

Investigation of batch-to-glass conversion kinetics and heat transfer in all-electric glass melting



Richard Pokorny



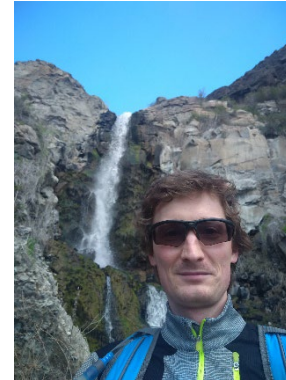
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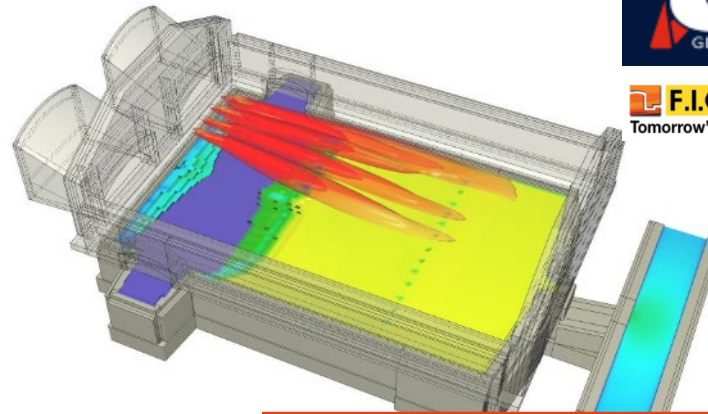


Mathematical modeling of batch melting

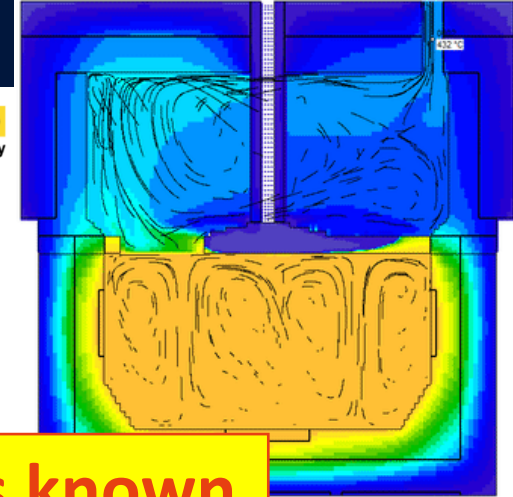


UCT PRAGUE

- ▶ Mathematical models of melters are commonly used for the simulation of melter behavior
 - ❑ Standard for practically all new furnaces
- ▶ Current weakness – oversimplification of the conversion layer (batch layer/cold cap)
 - ❑ Typical computational fluid dynamics (CFD) models use melting rate as an input condition
 - ❑ This might be reasonable when investigating phenomena in molten glass
 - ❑ Not OK, if you expect to process thousands of waste feed compositions
 - ❑ Not OK in electric or high-boasting furnaces, where heat flux to cold cap bottom is crucial
- ▶ Only with proper batch model, the melting rate can be predicted as a function of feed properties and melter operating conditions.
 - ❑ Electrode boosting power, fuel consumption, silica dissolution, spinel settling, RTD, plant upsets, online control,...



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**Surprisingly little is known
about heat flux to batch
from the melt...**



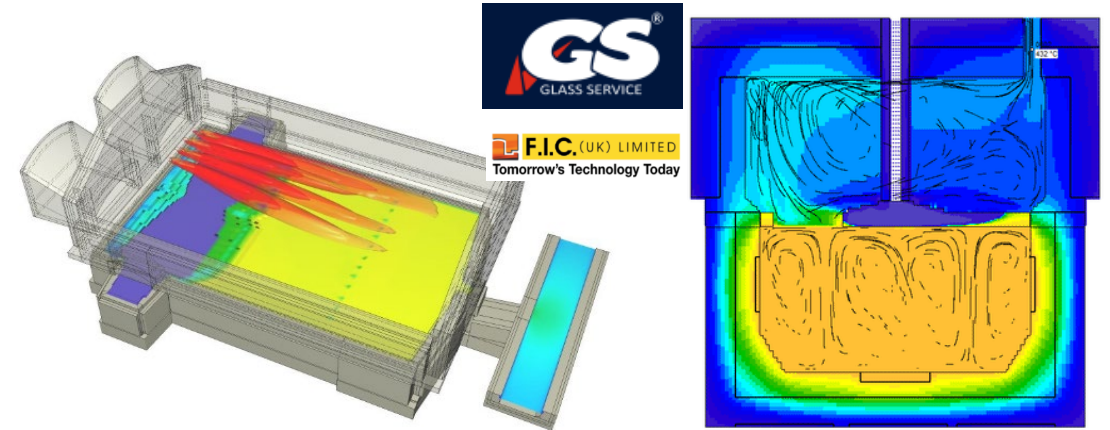
Objectives



UCT PRAGUE

► Improve predictive abilities of current CFD models

- By understanding how changes melter operating conditions affect the production rate in glass melting furnace



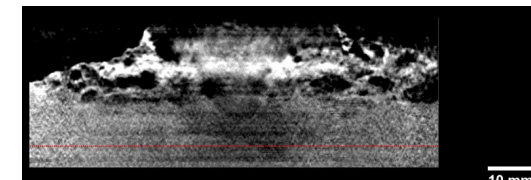
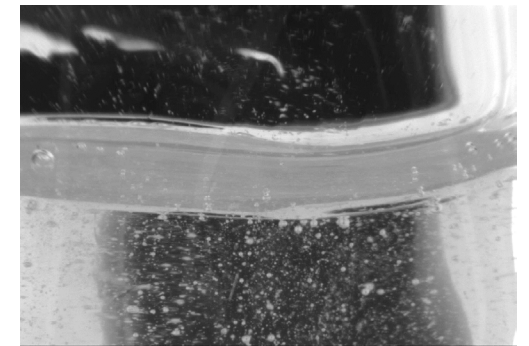
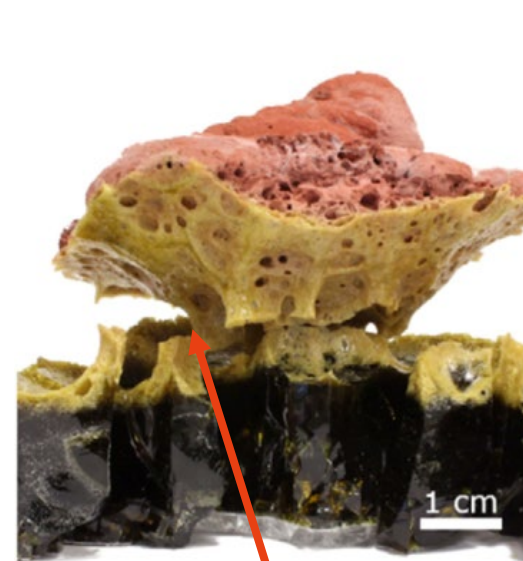
Regenerative end-port furnace for producing container glass

► 1) Develop advanced model for the batch-to-glass conversion

- Including both conversion kinetics (i.e., dependence of conversion on thermal history) and heat transfer in the batch

► 2) Understand the behavior of primary foam

- Especially the final foam decay



Extreme example of foam☺

Background & Motivation



UCT PRAGUE

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



Commissioning of WTP – Second melter heat up successfully completed, cold commissioning in progress (state as of April 2025)

Processing rate = waste loading x melting rate

Electric melters



Waste Treatment and Immobilization Plant (WTP)

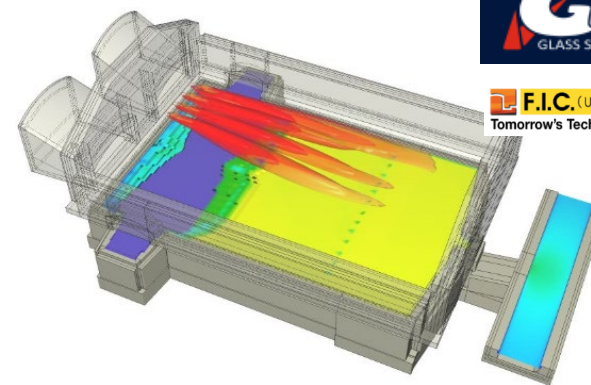
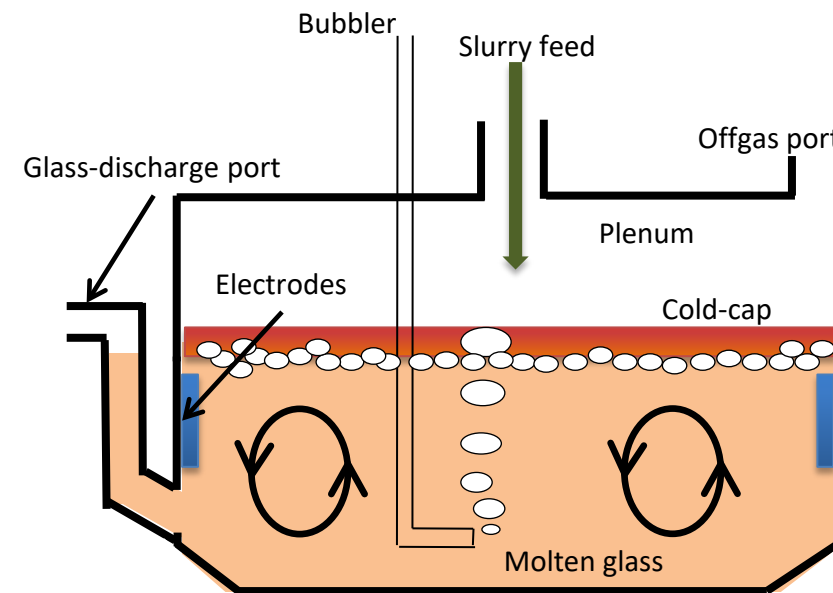


Slurry-fed Joule-heated Melter

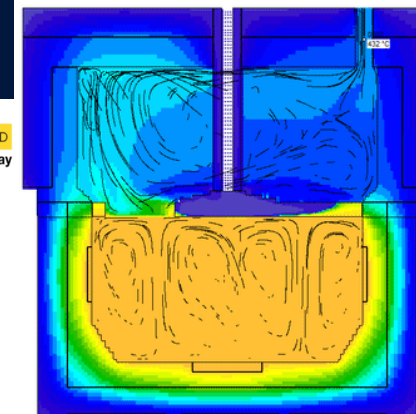


UCT PRAGUE

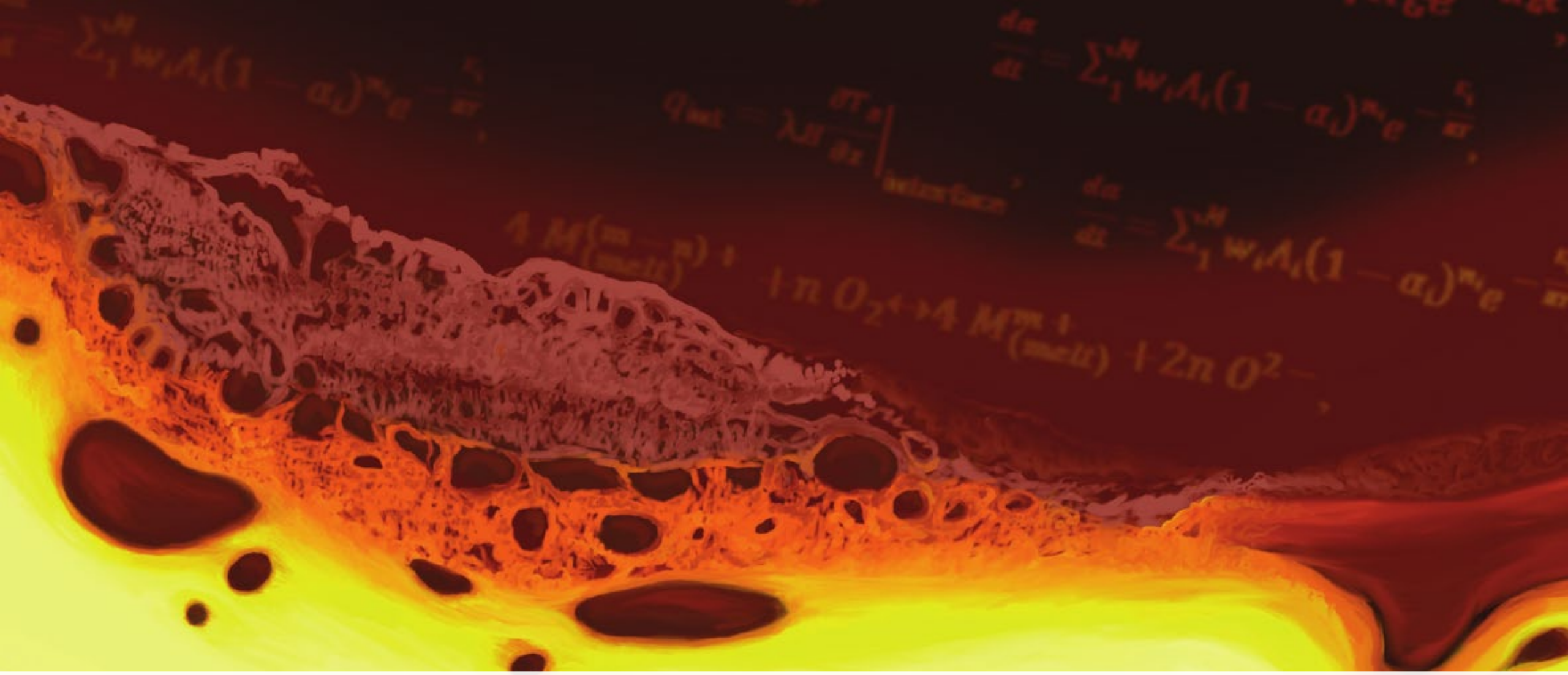
- ▶ Heat is delivered by Joule heating
- ▶ Glass melt is stirred by air bubbling
- ▶ Feed is poured from the top, dried slurry creates a layer of reacting materials (cold cap) floating on the melt
- ▶ Properties of cold-cap and molten glass determine the rate of melting



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Regenerative end-port furnace for producing container glass



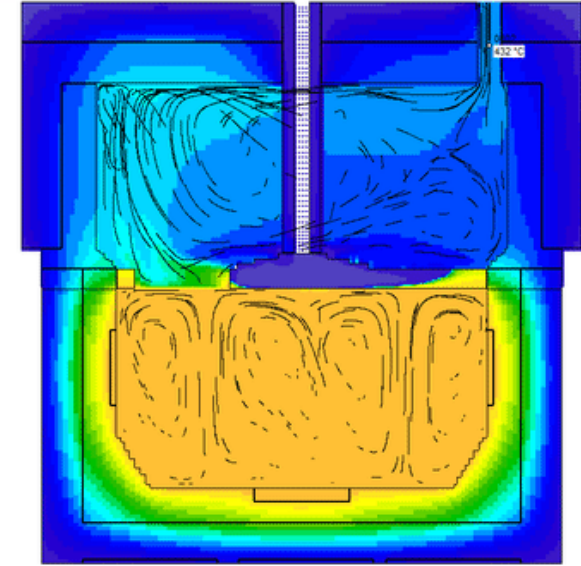
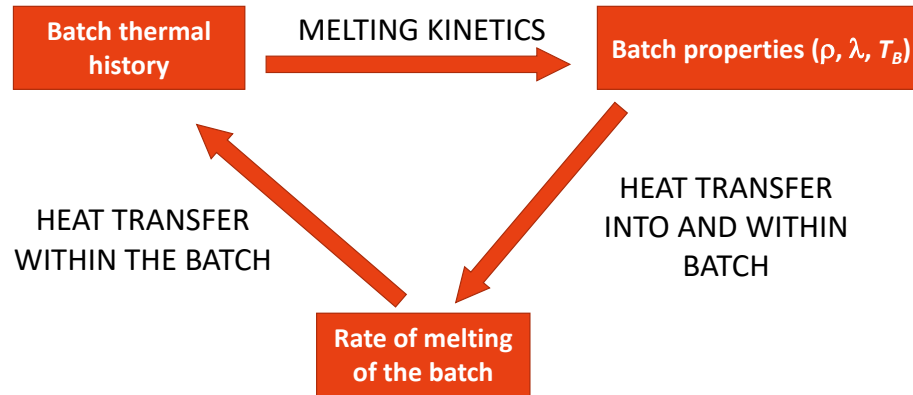
Kinetics of batch-to-glass conversion

Mathematical models of cold cap



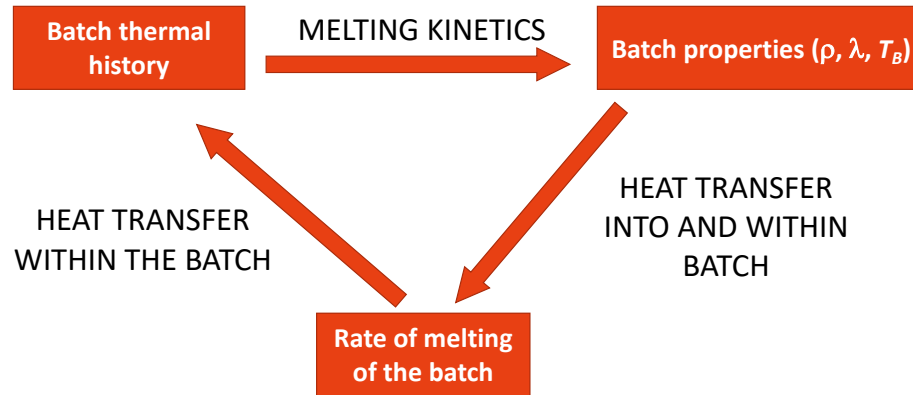
UCT PRAGUE

- Detailed model of a cold cap couples the energy and mass balances with equations describing the conversion kinetics

