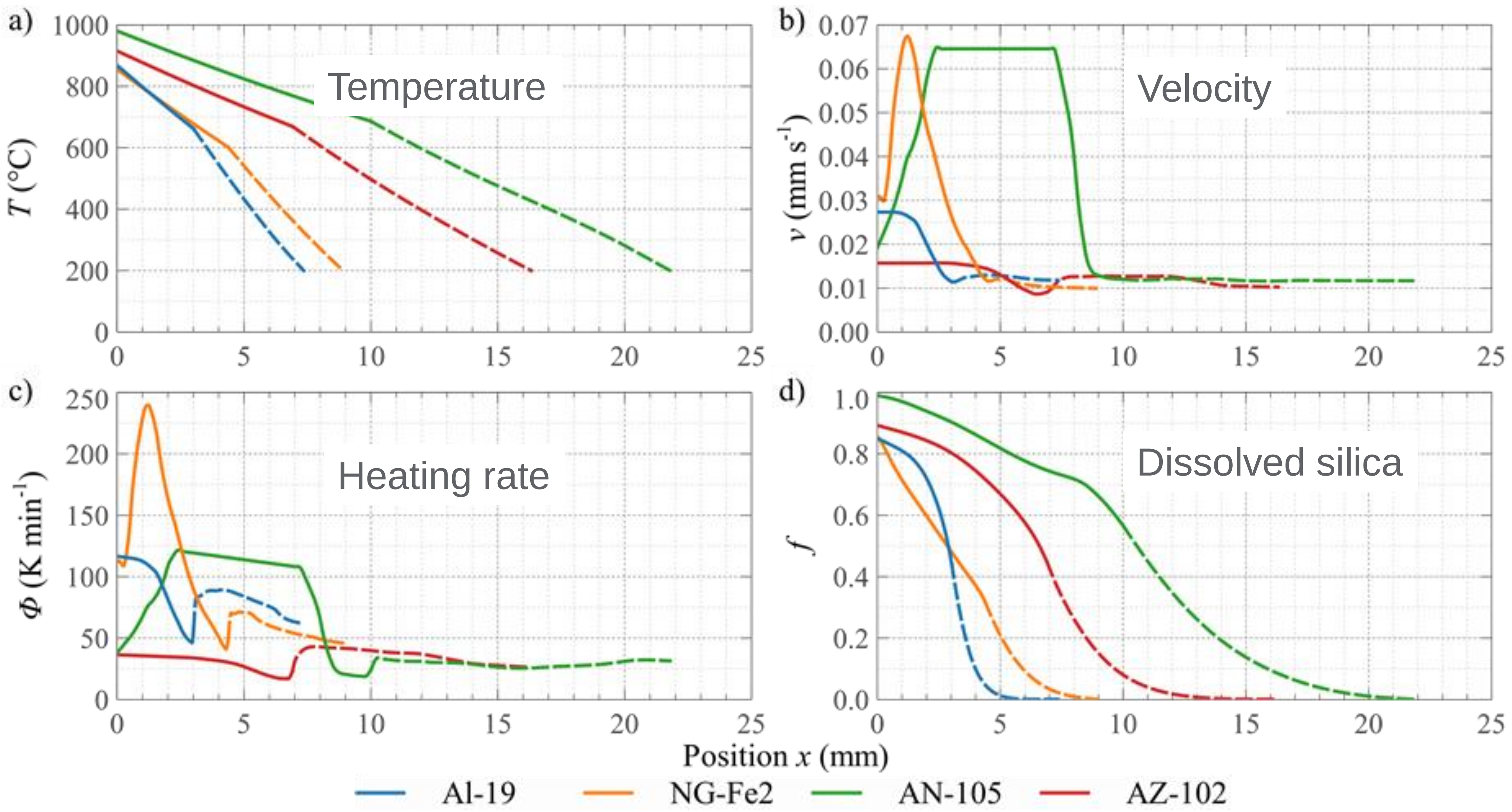
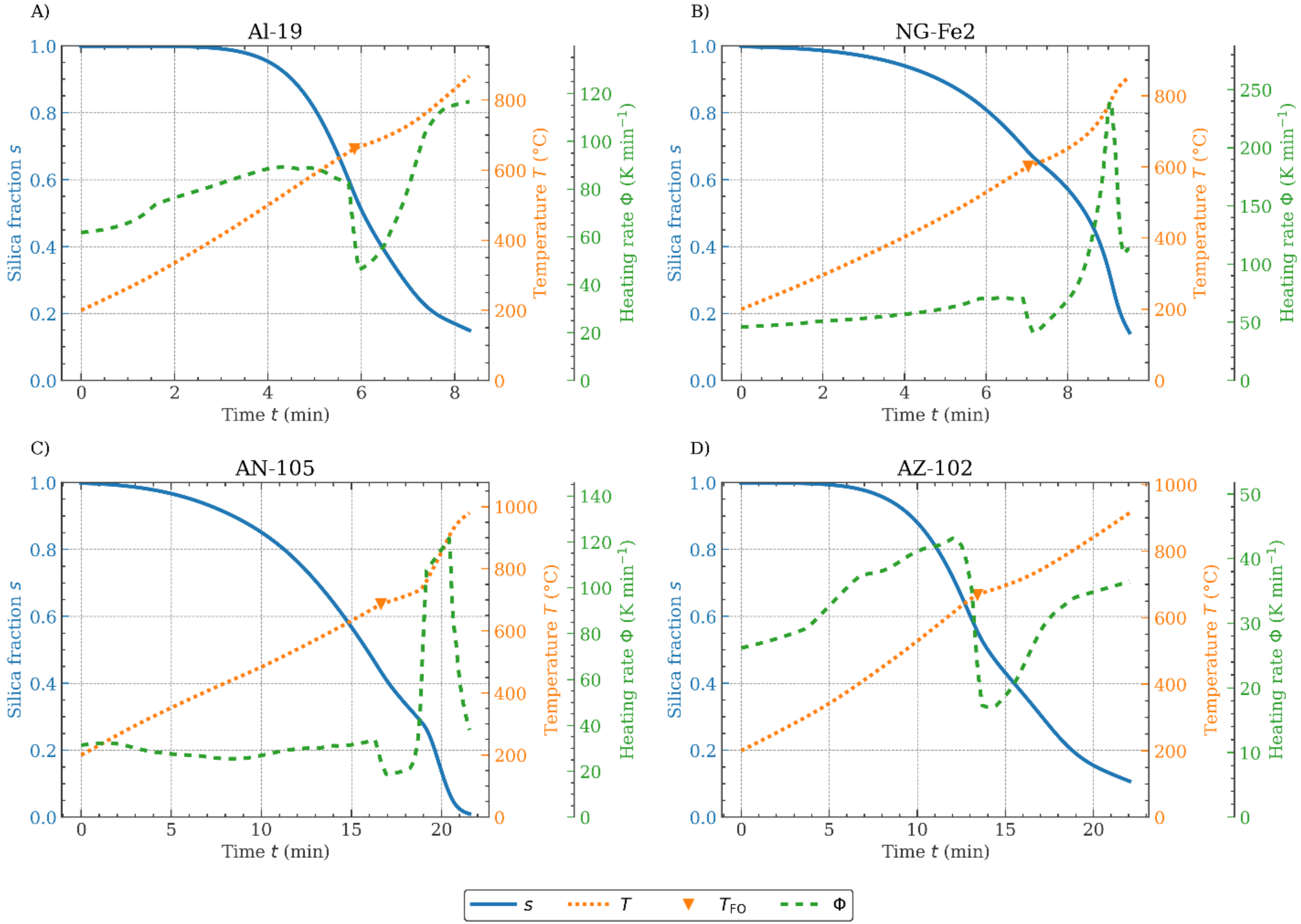
Distributions of Cold-cap Properties