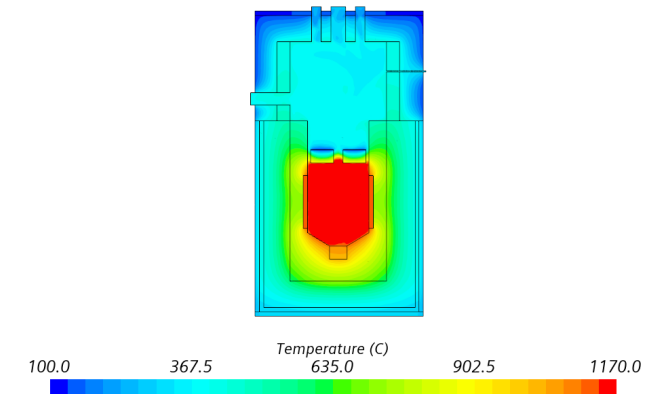
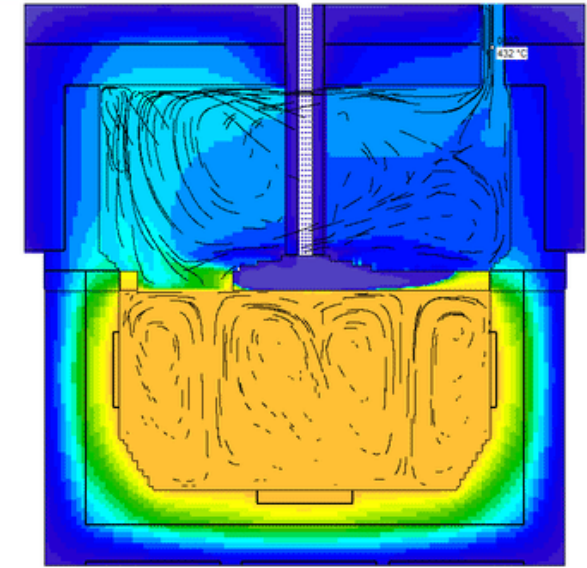


Mathematical models of cold cap

- ▶ Detailed model of a cold cap couples the energy and mass balances with equations describing the conversion kinetics



- ▶ While the general governing equations for the heat transfer and for the conversion kinetics are reasonably well understood, they are rarely coupled together
 - ❑ Without considering the batch thermal history, models are applicable only in a narrow range of conditions
- ▶ Cold cap model is linked to the CFD model using boundary conditions
 - ❑ Temperatures and heat fluxes at the cold cap bottom and top

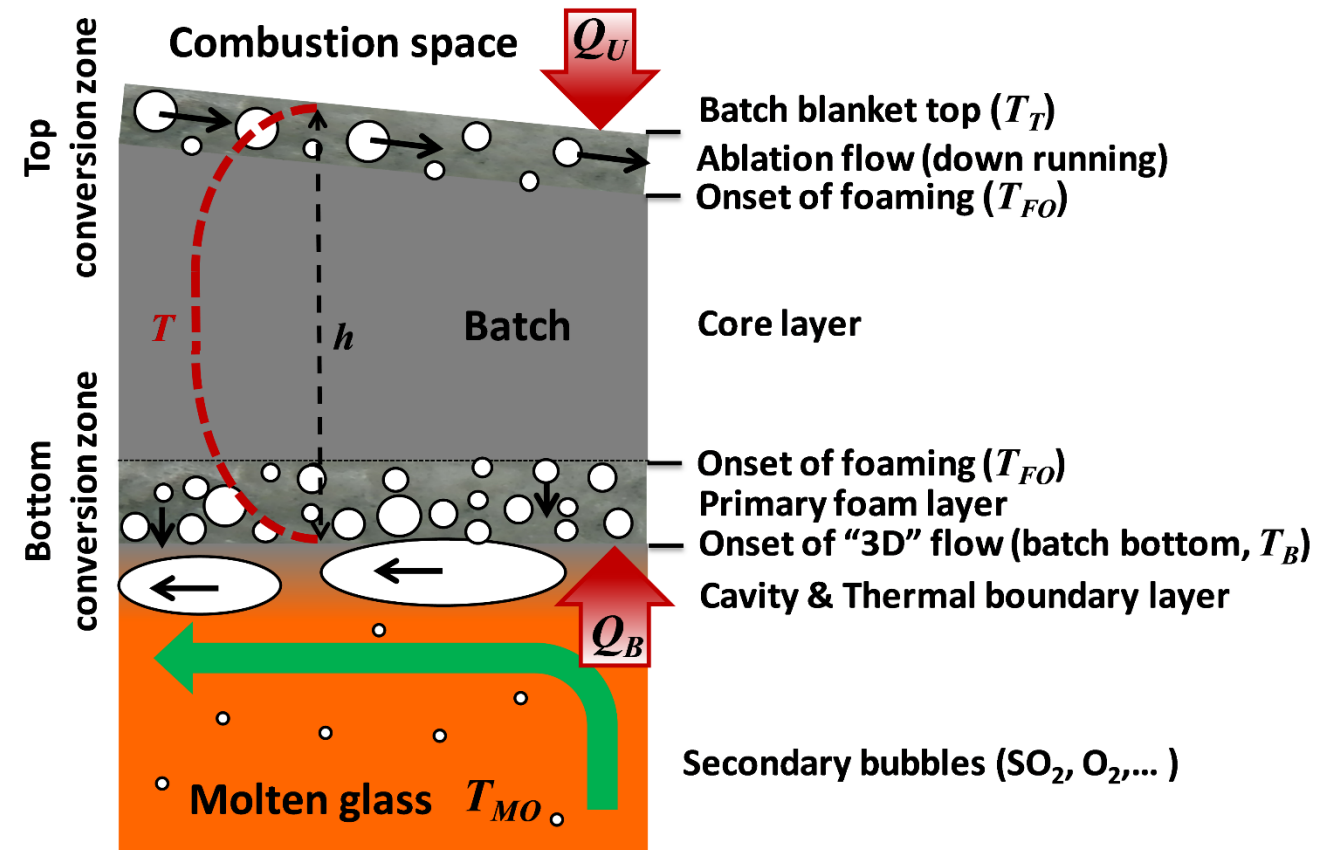


Analysis of kinetics of melting



UCT PRAGUE

- ▶ Processes occurring during batch melting are numerous and complex
 - ❑ Batch reactions leading to the production of glass-forming melt
 - ❑ Evolution of primary foam, its growth and collapse
 - ❑ Dissolution of solid particles (silica)
- ▶ Measure the kinetics of silica dissolution (XRD), gas evolution (TGA & EGA), and foam formation (FET & EGA)
- ▶ Estimate the effect of the conversion kinetics on the rate of melting



X-Ray diffraction (XRD)

- 3g samples heated in crucible
- Milled to powder
- PANalytical X'Pert3 Powder



Thermal Gravimetry (TGA)

- 1.5 g of batch
- N₂ atmosphere
- QMS 403C, NETZSCH



Evolved Gas Analysis (EGA)

- 1g heated in test tube with He gas flux
- Off-gases analyzed via GC-MS (Agilent)



Feed expansion tests (FET)

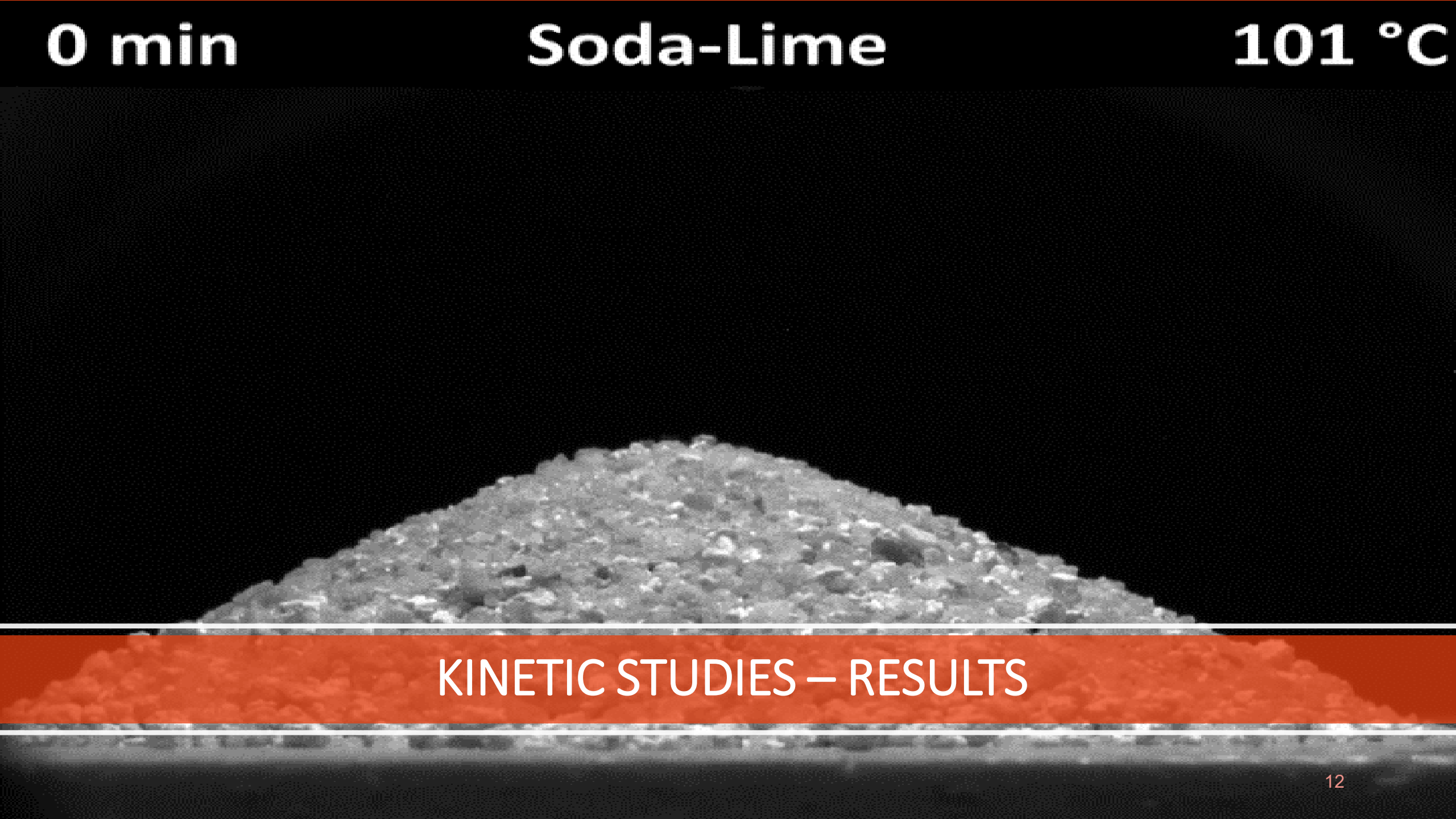
- 1.5 g batch in observation furnace
- Image analysis – sample volume



0 min

Soda-Lime

101 °C



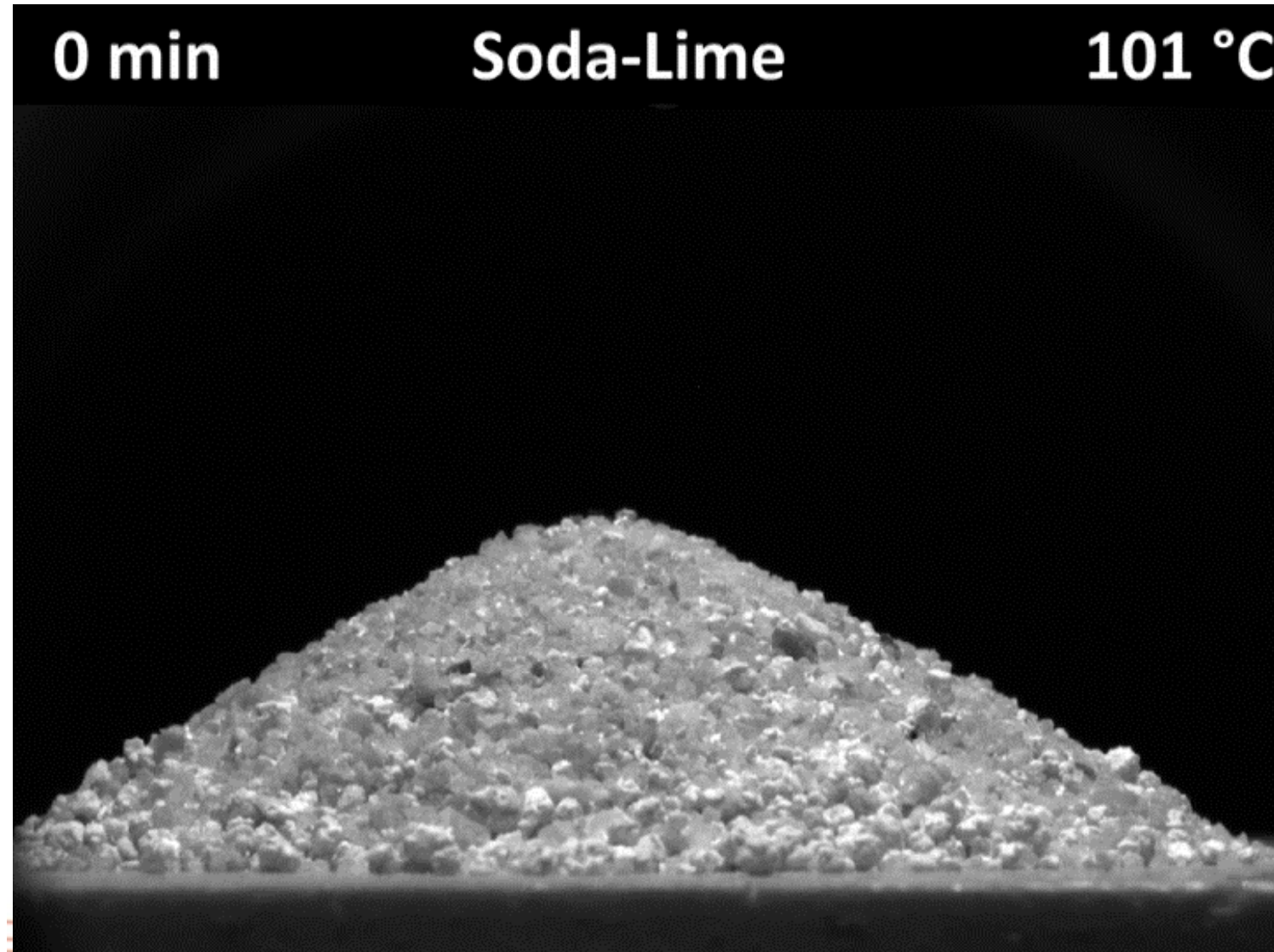
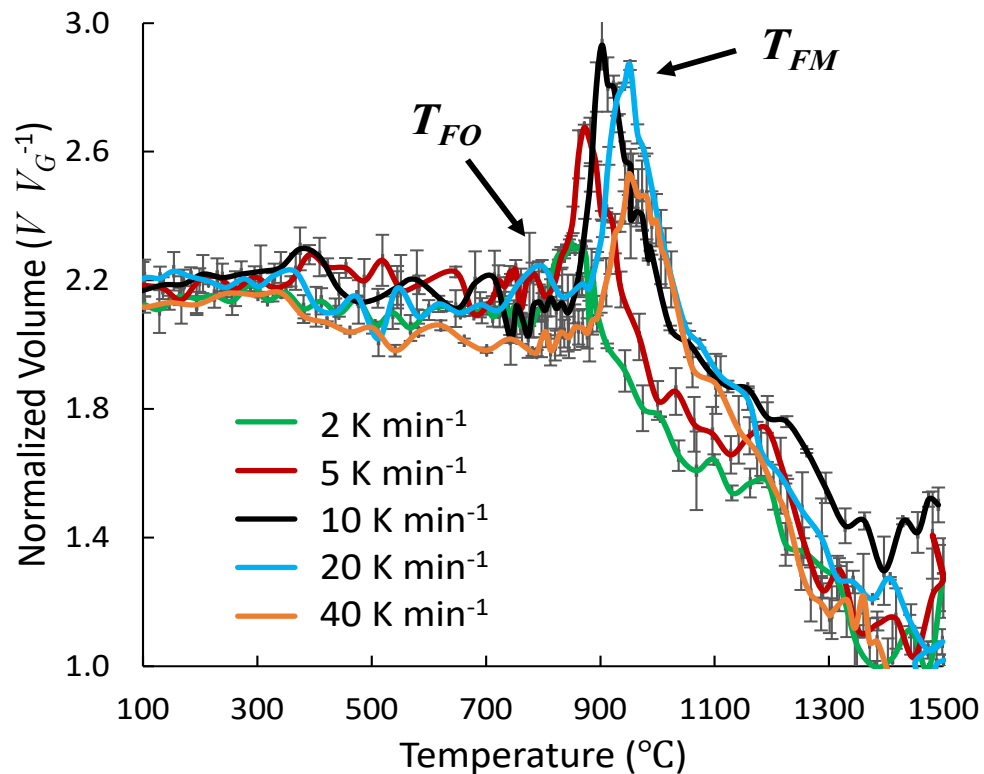
KINETIC STUDIES – RESULTS

Volume expansion – Feed expansion test



UCT PRAGUE

- ▶ The feed volume shifts to higher temperatures in response to faster heating

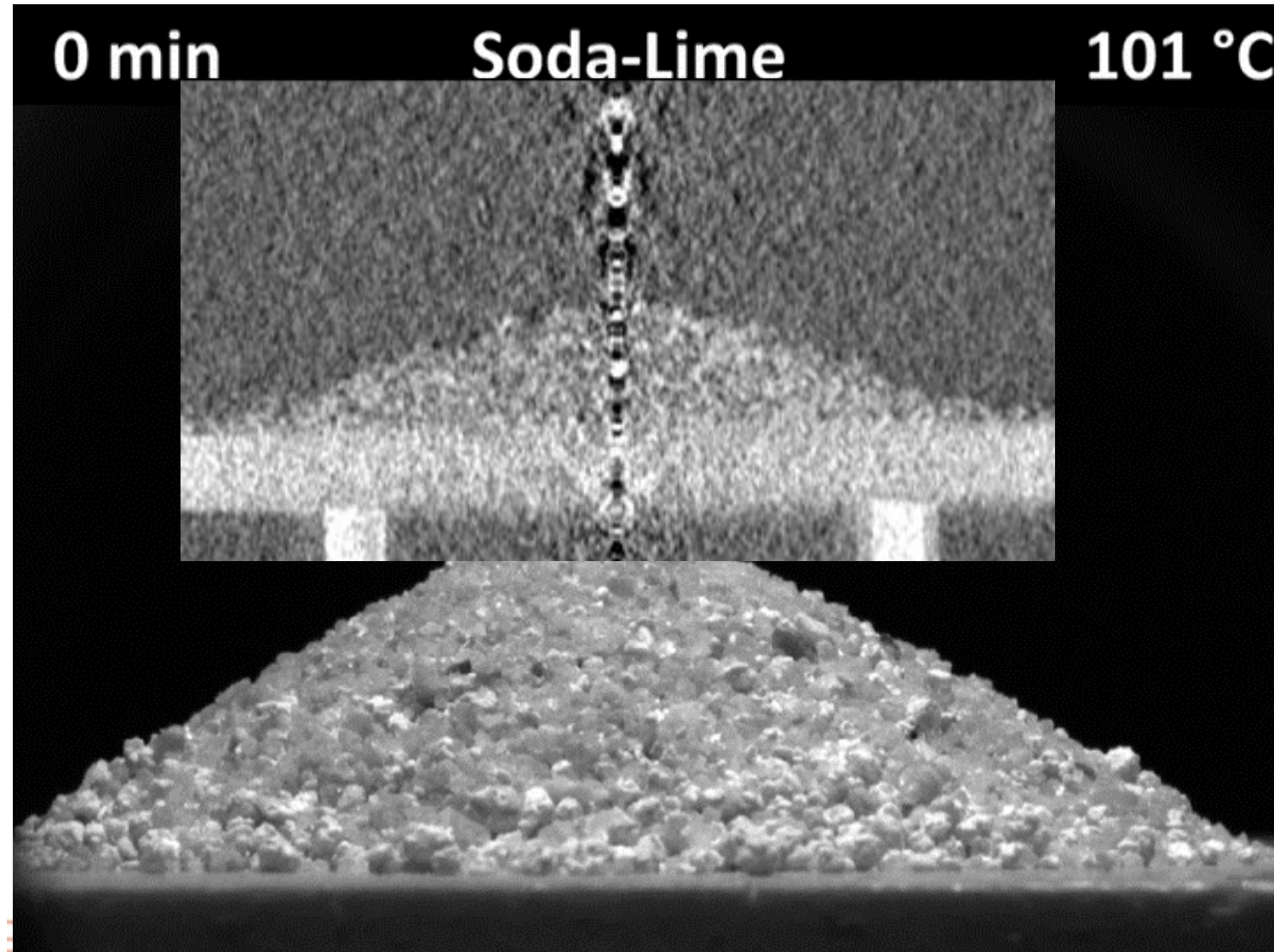
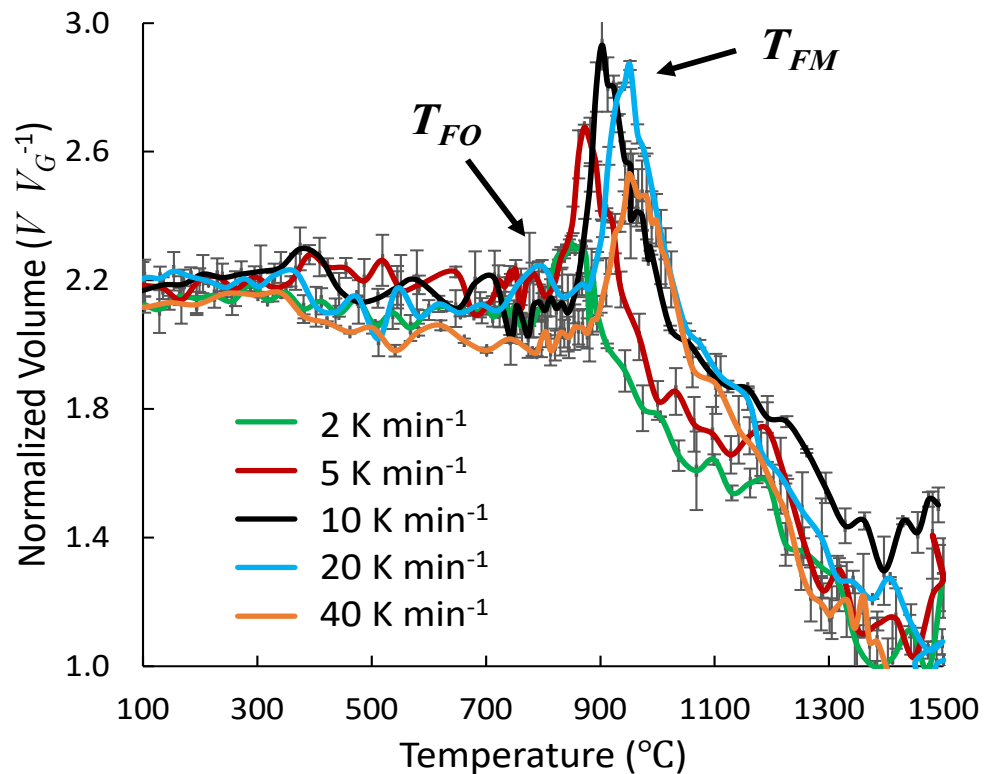


Volume expansion – Feed expansion test



UCT PRAGUE

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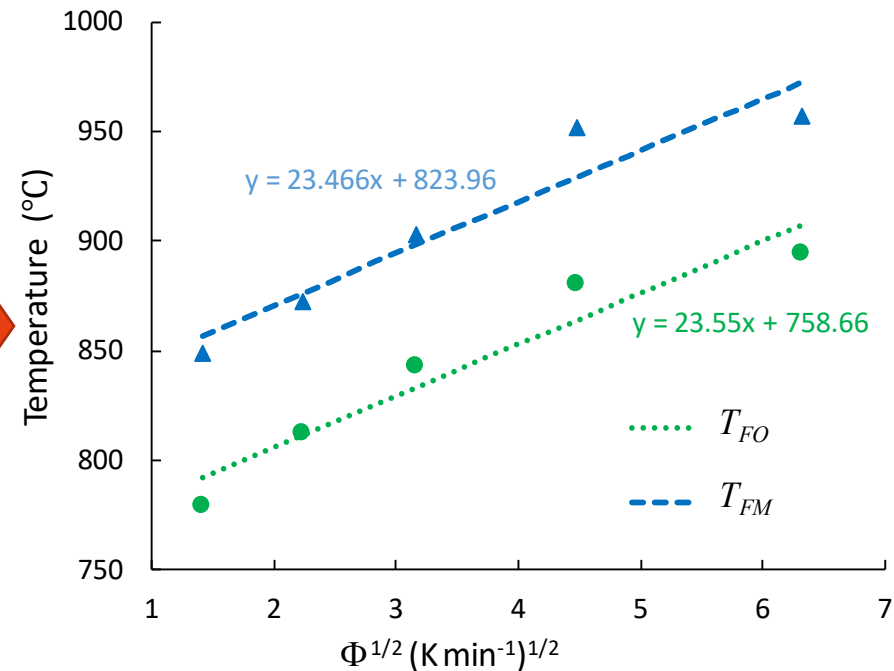
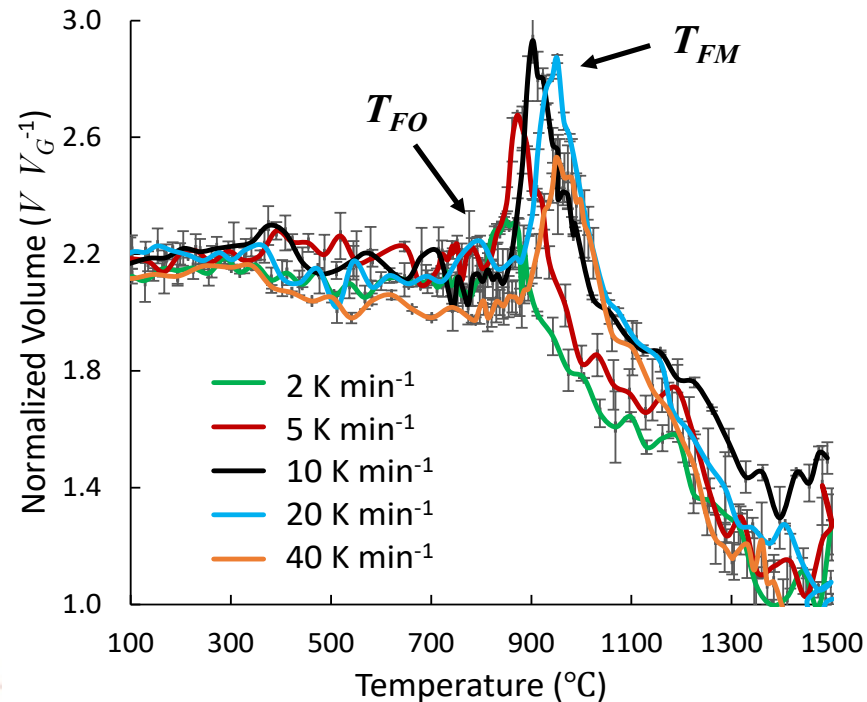


Volume expansion – Feed expansion test



UCT PRAGUE

- ▶ The foam onset and maximum temperatures increase with square root of heating rate
- ▶ The foam decay also shifts to higher temperatures

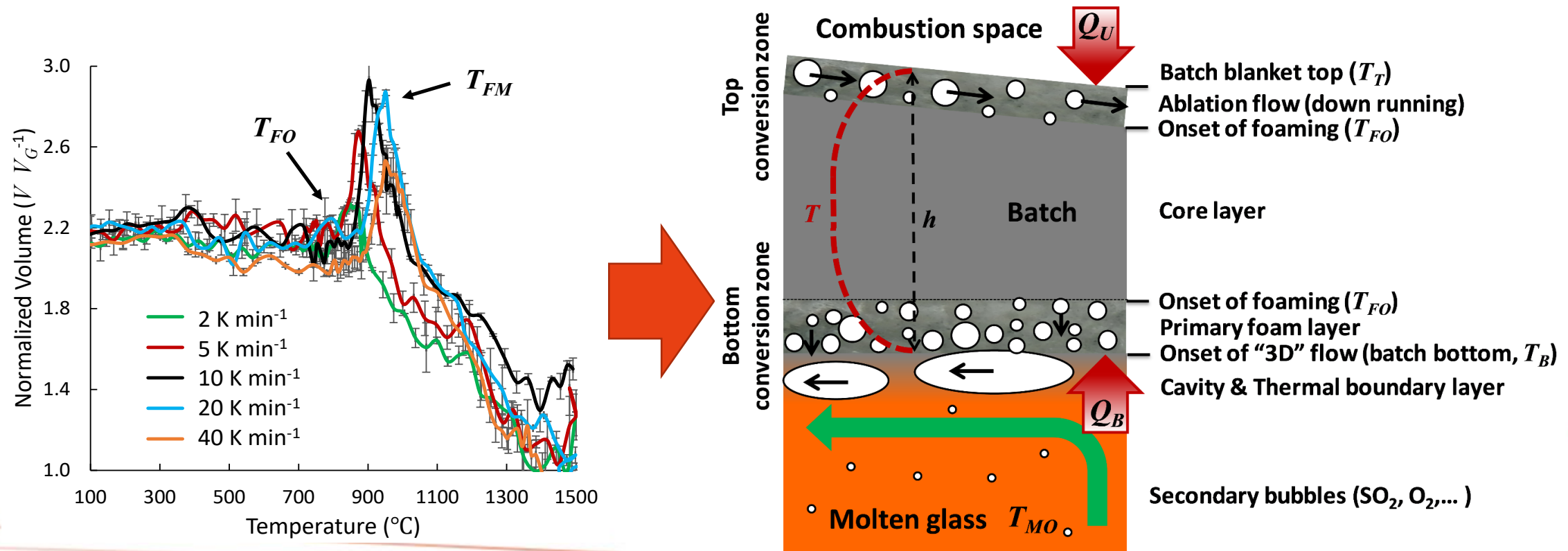


Volume expansion – Feed expansion test



UCT PRAGUE

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Volume expansion – Feed expansion test



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Cover Photo

Built in 1914 by Swiss architect Gustav Gull, the Zurich Amtshaus IV, housing council offices, has been thoroughly renovated from 2000 to 2003. In this project, the colour glass ARTISTA® of Schott Spezialglas AG was applied for rebuilding the glass ceiling of the central courtyard. Modelled on the original panes, ARTISTA® was especially converted into a seemingly historic, ornamented cast glass in order to retain the overall historical impression. In total, 161 type "White 0189" panes (135.6 m²) of thickness 6 mm were produced. The largest of these panes are (62.0 × 160.4) cm² in size. In order to ensure security regarding the overhead glazing, the panes are coated with a splinter protection foil. (Photo: M. Rothkegel)

Glaswerkstätte & Leuchtenmanufaktur M. Rothkegel OHG, Huberstraße 2a, D-97064 Würzburg, Tel.: +49(0)931 60096-0, Fax: +49(0)931 60096-19, E-mail: info@glaswerkstaette.de

SCHOTT Spezialglas AG, Hüttenstraße 1, D-31073 Grünspan, Tel.: +49(0)5187 771-413, Fax: +49(0)5187 771-1413, E-mail: udo.ahlers@schott.com

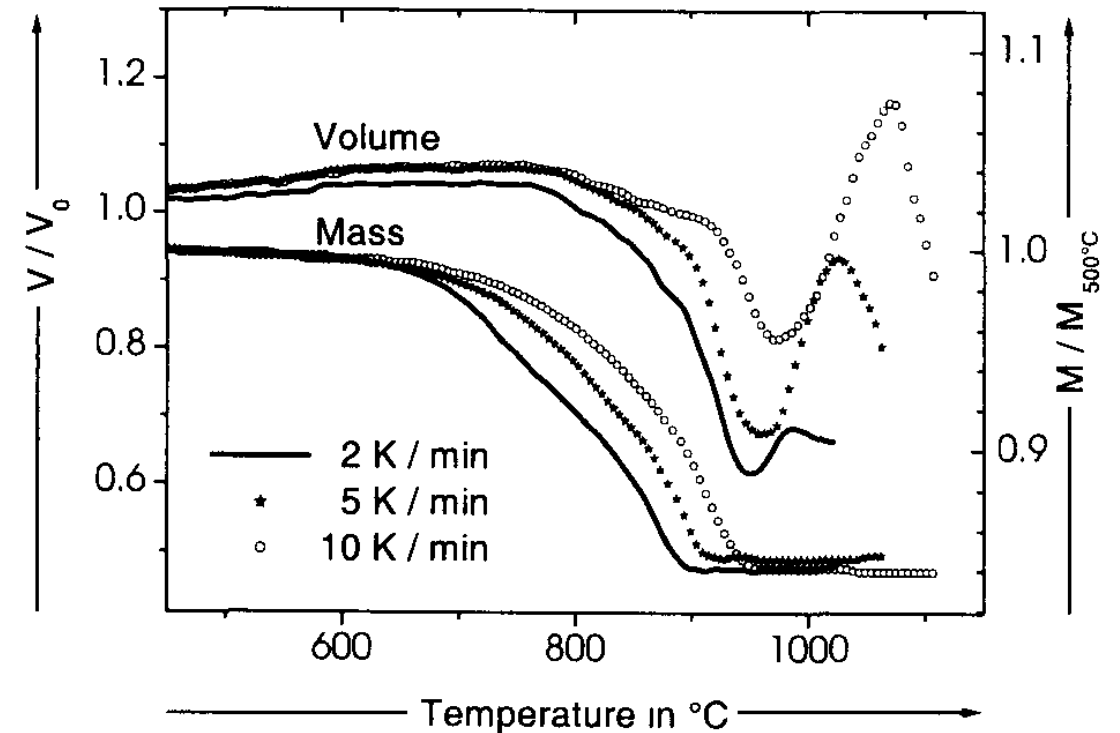


Figure 5. Volumetric and mass change during heating of type 1 batch with different heating rates.

Raether, F. and M. Krauss, *In Situ Measurements of Batch Glass During Melting*. Glass Science and Technology, 2004. **77**: p. 118-123.