Dashed lines: open-porosity reaction layer   Cold-cap bottom: $x = 0$

Ferkl, P., et al. (2023). "Effect of material properties on batch-to-glass conversion kinetics." International Journal of Applied Glass Science 14(4): 491-501.

Evolution of Temperature and Silica Fraction



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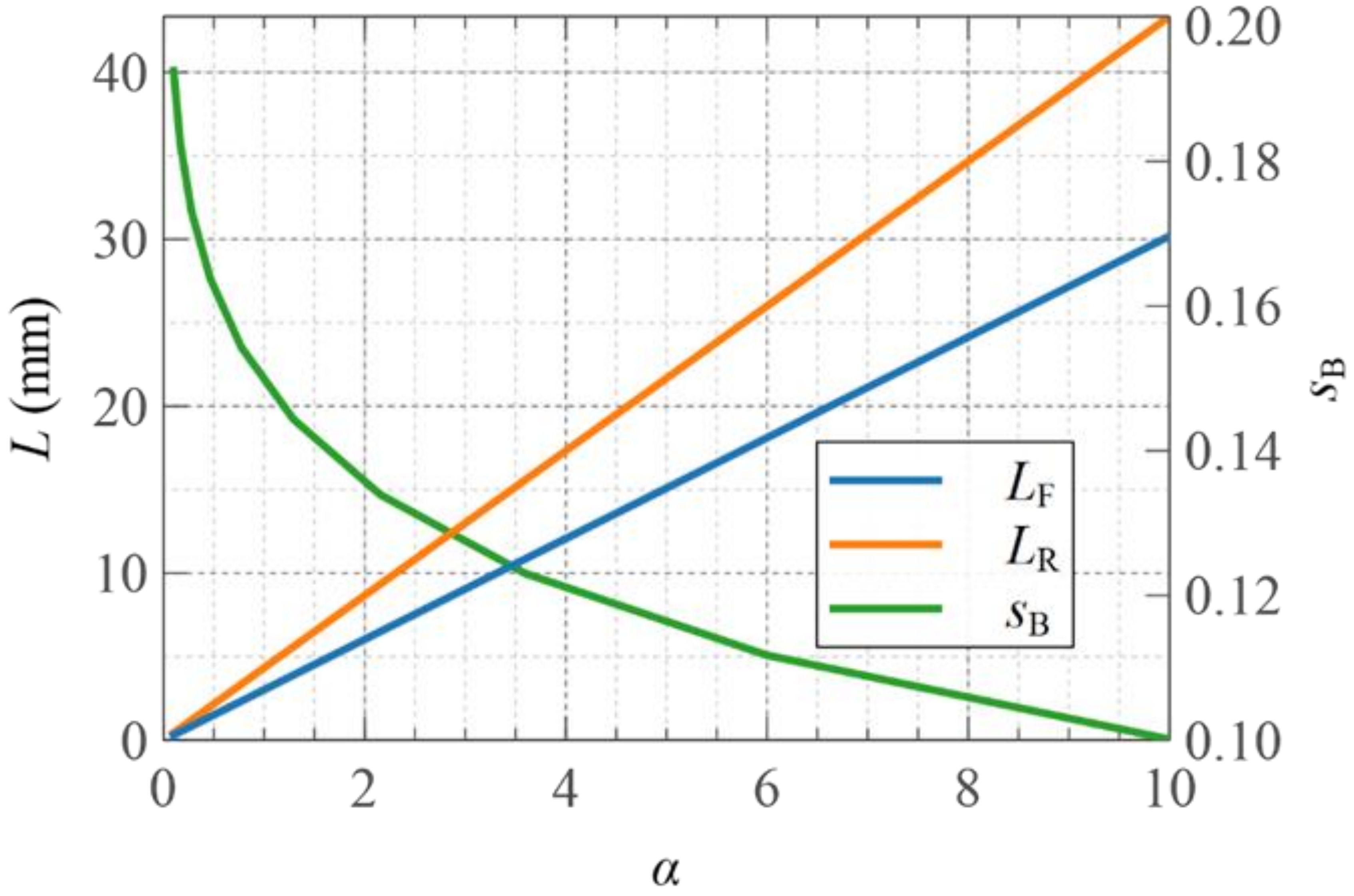
Thermal Conductivity of Cold cap

- Thermal conductivity of the cold-cap is difficult to measure
- Affects thickness of both reaction and foam layers
- Has an effect on undissolved amount of silica entering melt from the cold cap

$$\lambda = \alpha\lambda_0$$



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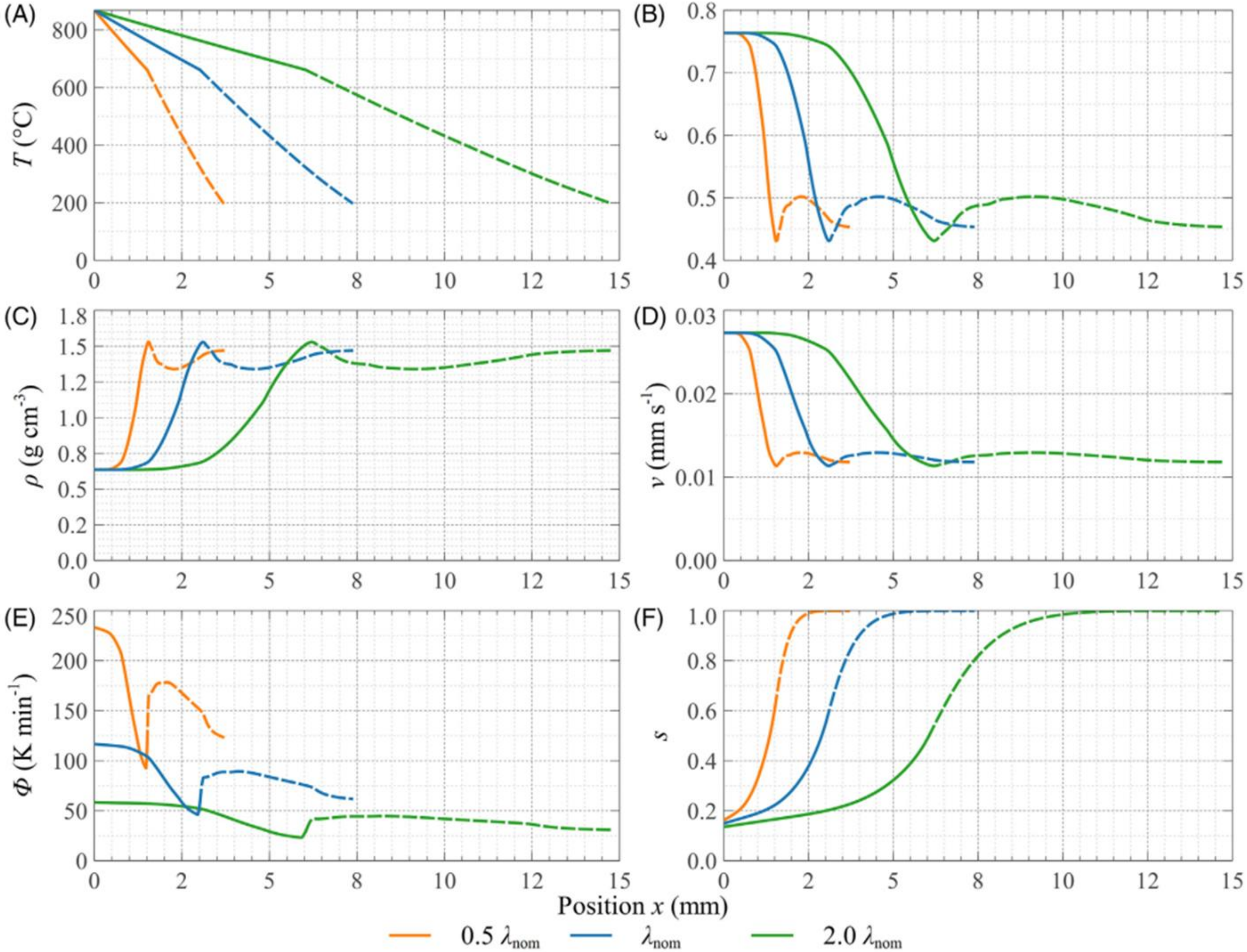
Thermal Conductivity of Cold cap

- Thermal conductivity changes heating rate profiles in the cold cap, which affect the kinetics of conversion processes



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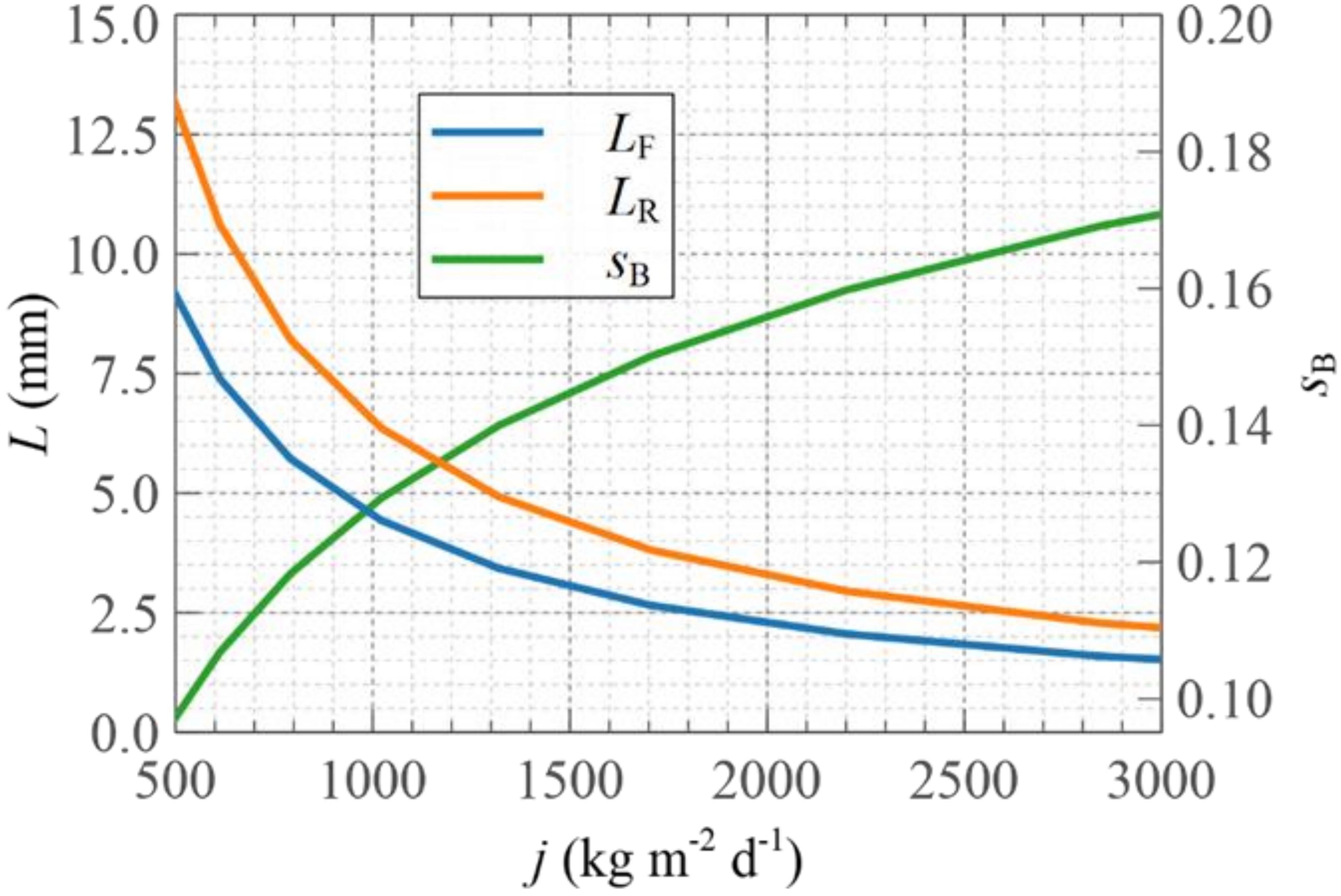
Effect of Glass Production Rate on Cold cap