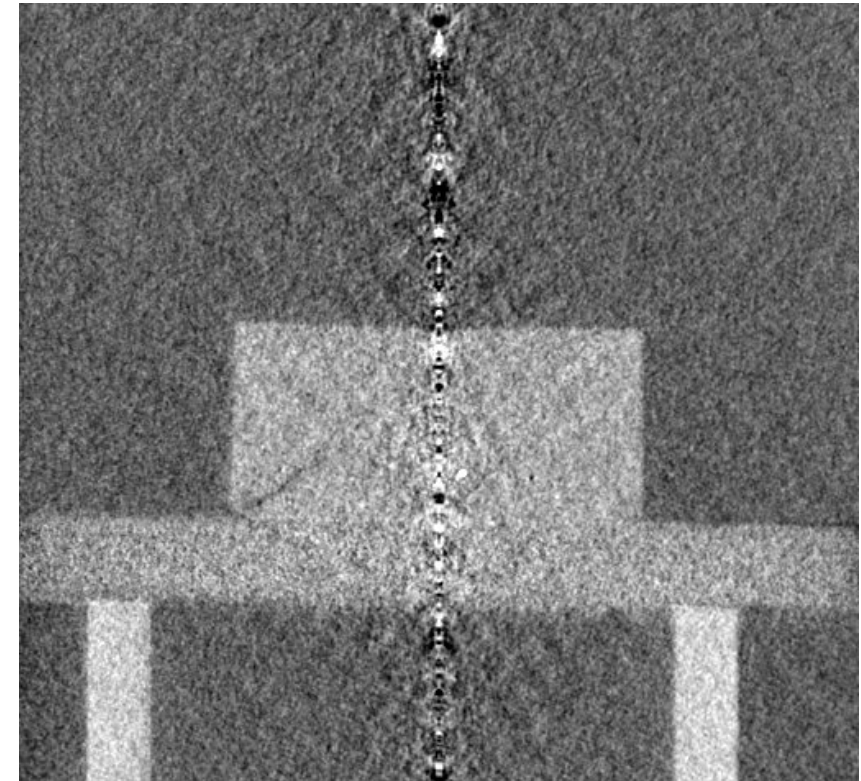
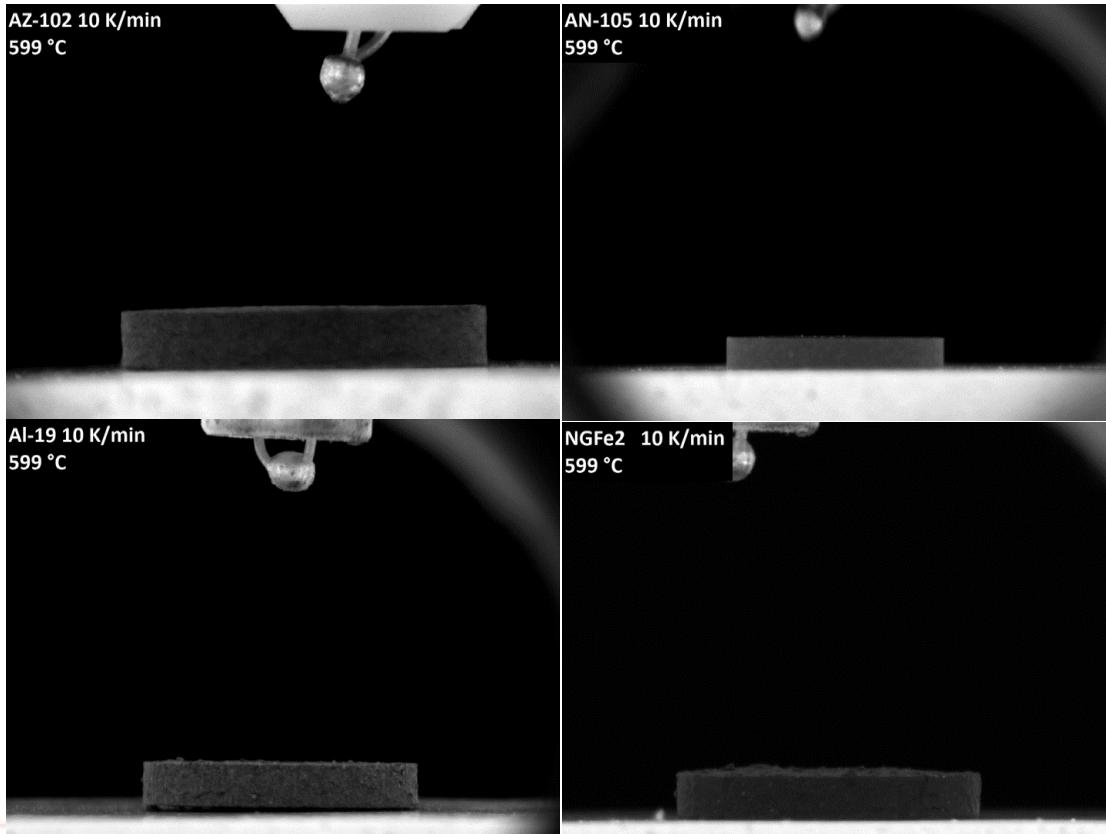
Foaming experiments

Al-19 (nuclear waste feed)



UCT PRAGUE

- ▶ HTVO
- ▶ X-ray CT observation



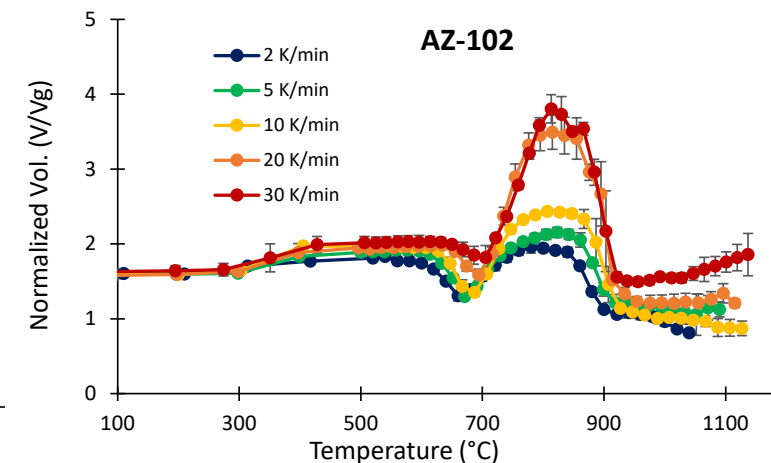
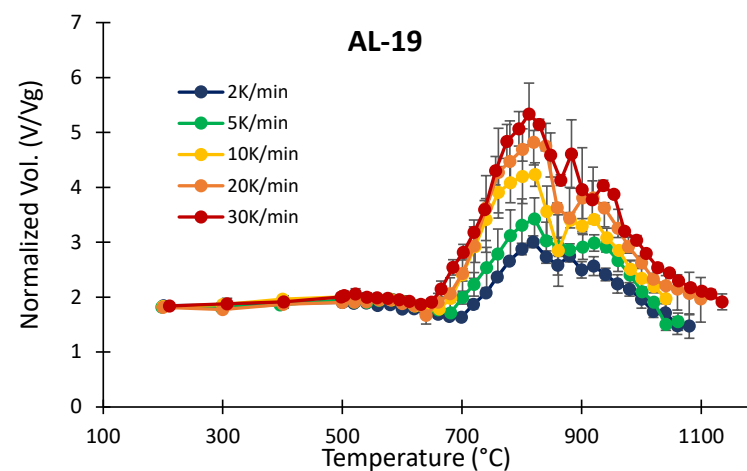
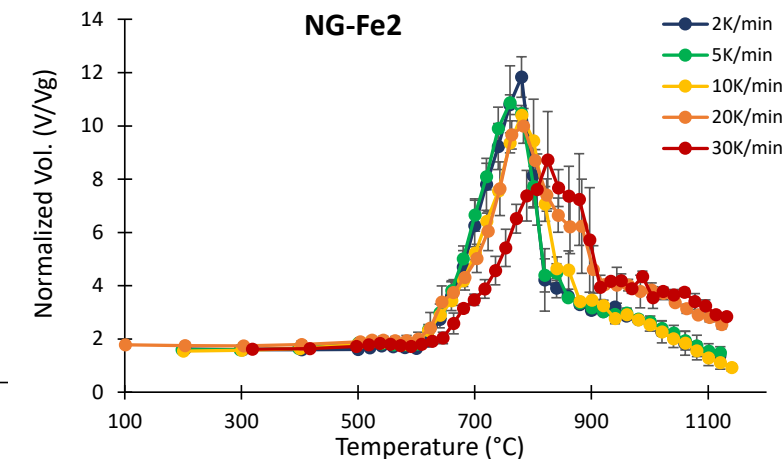
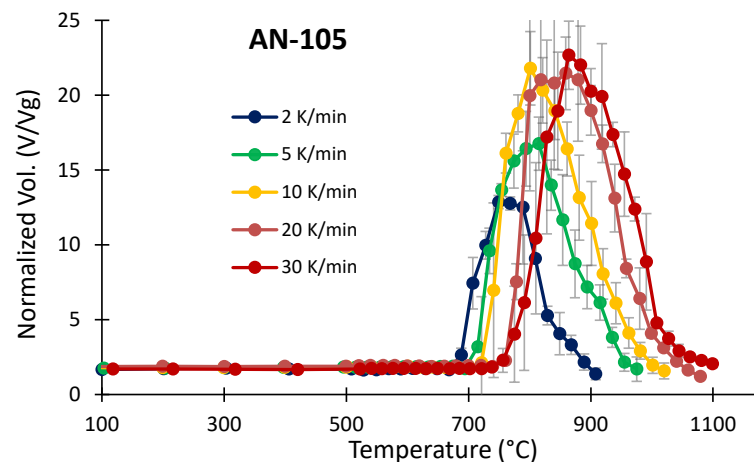
Kinetics of melting –nuclear waste feeds



UCT PRAGUE

- ▶ Kinetic processes dependent on temperature history (heating rate)
- ▶ In thermally activated processes, characteristic temperatures increase with increasing heating rate (such as gas evolution peaks observed by TGA and EGA)

□ In our previous work, we found that characteristic temperatures related to gas evolution, silica dissolution, and foaming all depend on the thermal history in a similar way

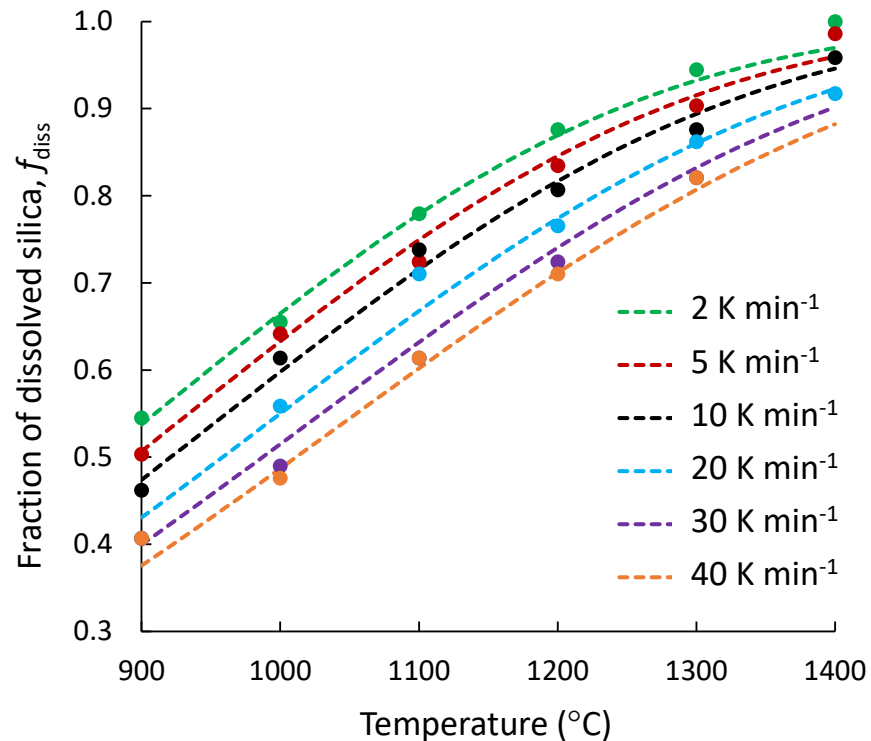


Dissolution of silica (XRD) – Container glass

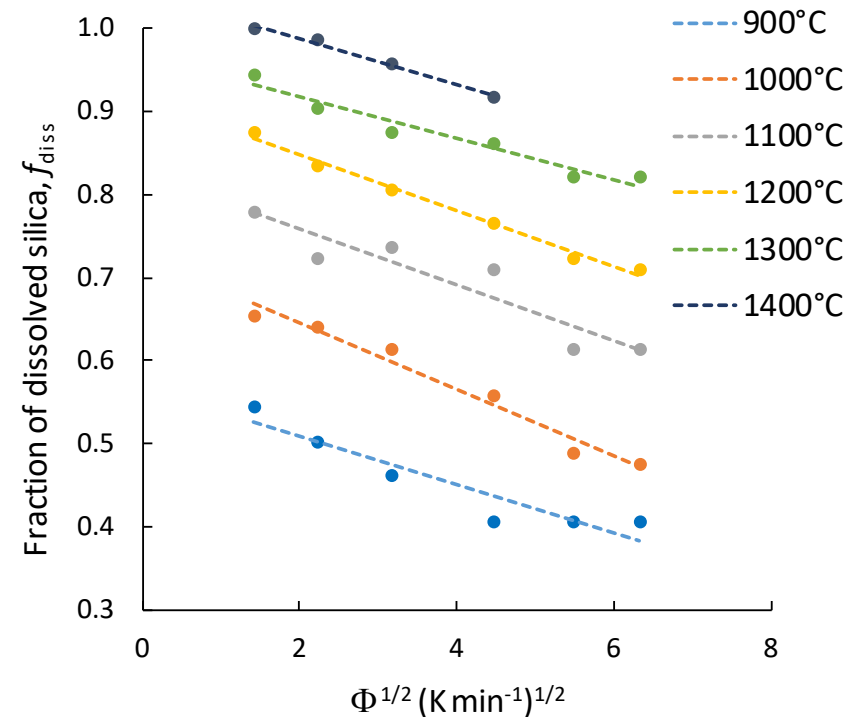


UCT PRAGUE

- Fraction of silica dissolved, f_{diss} , shifts to higher temperatures in response to faster heating
- ▣ At a constant temperature, f_{diss} depends almost linearly on the square root of heating rate



$$f_{diss} = 1 - \exp \left[- \left(\frac{T/T_0}{(1 + \sqrt{\Phi/\Phi_f})} \right)^{p_1} \right]$$



T Temperature
 Φ Heating rate
 T_0, Φ_f, p Fitting parameters

Gas Evolution (TGA and EGA)



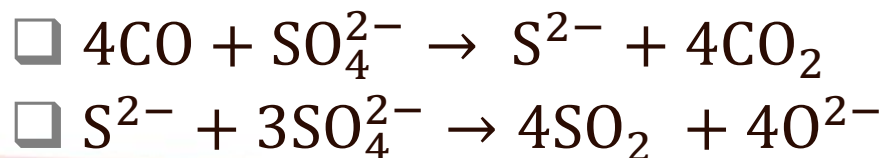
UCT PRAGUE

► Limestone decrepitation $\sim 400^\circ\text{C}$

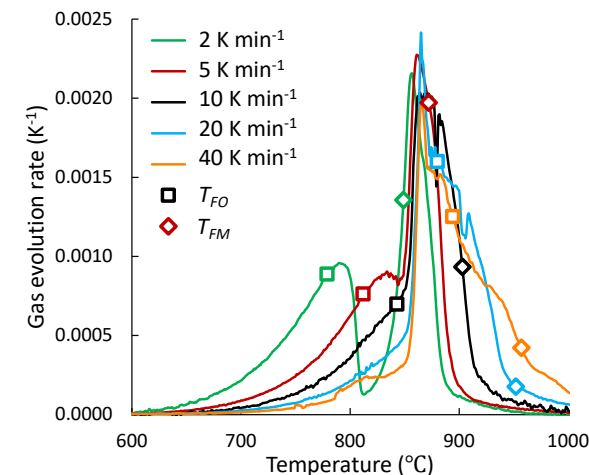
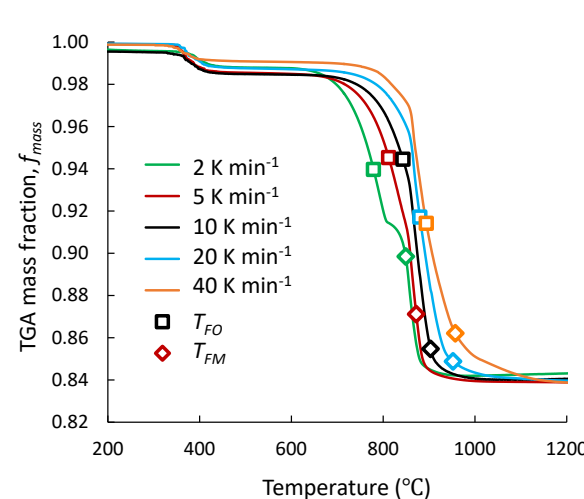
► CO_2 begins to evolve at $\sim 600^\circ\text{C}$ and continues up to $\sim 1100^\circ\text{C}$

- Two peaks visible at slower rates – first peak corresponds to decomposition of CaCO_3 and its reaction with solid silica sand, second peak occurs when melting soda considerably accelerates its reaction with silica
- Decrease between the two peaks caused by the formation of double carbonate

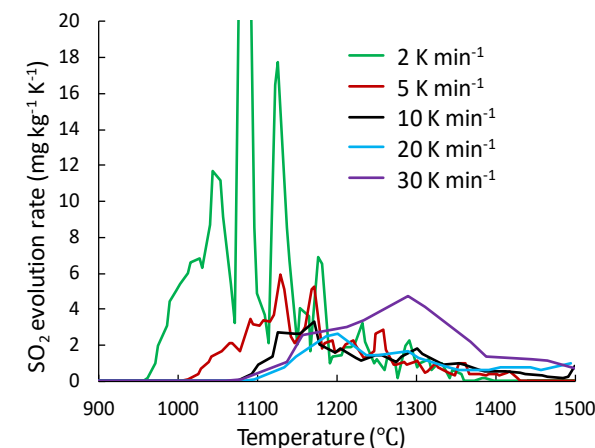
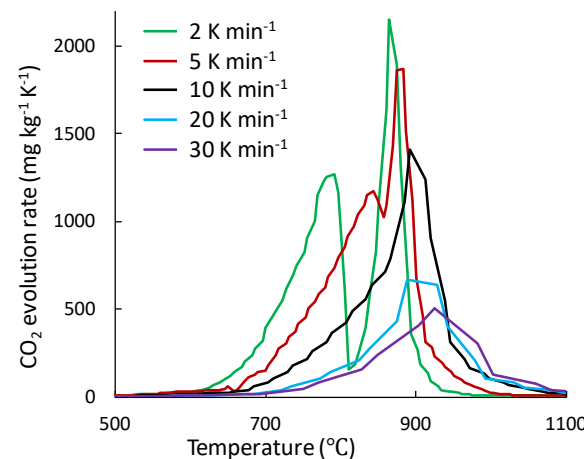
► SO_2 is produced starting from 1000°C