- Glass production rate affects the cold-cap thickness and amount of undissolved silica
- Changes heating rate profiles in the cold cap



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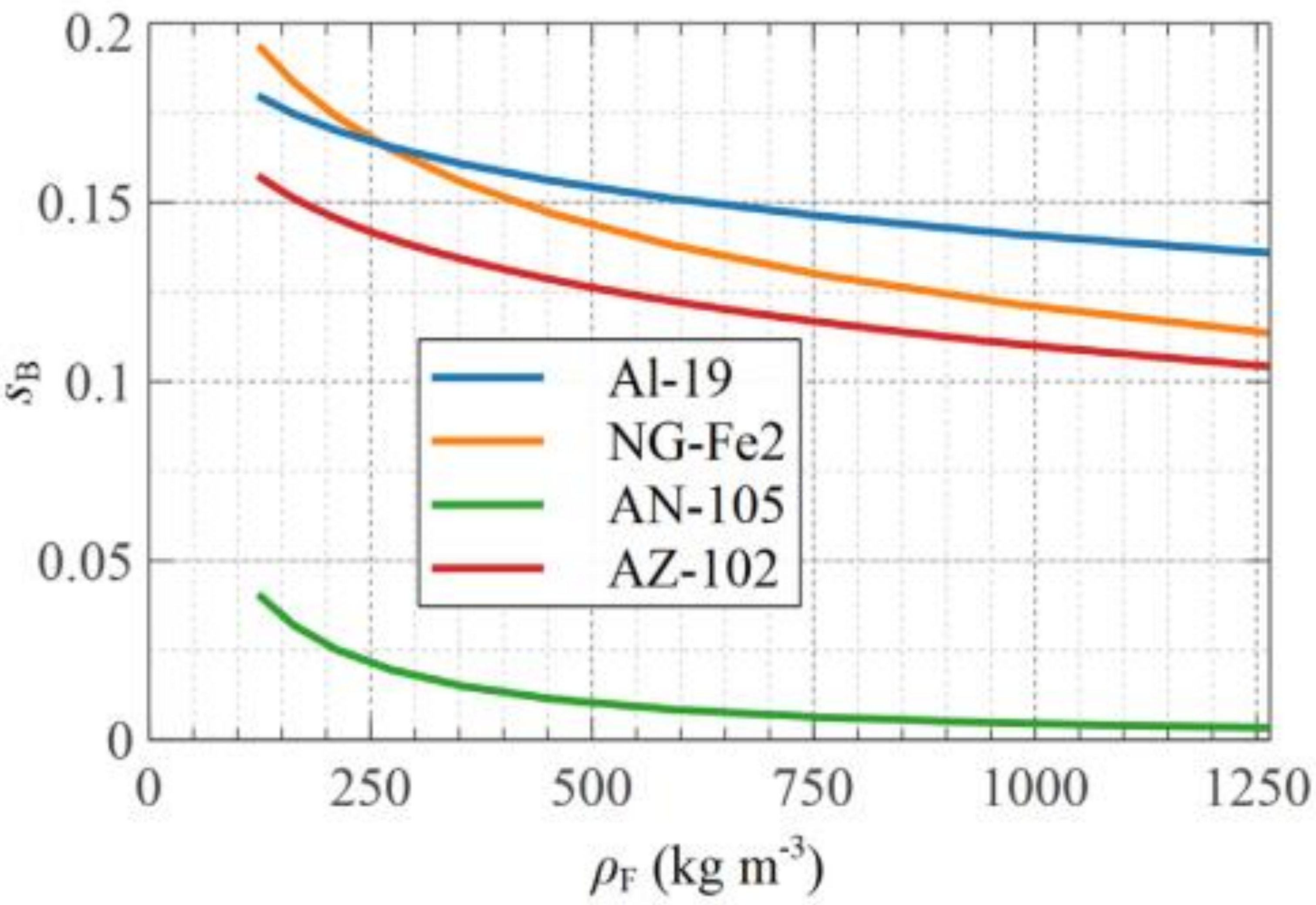
Effect of Density on Cold cap

- Density affects the amount of undissolved silica
- Changes heating rate profiles in the cold cap
- No effect on cold-cap thickness
- Velocity changes in proportion to the density