TGA



EGA

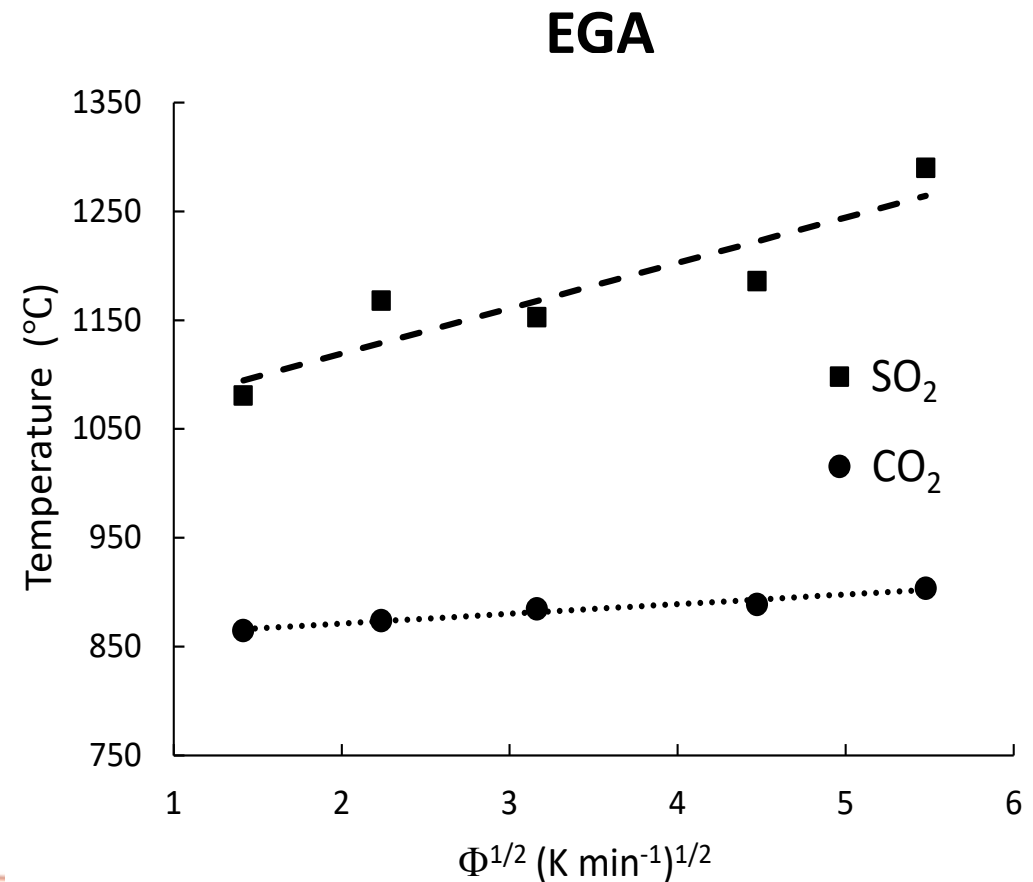
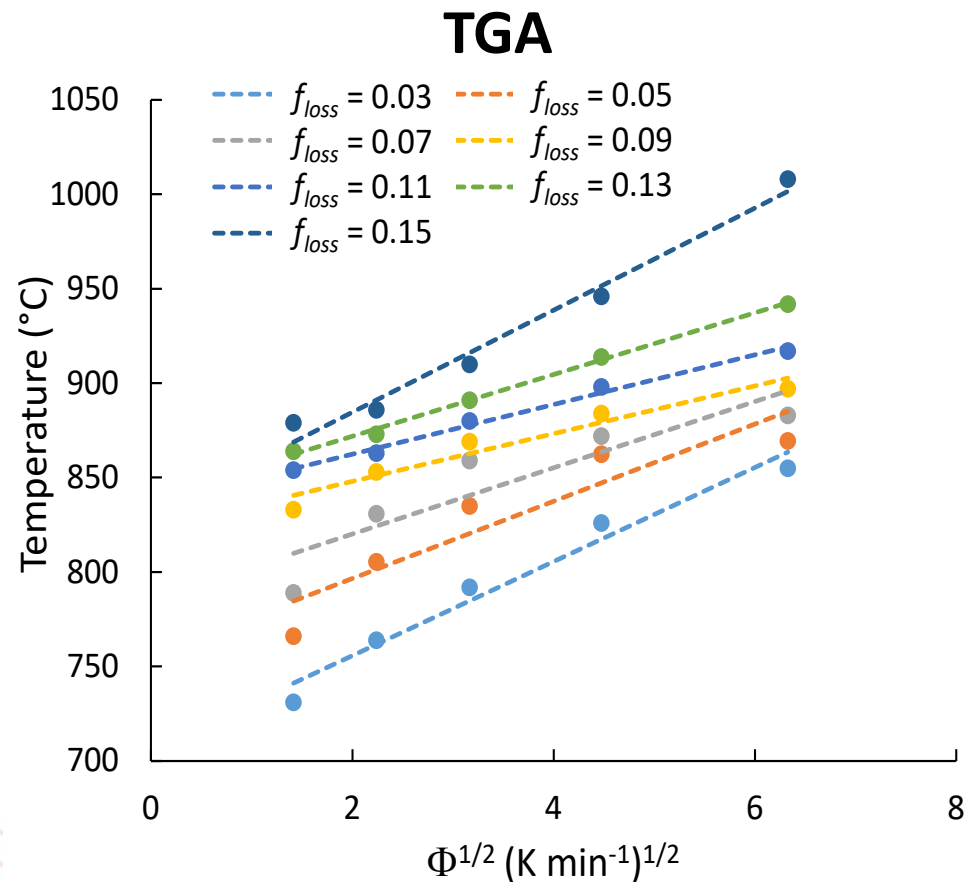


Gas Evolution (TGA and EGA)



UCT PRAGUE

- The gas evolving reactions shift to higher temperatures linearly with the square root of the heating rate – this dependence is nearly identical to that of silica dissolution





DISCUSSION

Effects of kinetics on melting rate

- ▶ The melting rate depends on the heat flux to the batch from below and above

$$j_B = \xi_B (T_{MO} - T_B) \Delta H^{-1}$$

- ▶ Characteristic temperatures increase with the square of root of heating rate

$$T_B = T_{B0} [1 + (\Phi / \Phi_B)^{1/2}]$$

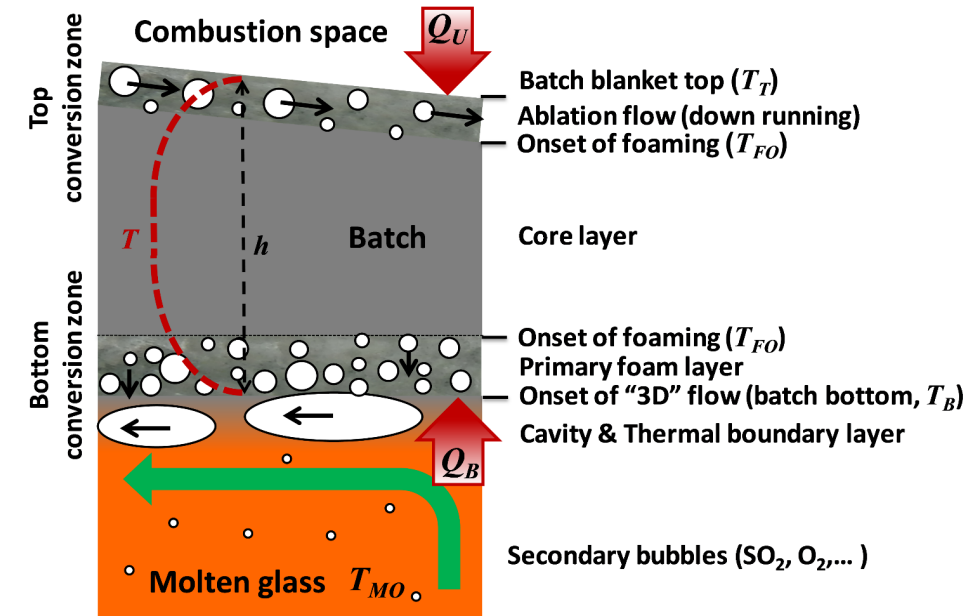
- ▶ Within the batch blanket, heating rate increases with the square of melting rate

- ❑ Higher melting rate – particles move faster downwards
- ❑ Higher heat flux – the reaction layer is thinner

$$\Phi \sim C j^2$$

- ▶ This means that characteristic temperatures increase approx. linearly with melting rate

$$T_B = T_{B0} [1 + K j_B]$$



Effects of kinetics on melting rate

- ▶ The melting rate depends on the heat flux to the batch from below and above

$$j_B = \xi_B (T_{MO} - T_B) \Delta H^{-1} \quad \longrightarrow \quad j_B = \xi_B (T_M - T_{B0} [1 + K j_B]) \Delta H^{-1}$$

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$$T_B = T_{B0} [1 + (\Phi / \Phi_B)^{1/2}]$$

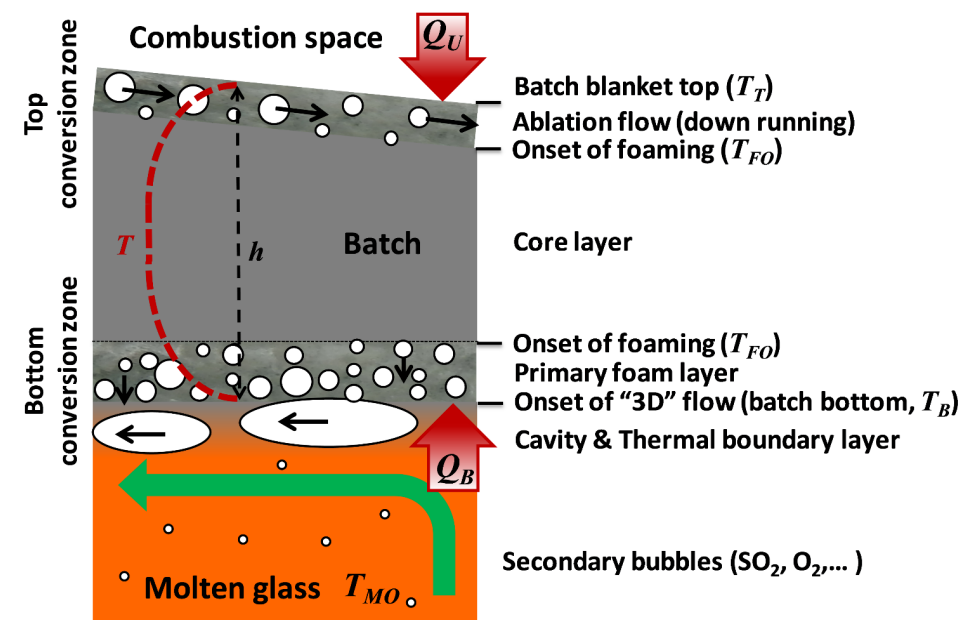
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Effects of kinetics on melting rate

- ▶ The melting rate depends on the heat flux to the batch from below and above

$$j_B = \xi_B (T_{MO} - T_B) \Delta H^{-1} \quad \longrightarrow \quad j_B = \frac{\xi_B (T_M - T_{B0}) \Delta H^{-1}}{1 + \xi_B K T_{B0} \Delta H^{-1}}$$

- ▶ Characteristic temperatures increase with the square of root of heating rate

$$T_B = T_{B0} [1 + (\Phi / \Phi_B)^{1/2}]$$

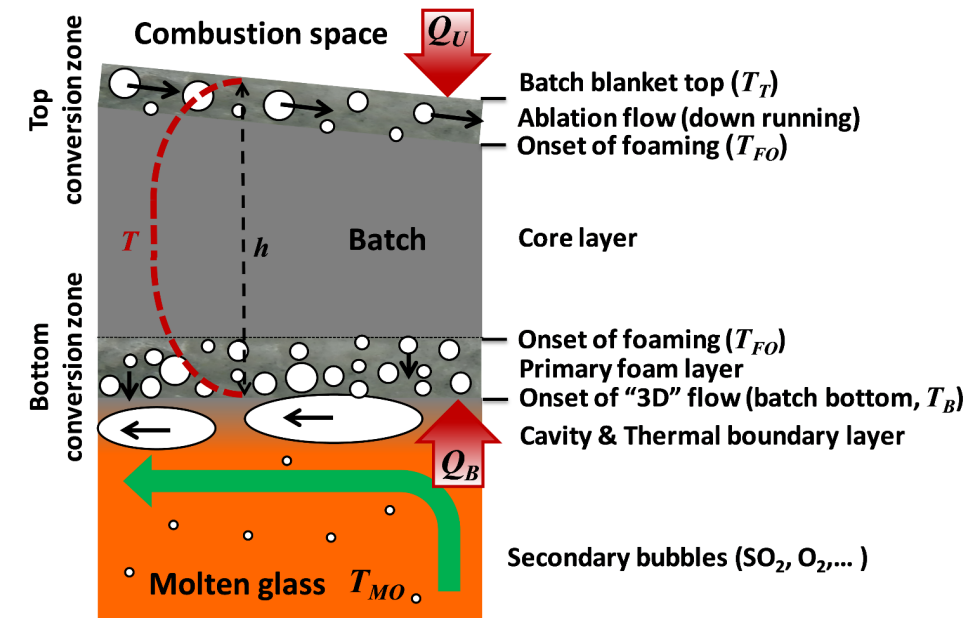
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- ▶ This means that characteristic temperatures increase approx. linearly with melting rate

$$T_B = T_{B0} [1 + K j_B]$$



Effects of kinetics on melting rate

- The melting rate depends on the heat flux to the batch from below and above

$$j_B = \xi_B (T_M - T_{B0} [1 + K j_B]) \Delta H^{-1} \quad \longrightarrow \quad j_B = \frac{\xi_B (T_M - T_{B0}) \Delta H^{-1}}{1 + \xi_B K T_{B0} \Delta H^{-1}}$$

Effects of kinetics on melting rate

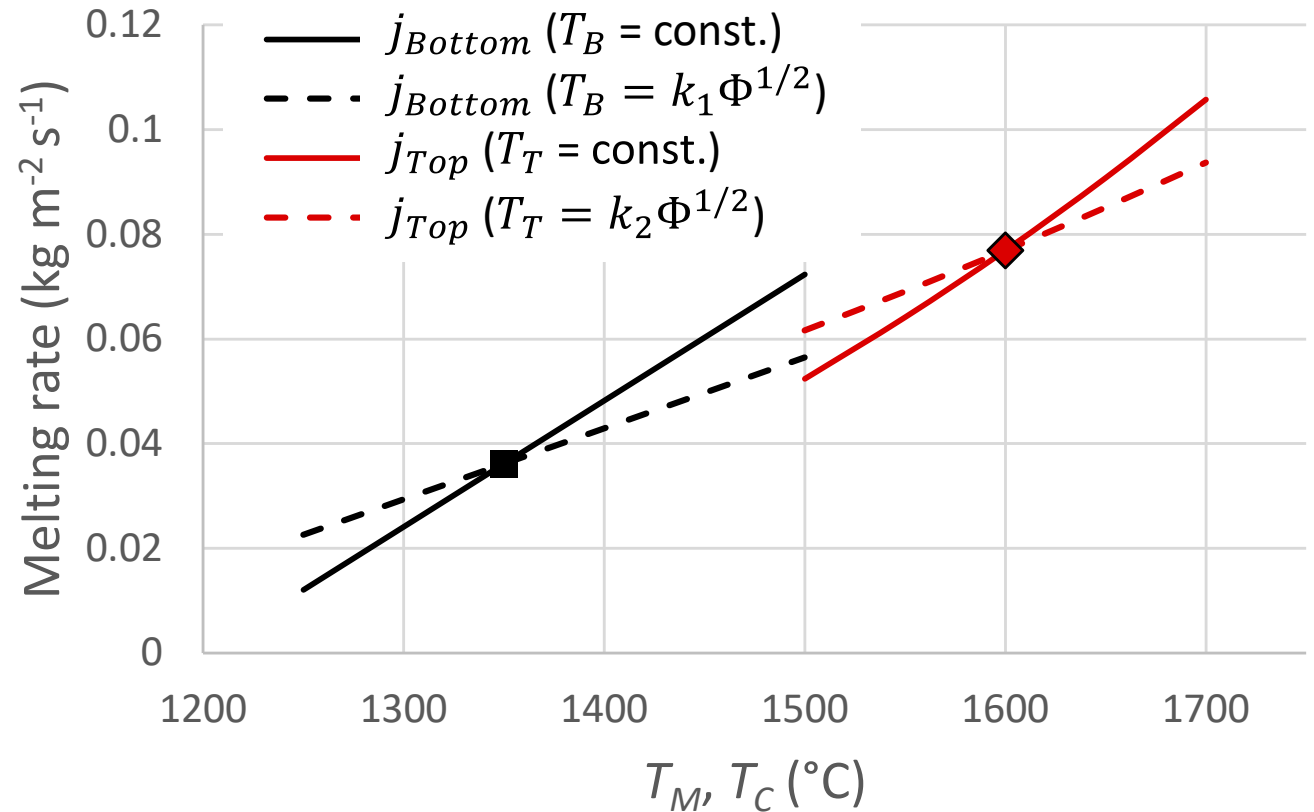
► Black dashed line

$$j_B = \frac{\xi_B(T_M - T_{B0})\Delta H^{-1}}{1 + \xi_B K T_{B0} \Delta H^{-1}}$$

► Black solid line

$$j_B = \xi_B(T_{MO} - T_B)\Delta H^{-1}$$

► Melting rate affected less when effect of kinetics is considered



Kinetic models



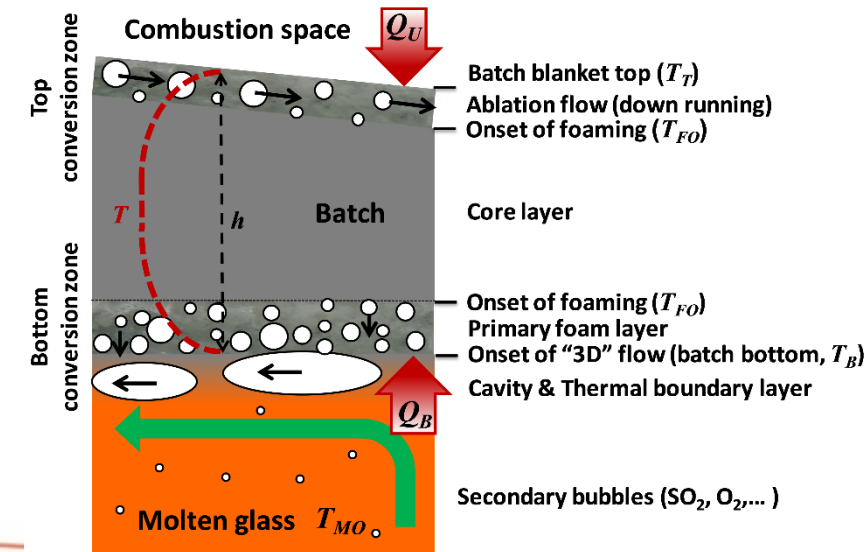
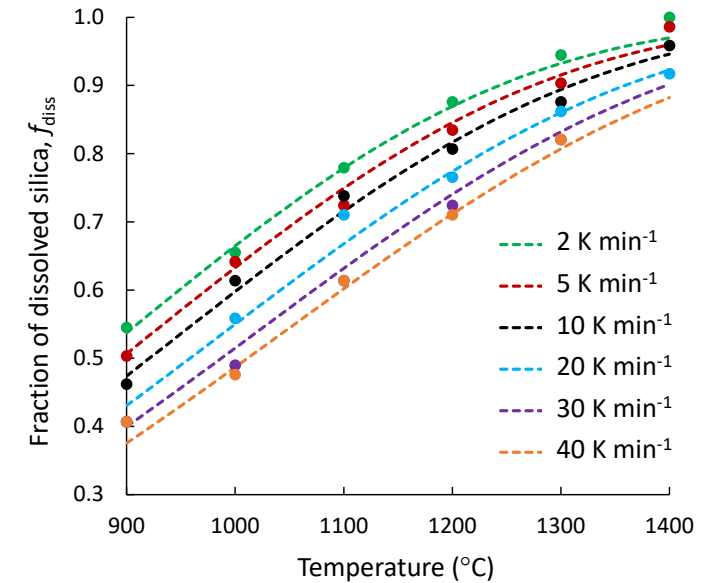
UCT PRAGUE

$$f_{diss} = 1 - \exp \left[- \left(\frac{T/T_0}{(1 + \sqrt{\Phi/\Phi_f})} \right)^{p_1} \right]$$

T Temperature
 Φ Heating rate
 T_0, Φ_f, p Fitting parameters

- ▶ Valid only for constant Φ
- ▶ In general, Φ increases exponentially during melting
- ▶ To describe the conversion process in the batch layer, we need a classical kinetic equation

$$\frac{df}{dt} = F[f(t), T(t)]$$



Kinetic models



UCT PRAGUE

$$f_{diss} = 1 - \exp \left[- \left(\frac{T/T_0}{(1 + \sqrt{\Phi/\Phi_f})} \right)^{p_1} \right]$$

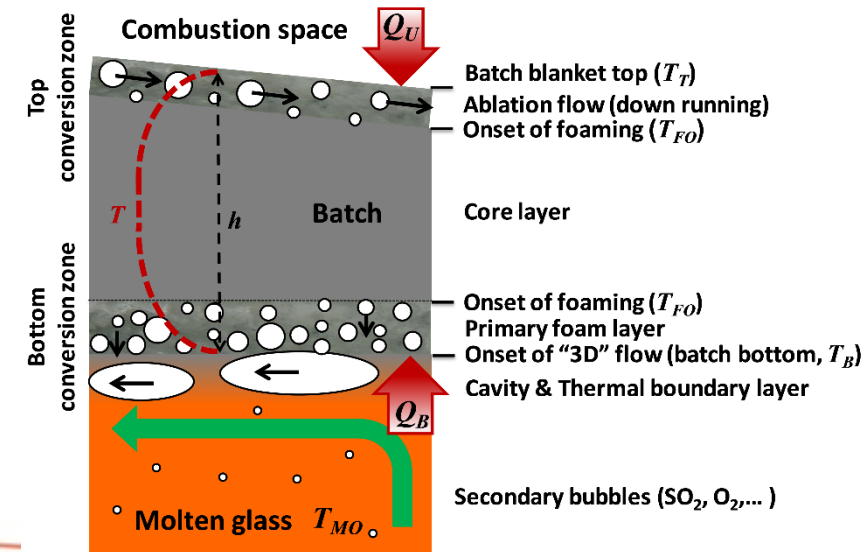
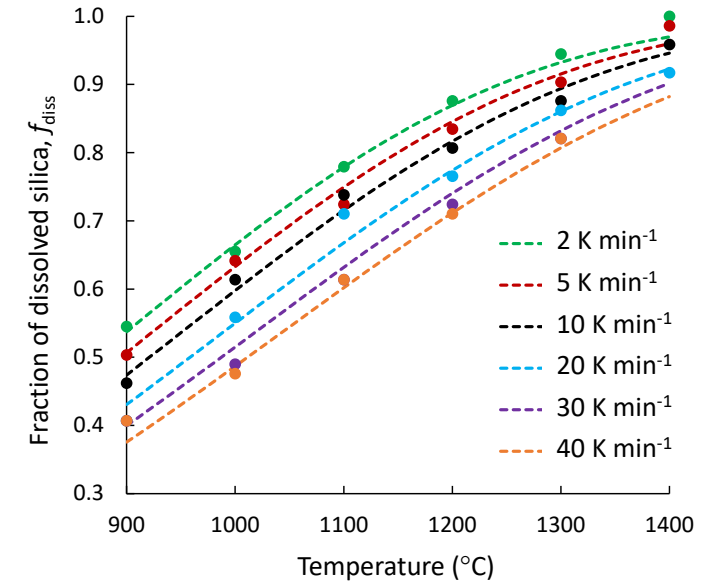
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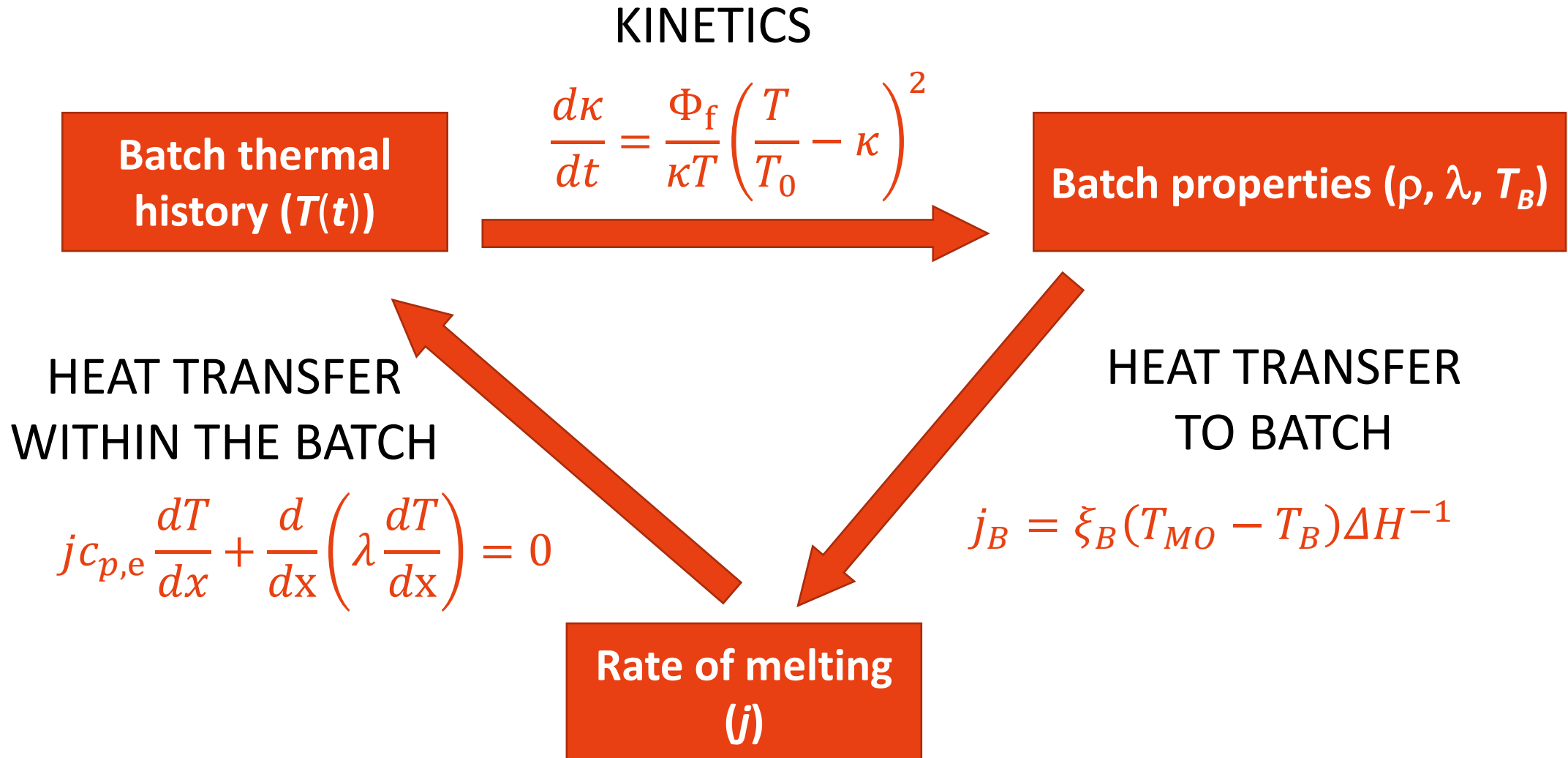
- To describe the conversion process in the batch layer, we need a classical kinetic equation $\frac{df}{dt} = F[f(t), T(t)]$

❑ Stretched-Exponential $\frac{d\kappa}{dt} = \frac{\Phi_f}{\kappa T} \left(\frac{T}{T_0} - \kappa \right)^2 \quad \kappa = (-\ln(1 - f))^{\frac{1}{p}}$

❑ Sestak-Berggren $\frac{df_i}{dt} = A_i f_i^m (1 - f_i)^n \exp \left(- \frac{E_i}{RT} \right)$



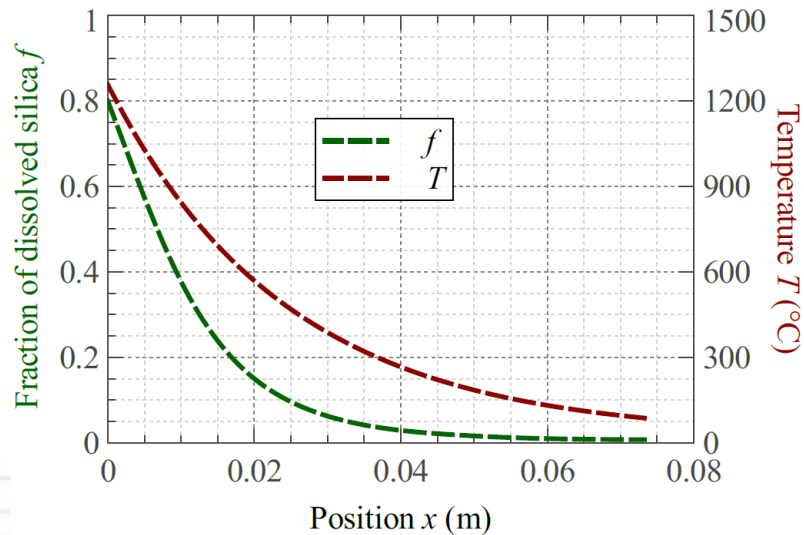
Batch melting Triangle



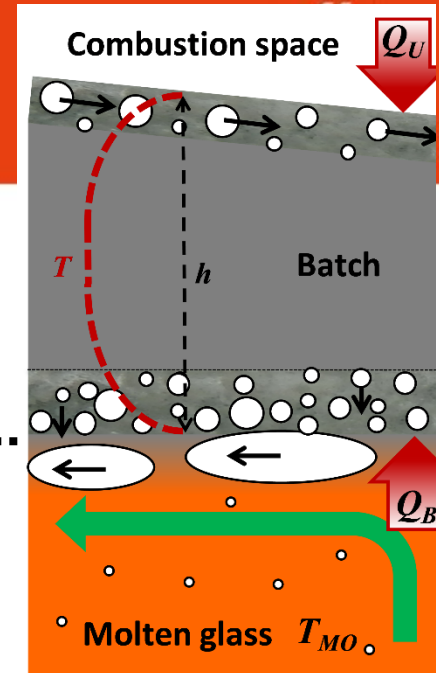
Results

► Temperature profile and silica dissolution

- ▣ Using constant batch properties, exponential profiles



T_B, f_B
($x = 0$)

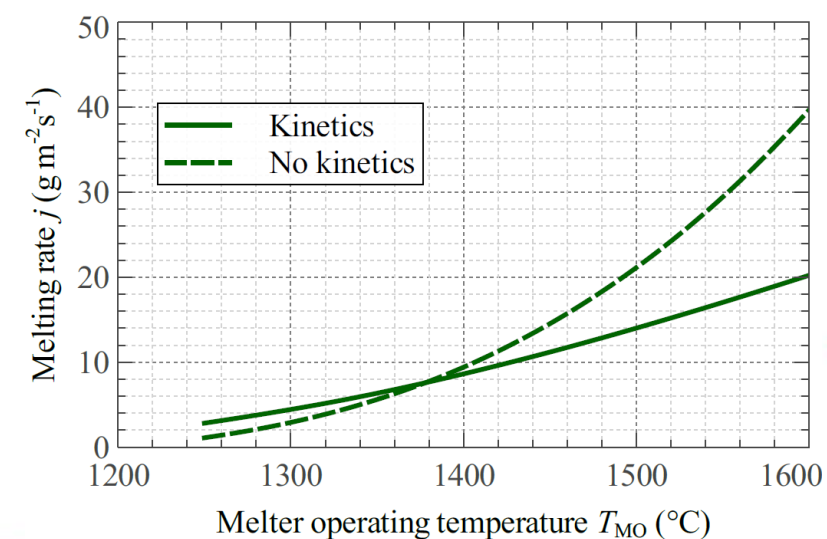
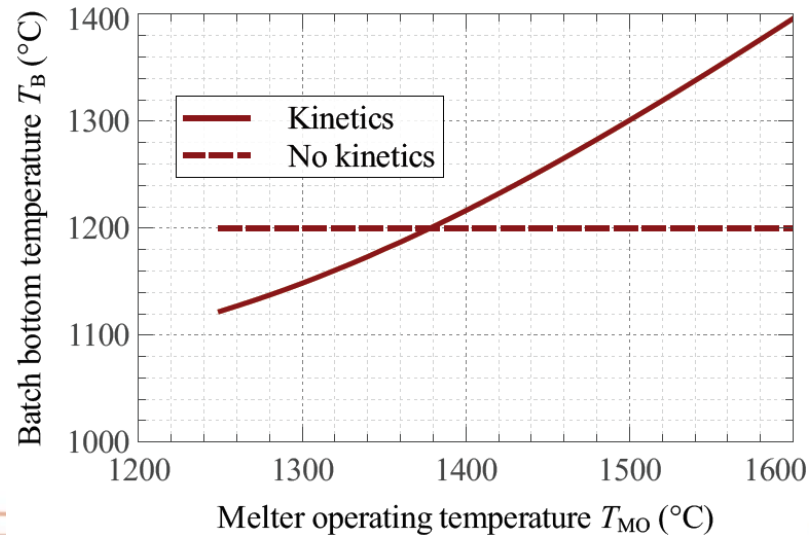
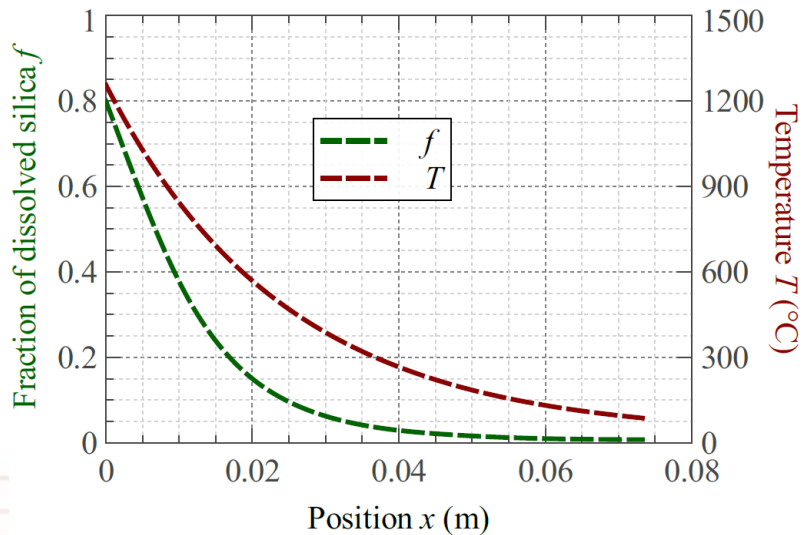
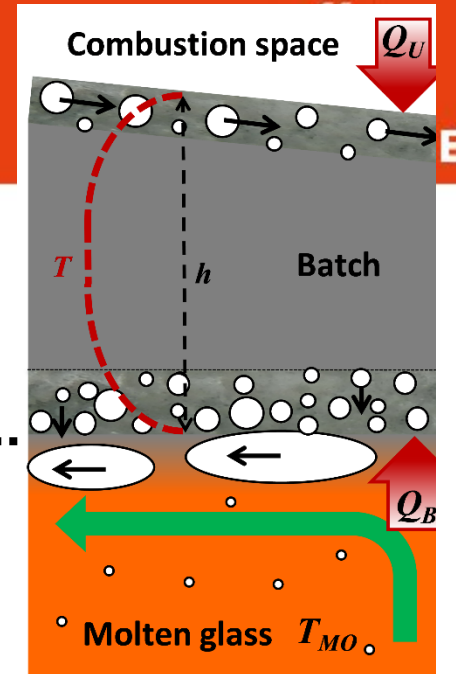


Results

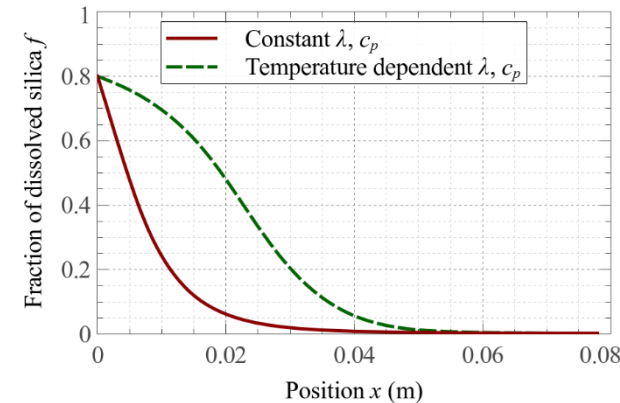
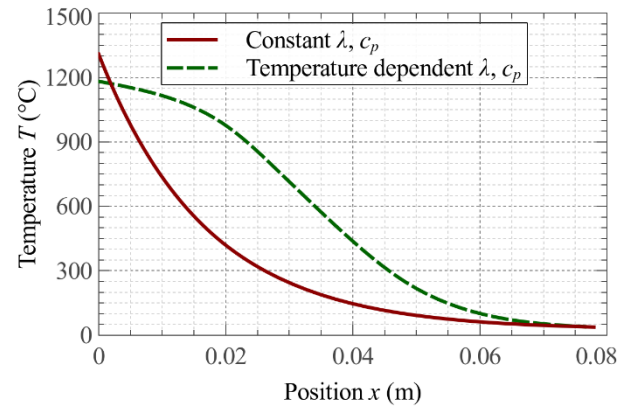
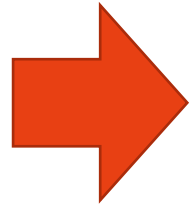
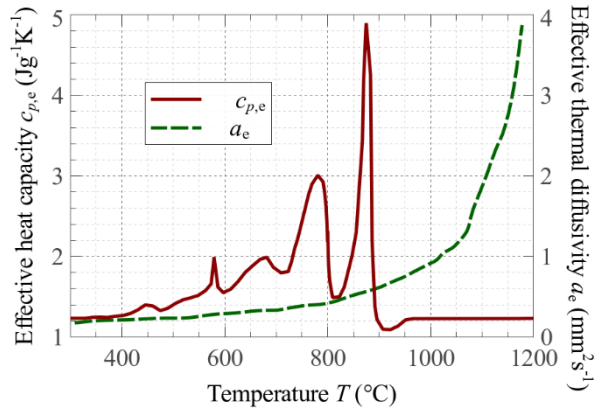
► Temperature profile and silica dissolution