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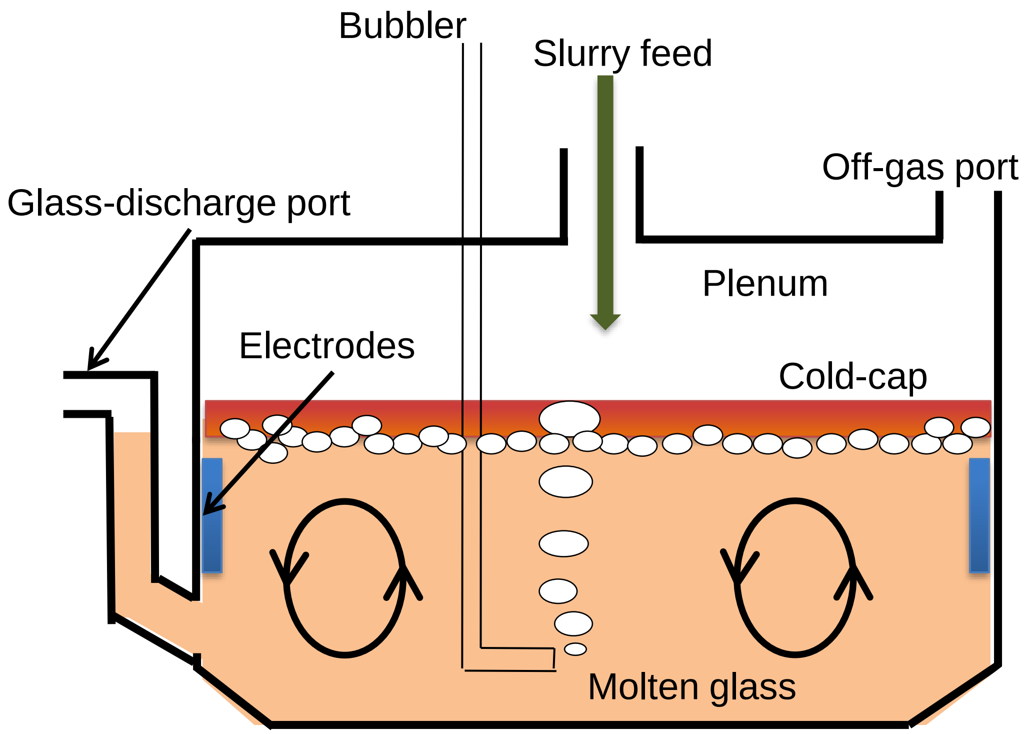
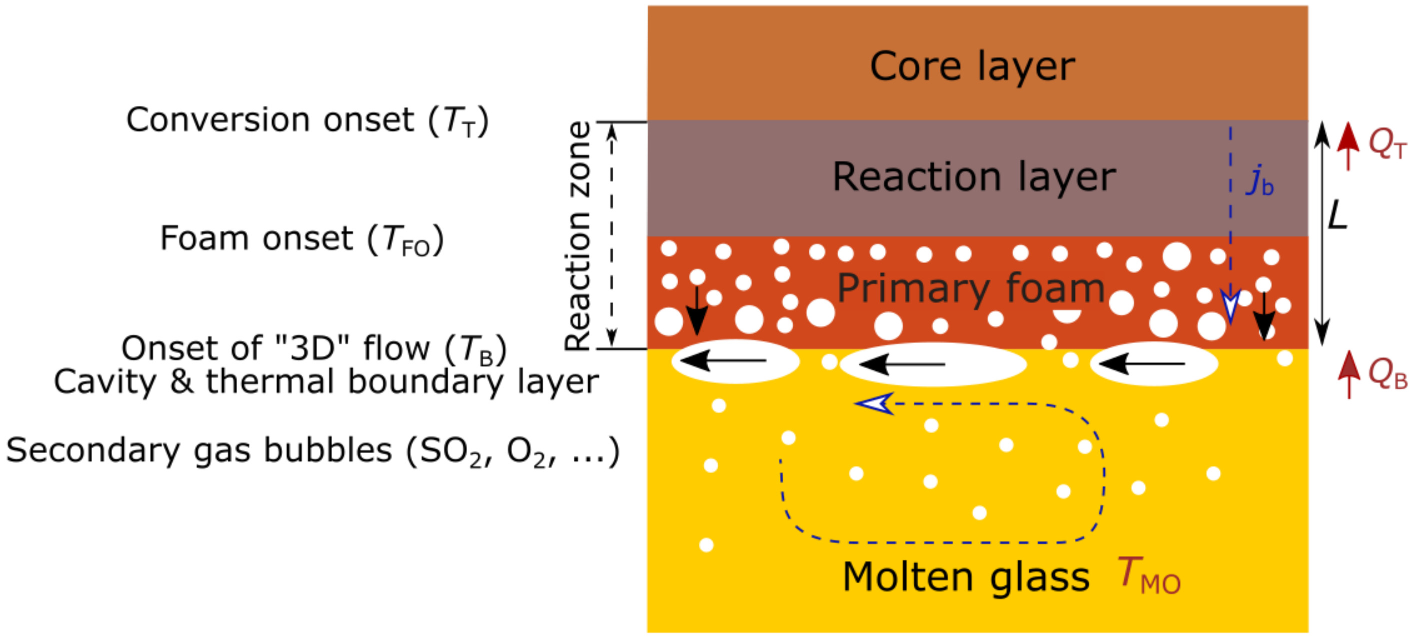
Conclusions

- Heat transfer in cold cap, conversion reactions, properties, and structure of the cold cap are interdependent.
- Expanding datasets of feed properties and gathering data from melter tests is crucial for customizing the mathematical/numerical models for application to feeds of interest.