▣ Using constant batch properties, exponential profiles

► When kinetics is considered, temperature at the batch bottom is changing, and melting rate increases less than when kinetics is not considered

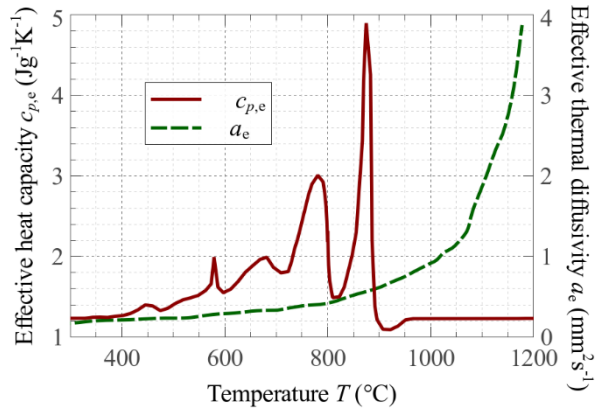


► Temperature-dependent material properties

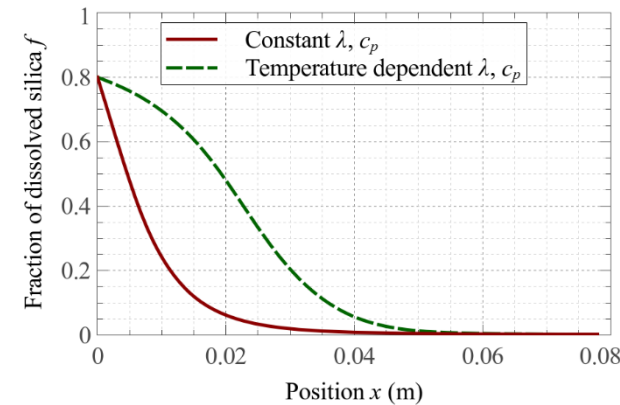
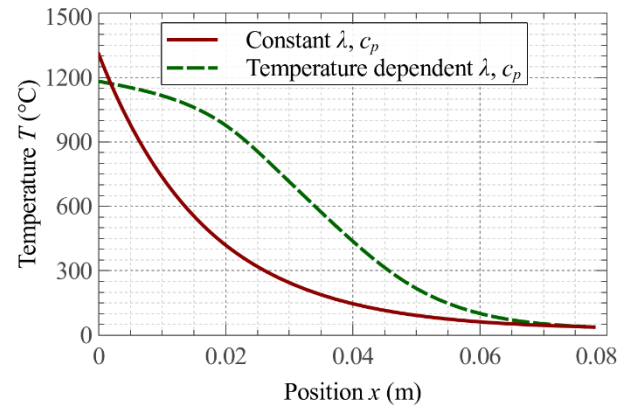
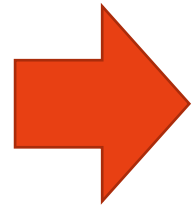


Doi, Y., et al. (2018). "Thermal diffusivity of soda-lime-silica powder batch and briquettes." *Glass Technology - European Journal of Glass Science and Technology Part A* 59(3): 92-104.

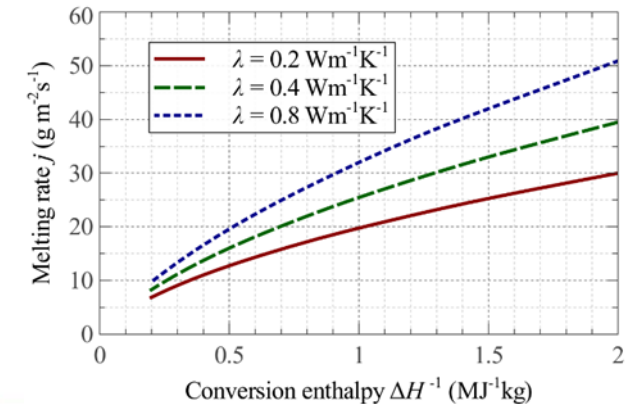
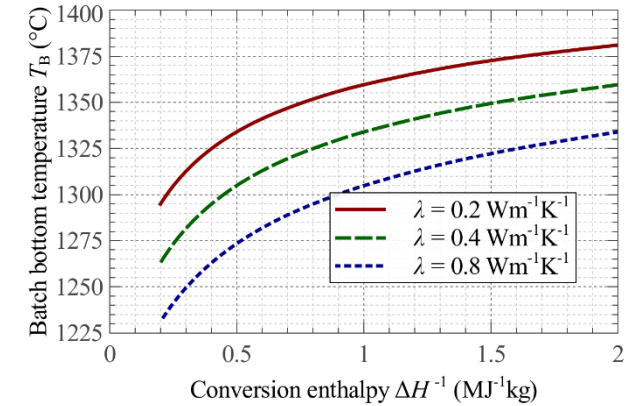
► Temperature-dependent material properties



Doi, Y., et al. (2018). "Thermal diffusivity of soda-lime-silica powder batch and briquettes." *Glass Technology - European Journal of Glass Science and Technology Part A* 59(3): 92-104.



► Effect of heat conductivity

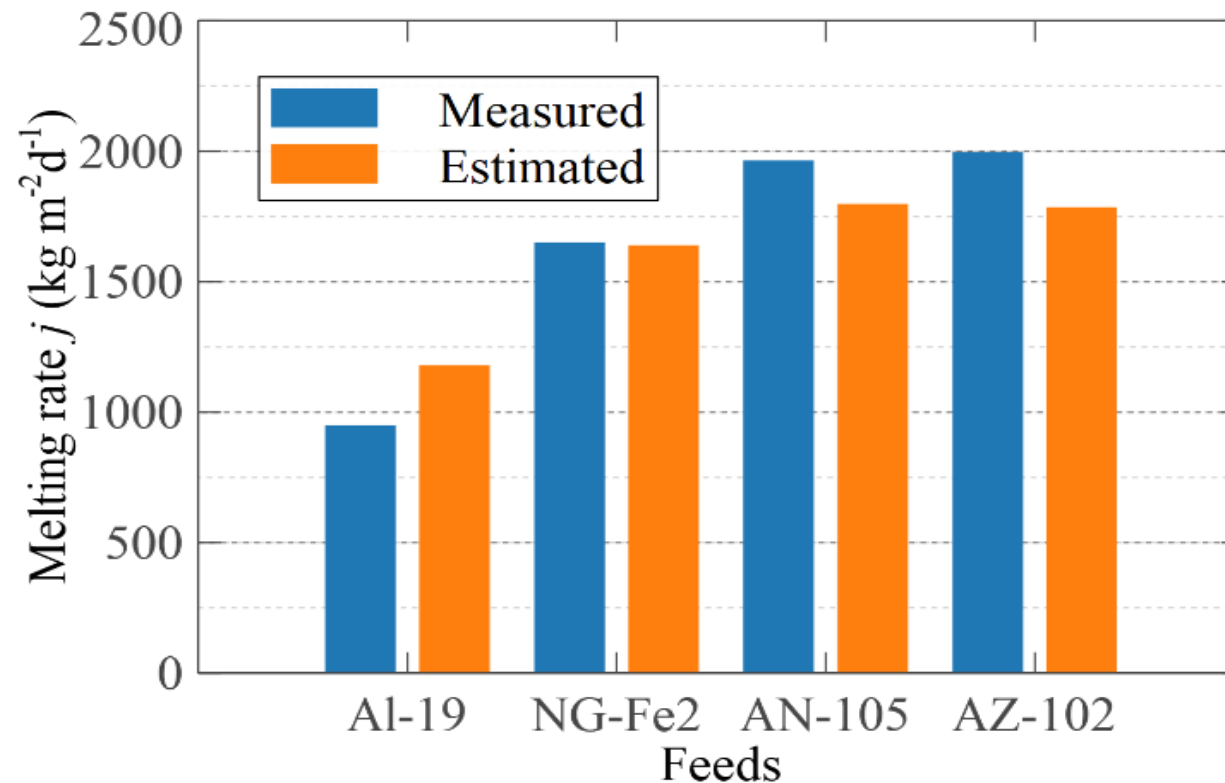


Comparison with melter results

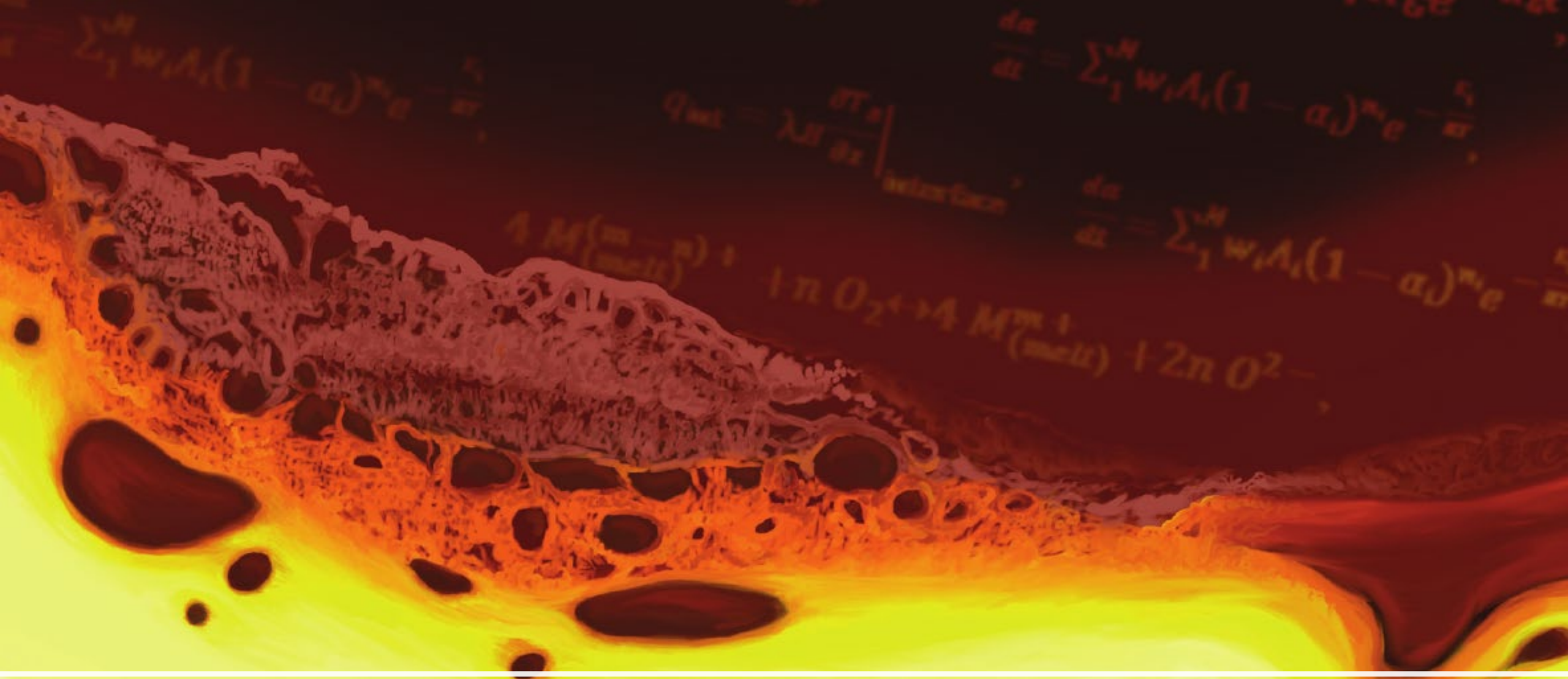


UCT PRAGUE

- ▶ Relatively good agreement between measured and estimated glass production rate



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



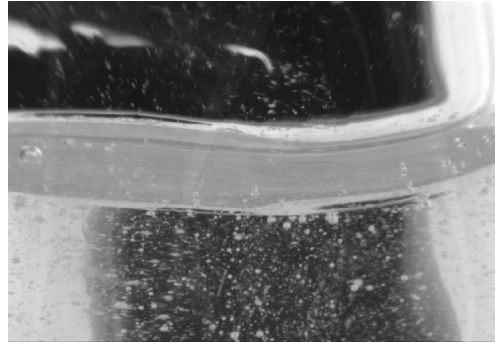
Next challenge – foam collapse in electric and hybrid melters

Analysis of primary foaming



UCT PRAGUE

- ▶ How does the colder atmosphere in hybrid melters affect the decay of primary foam?
- ▶ Visual and x-ray observation of feed pellet melting on the surface of molten glass

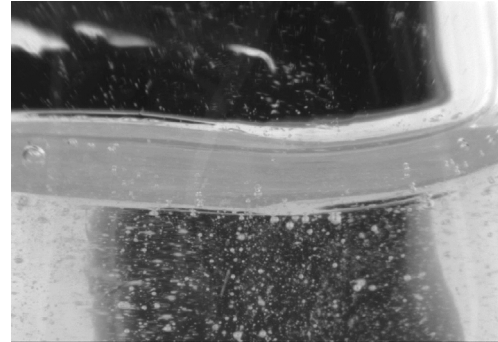


Analysis of primary foaming



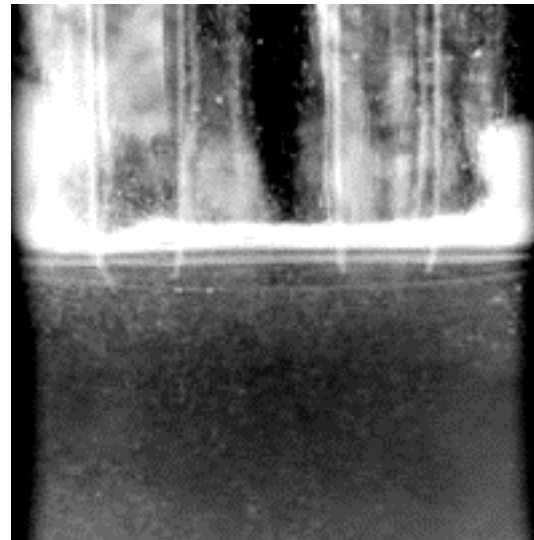
UCT PRAGUE

- ▶ How does the colder atmosphere in hybrid melters affect the decay of primary foam?

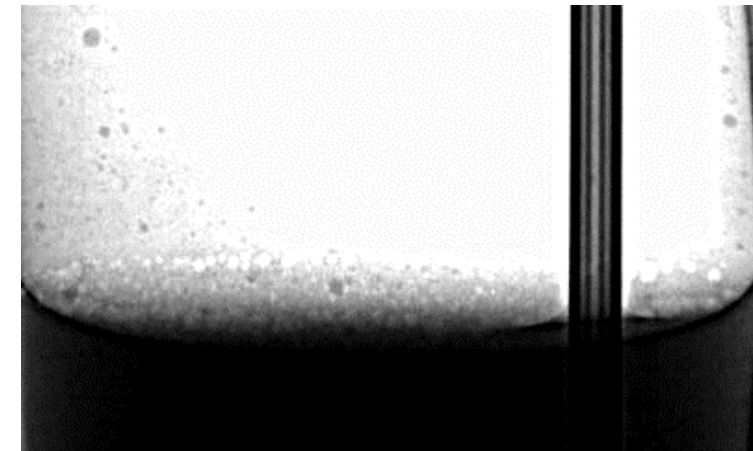


- ▶ Visual and x-ray observation of feed pellet melting on the surface of molten glass

28mm diameter
5 g
~4.75 mm height
~40% coverage



Visual observation



X-Ray radiography

AN-102 1150°C

Analysis of primary foaming

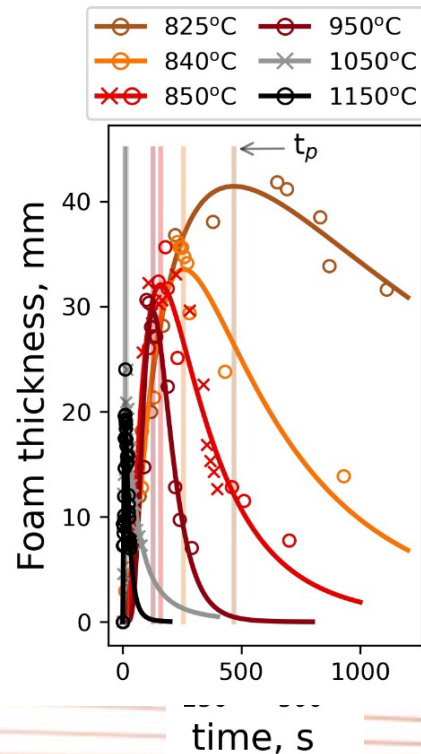


UCT PRAGUE

► Visual and x-ray observation

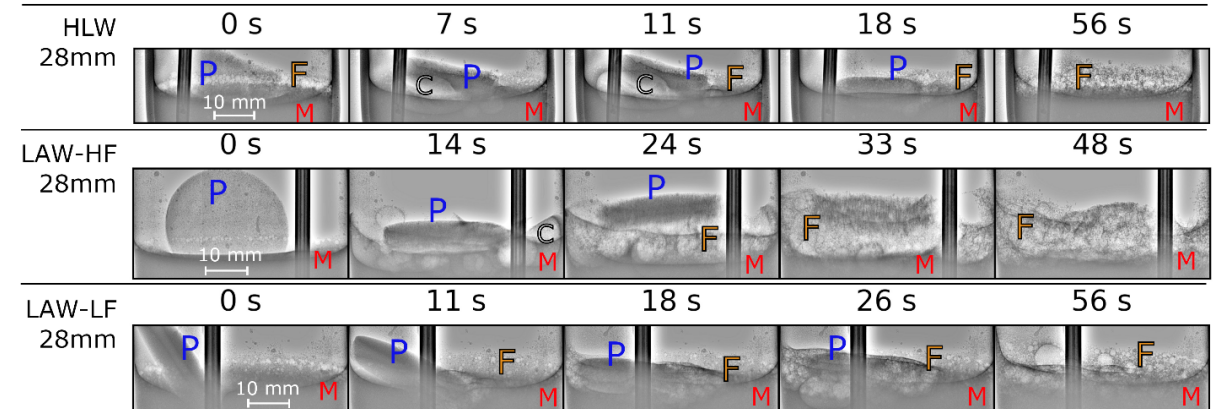
- Different feeds (low-foaming, high-foaming)
- Different temperatures (850 – 1150 °C)