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- Collaborators
  - Pacific Northwest National Laboratory (PNNL)
    - Mark Hall, Will Eaton, Derek Dixon, Steven Luksic, Jose Marcial, Seung Min Lee, Jaimie George, Tongan Jin
  - Idaho National Laboratory (INL)
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  - University of Chemistry and Technology, Prague (UCT)
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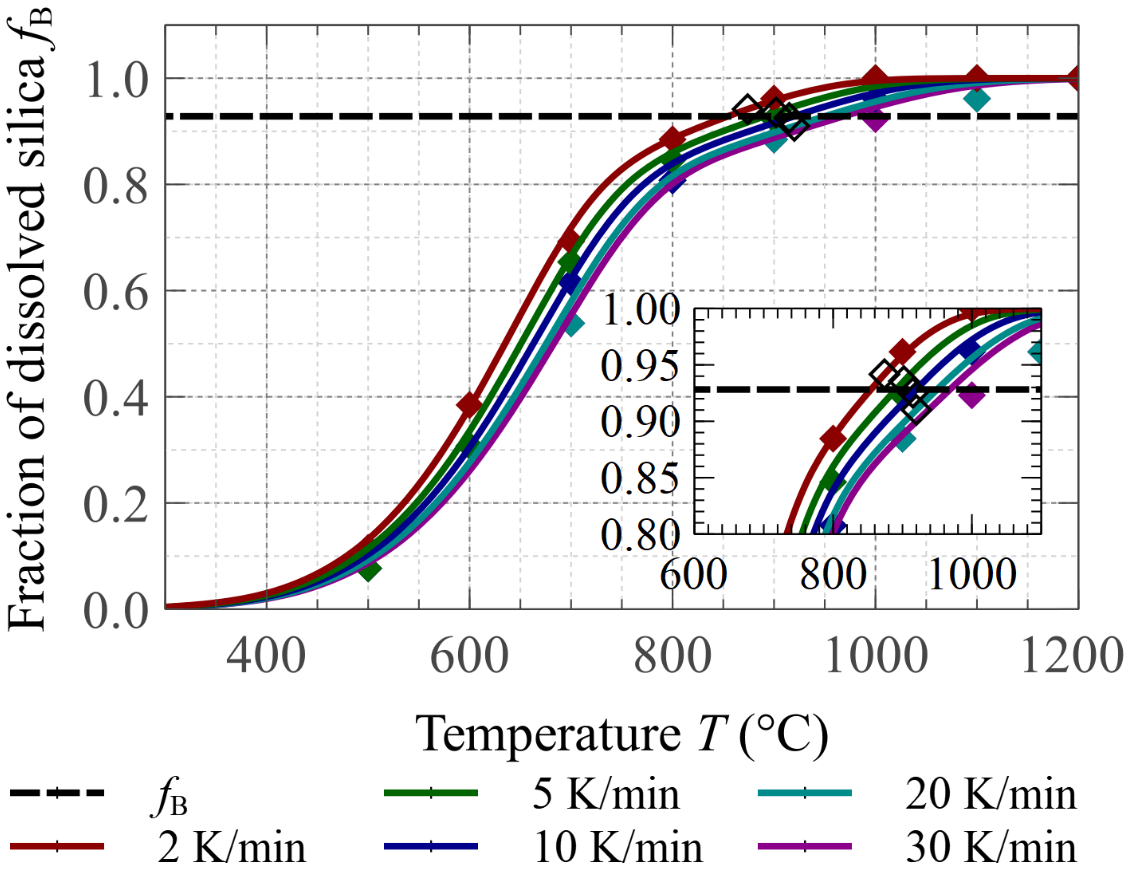
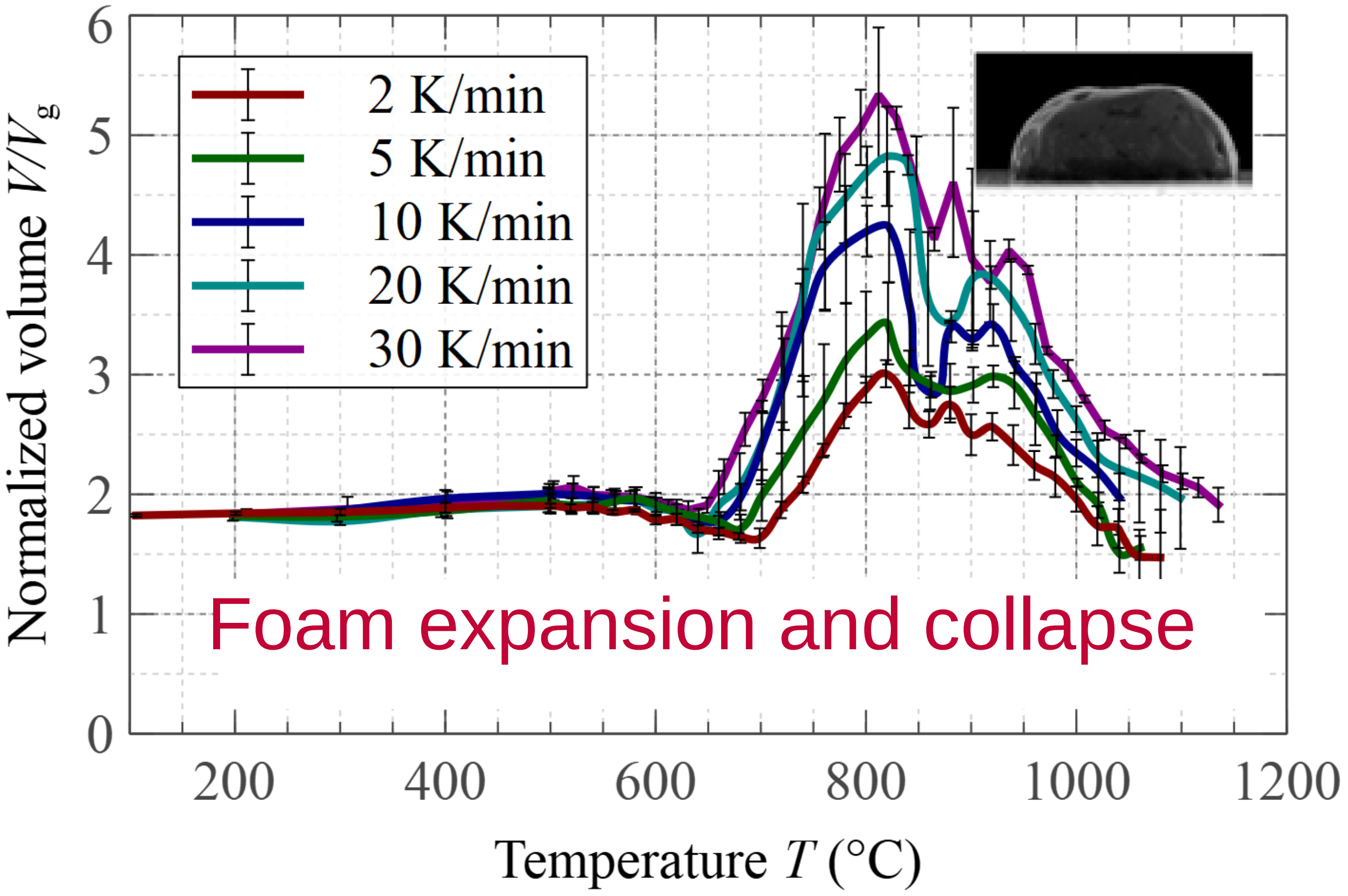
  - AttainX, General Service Support Contractor to the Office of River Protection
    - Pavel Hrma

Appendix

X-ray diffraction



Silica dissolution, XRD data



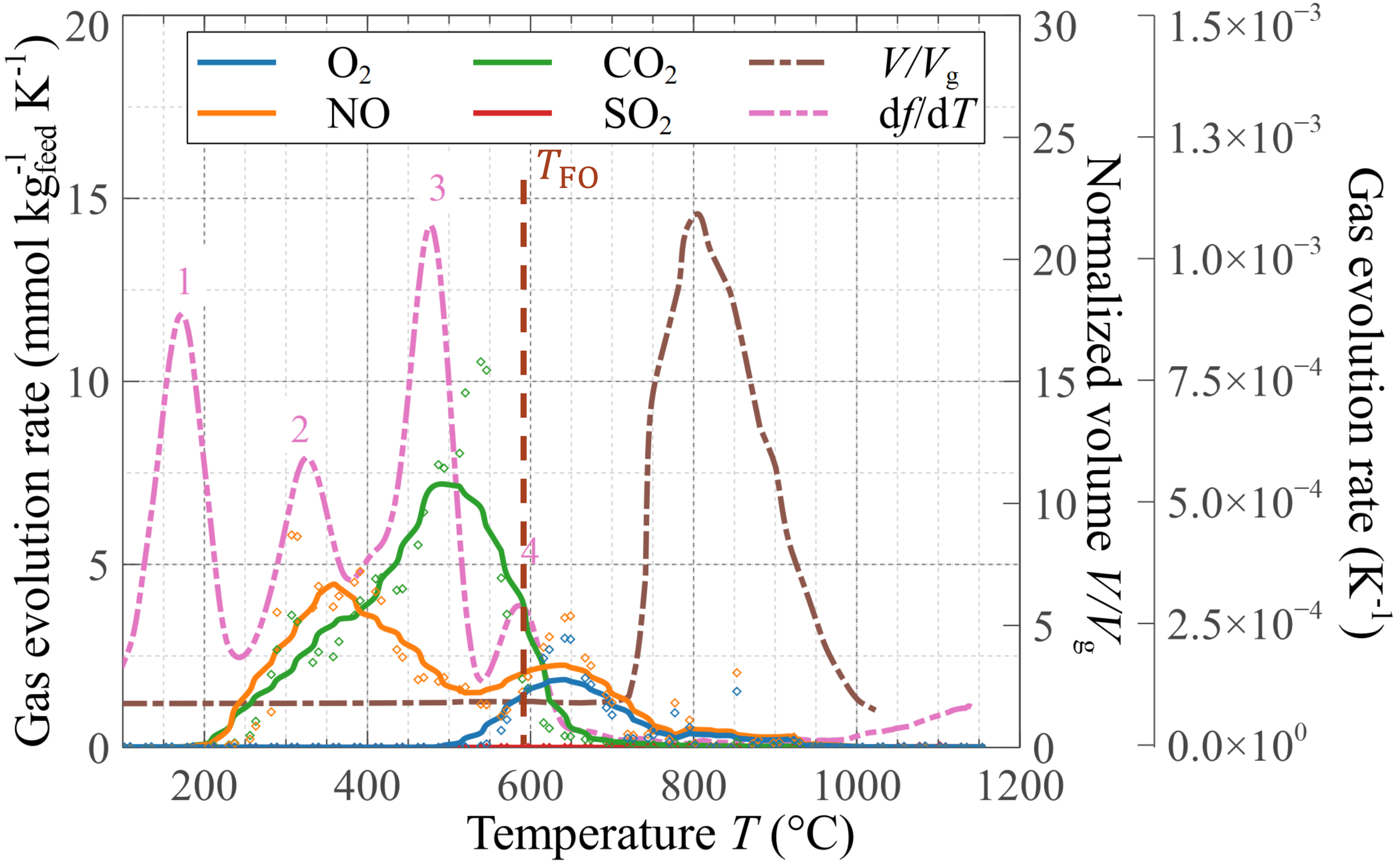
Foam expansion and collapse

- The motion of condensed phase changes from predominantly vertical (inside the cold-cap) to predominantly horizontal (below the cold-cap)
- Foam collapses at the bottom of the cold-cap
- Melter feed solids (such as silica) are mostly dissolved at cold-cap bottom

P. Ferkl, et al., Conversion kinetics during melting of simulated nuclear waste glass feeds measured by dissolution of silica, Journal of Non-Crystalline Solids, 579 (2022) 121363.

Thermogravimetric & Evolved Gas Analysis

- Most of the gas is evolved below temperature of foam onset (T_{FO}) and escapes through open porosity
- Gases evolved above T_{FO} cause foaming



As foam collapses, secondary gases are detected

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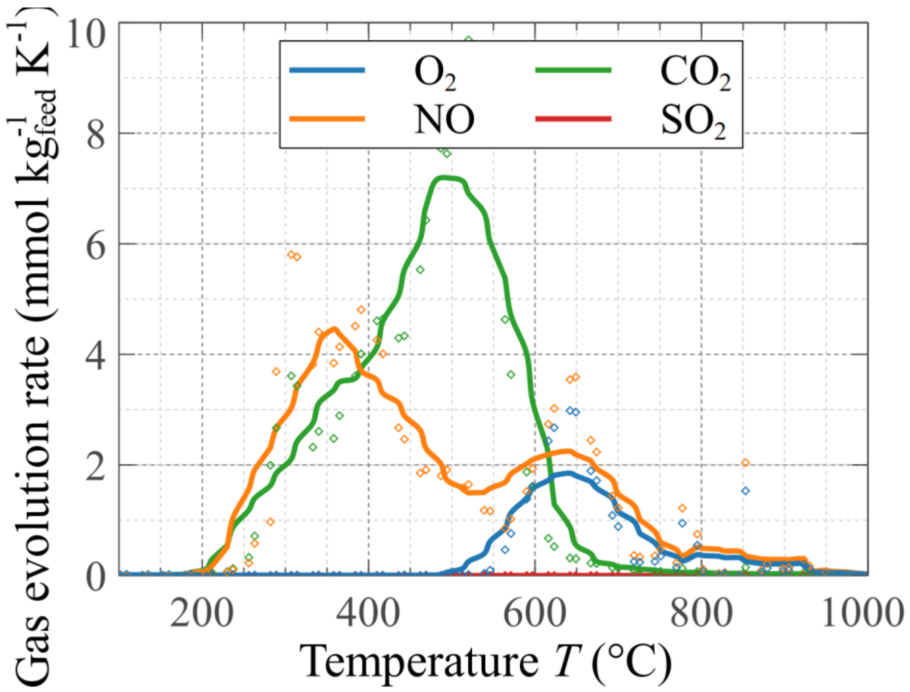
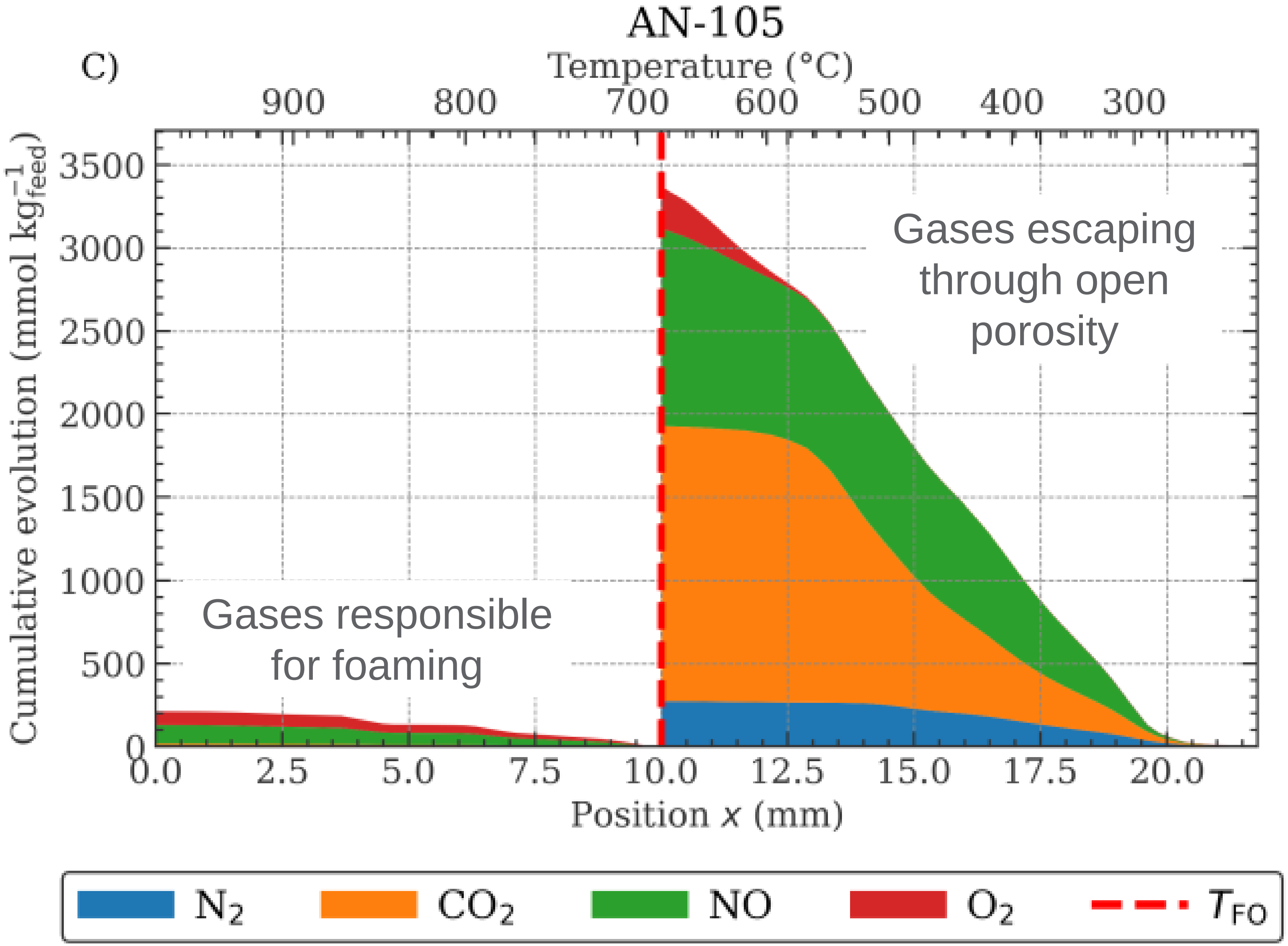
Gas Evolution in Cold Cap

- Fraction of gas evolved below T_{FO}:
  - N_2: 0.97
  - CO_2: 0.98
  - NO: 0.88
  - O_2: 0.68





Gases escaping through open porosity

Gases responsible for foaming

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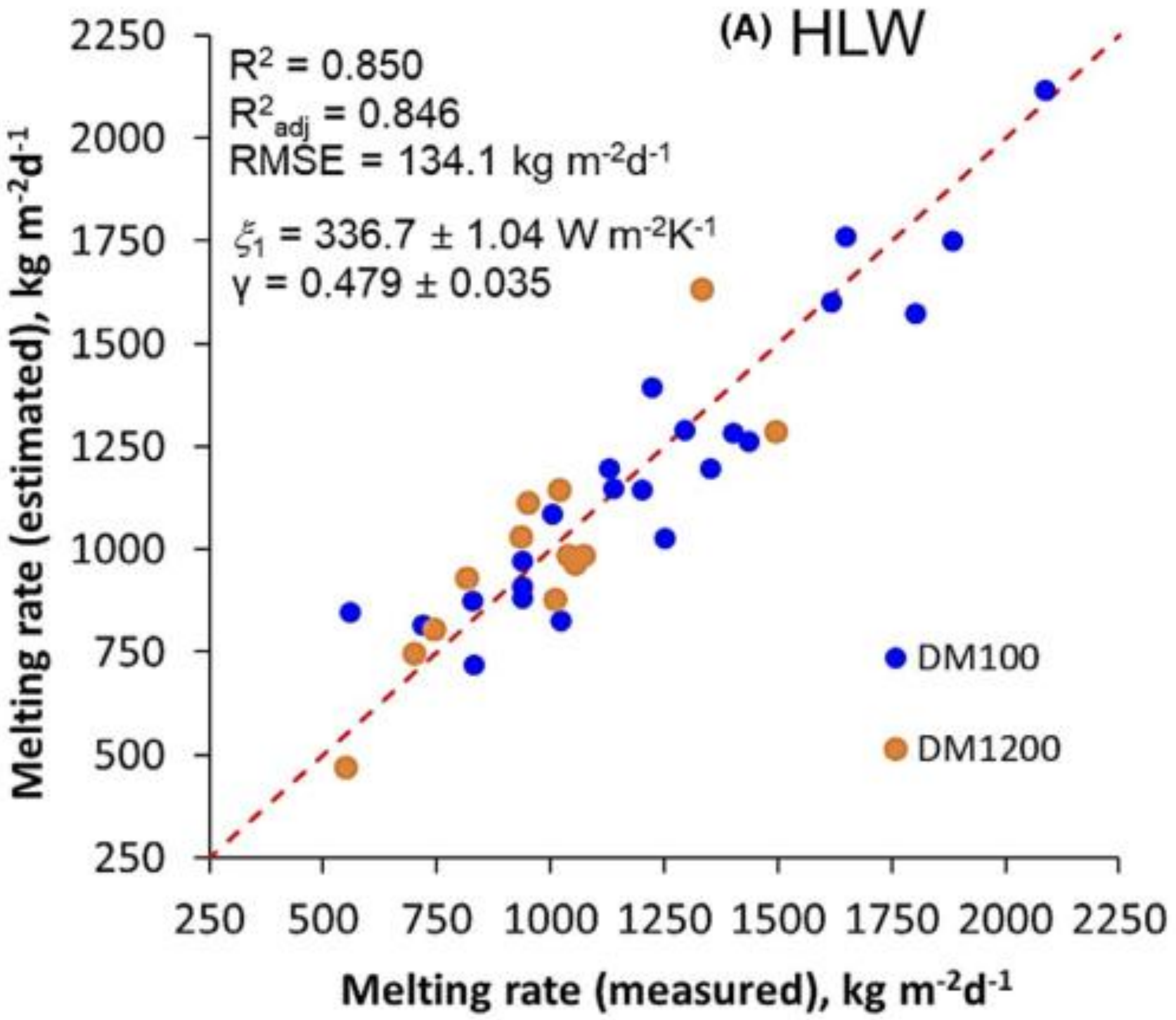
Melting Rate (j) Correlation Equation

$$j = \xi \mathrm{Re}^{\gamma} \frac{T_{\mathrm{MO}} - T_{\mathrm{B}}}{\Delta H} \qquad \mathrm{Re} = \frac{v \rho h}{\eta}$$

- Melter geometry and operating conditions:
  - v bubbling rate
  - h melt pool depth
  - T_{MO} melter operating temperature
- Glass melt properties:
  - ρ melt density
  - η melt viscosity
- Melter feed properties:
  - ΔH conversion enthalpy
  - T_B cold cap bottom temperature
- Adjustable parameters: ξ and γ



S. Lee, et al., Melting rate correlation with batch properties and melter operating conditions during conversion of nuclear waste melter feeds to glasses, International Journal of Applied Glass Science, 12 (2021) 398-414.