► Foam thickness measured vs. time

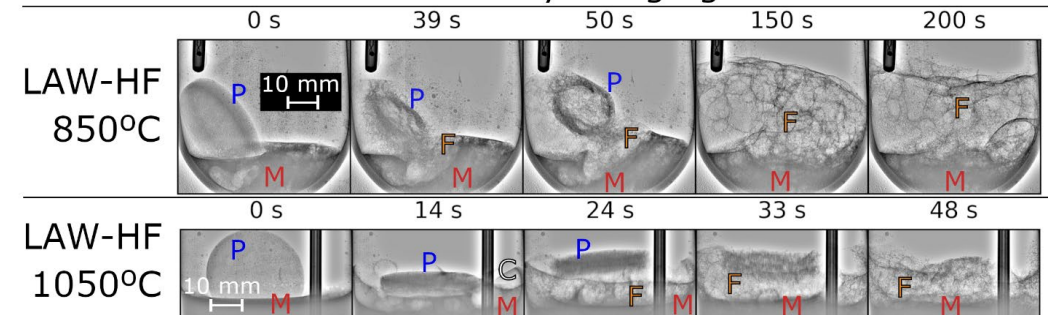


Data from visual observation are shown as circles (o) and data obtained through X-ray images shown as crosses (x)

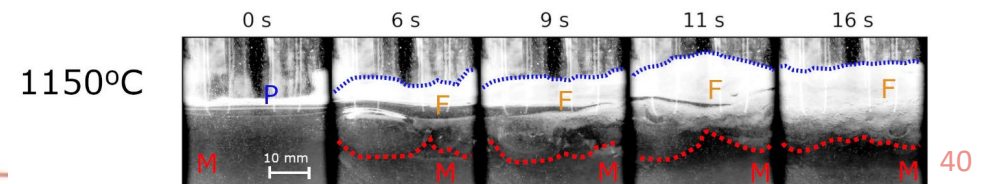
X-ray imaging 1050°C



X-ray Imaging



LAW-HF pellets (D:28mm H:4.75mm)



Analysis of primary foaming



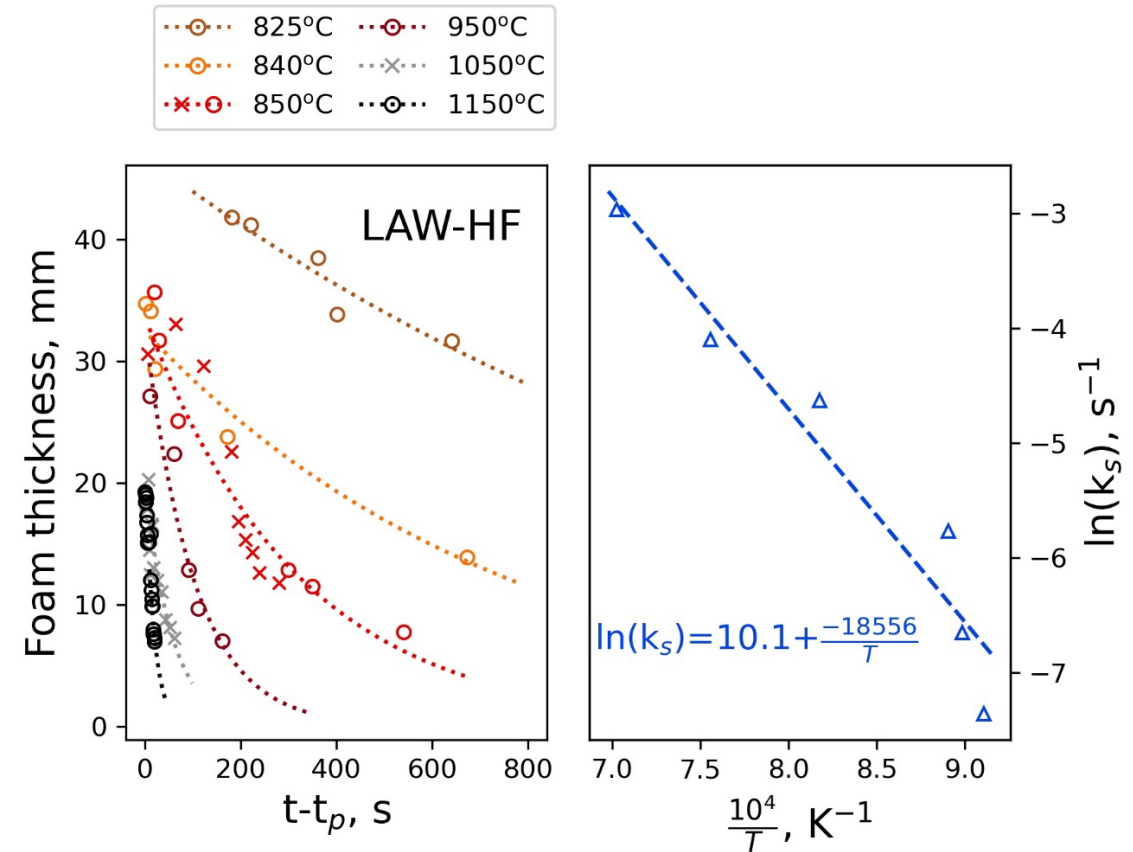
UCT PRAGUE

- ▶ Exponential fits of foam thickness versus time for pellets charged onto glass melts at various temperatures

- Allows to calculate the foam decay rate and foam decay coefficients

- ▶ The foam decay activation energy, $E_k = 154$ kJ/mol

- lower than the activation energy for viscous flow, $E_\eta = 156\text{--}198$ kJ/mol (estimated using viscosity models),
 - consistent with Kappel et al. [1] who attributed the difference to the foam lamellae break up.



$$h = h_0 \exp(-k_s (t - t_p))$$

h Foam height

t Time

t_p Time at maximum foam height

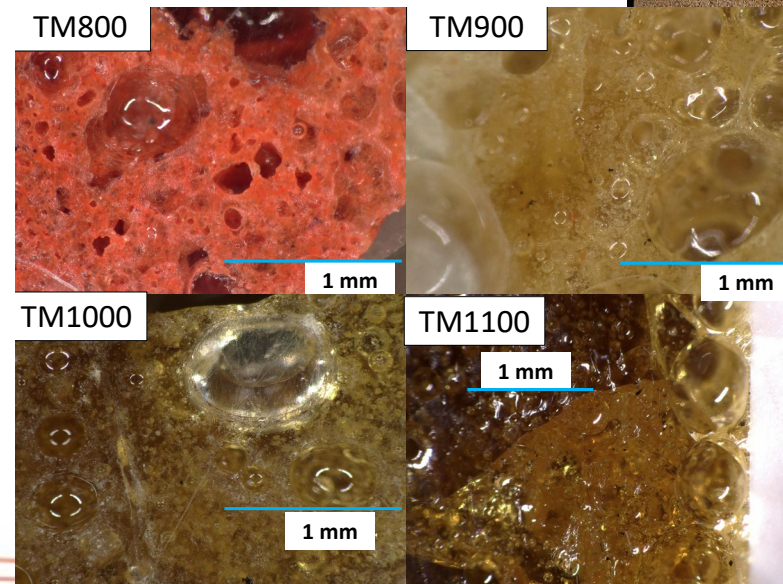
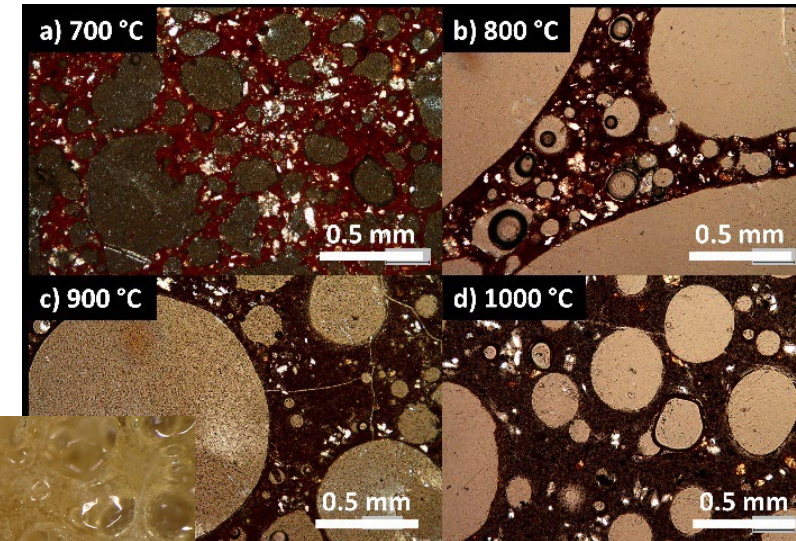
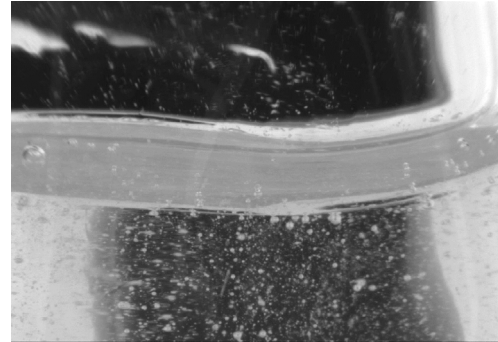
h_0, k_s Foam decay constants

Foam decay in melters with high boosting



UCT PRAGUE

- ▶ How does the colder atmosphere in hybrid melters affect the decay of primary foam?
- ▶ The foam stability depends mostly on the viscosity of the transient glass-forming melt
 - ❑ The transient glass-forming melt evolves as batch components react, melt, and dissolve upon heating
 - ❑ Once connected, transient melt encapsulates dissolving refractory particles, forming irregularly shaped pores that soon become spherical as temperature increases, turning the melt into primary foam



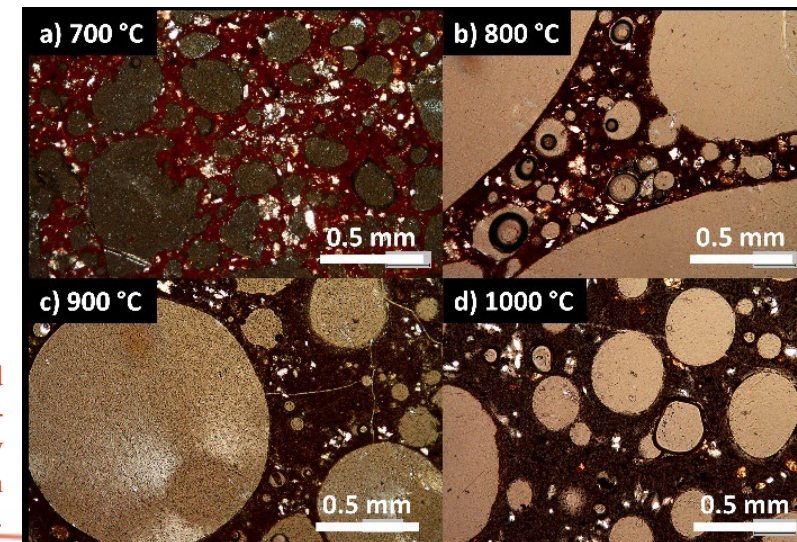
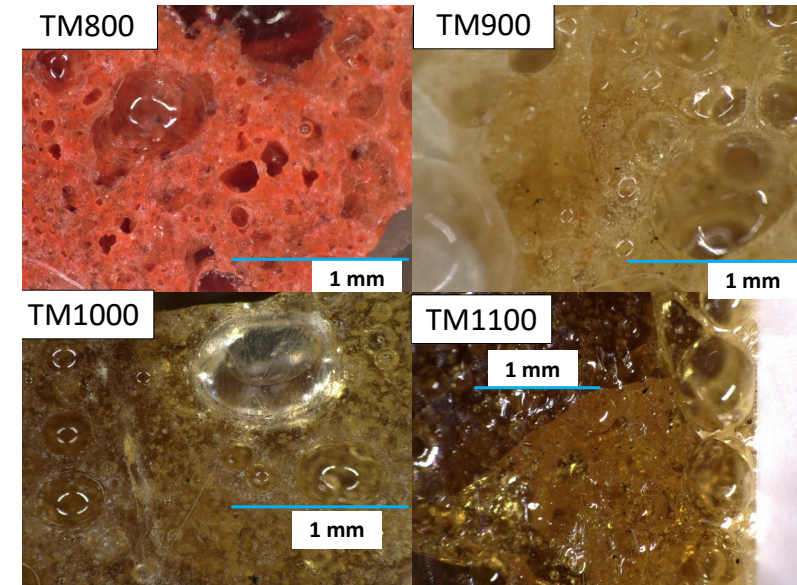
Microscopy image of the LAW (top) and HLW (bottom) feed samples heated to 700-1100 °C. Gas bubbles are separated by transient glass-forming melt, in which residual refractory particles are dissolving.

Transient glass-forming melt



UCT PRAGUE

- ▶ Stability of primary foam depends on transient melt viscosity, which depends on its composition and temperature
- ▶ Glass-forming melt composition can be determined as a function of temperature using X-ray diffraction (XRD) – the undissolved crystalline phases detected by XRD are subtracted from overall glass composition, obtaining the transient amorphous phase composition
- ▶ Evaluation of transient glass-forming melt viscosity:
 - ❑ Viscosity-composition models – VFT, Adam-Gibbs, MYEGA
 - ❑ Viscosity measurements – spindle viscometer, falling ball viscometry, hot stage microscopy



Microscopy image of the LAW (top) and HLW (bottom) feed samples heated to 700-1100 °C. Gas bubbles are separated by transient glass-forming melt, in which residual refractory particles are dissolving.

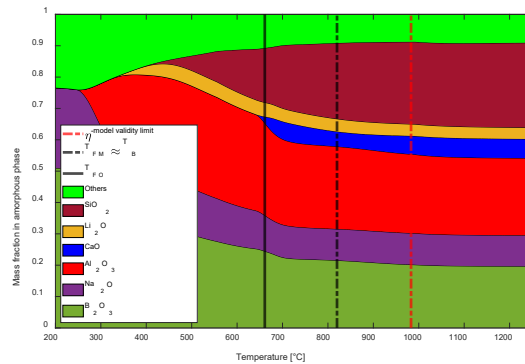
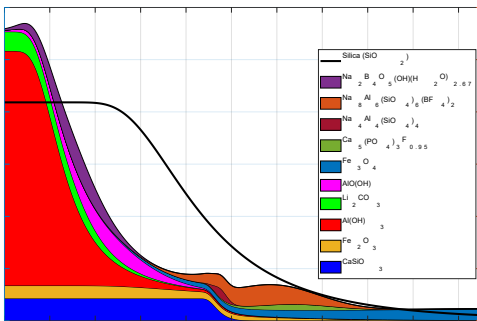
XRD – composition of transient melt



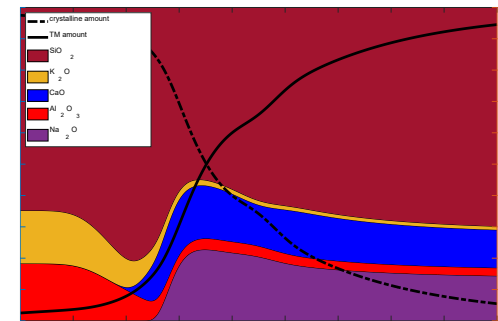
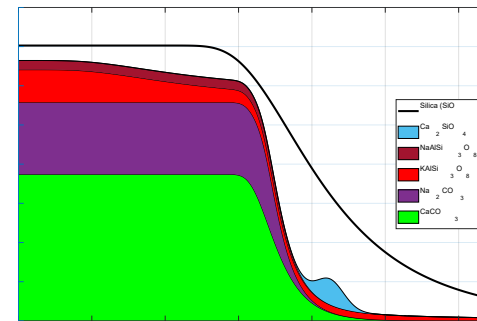
UCT PRAGUE

- Amorphous phase composition calculated by subtracting components in crystalline phase from the overall glass composition

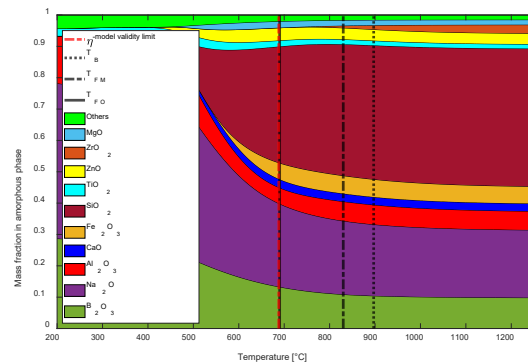
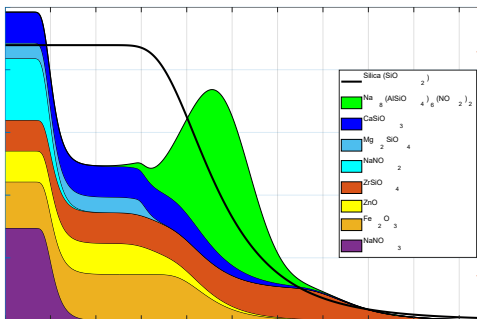
High-alumina High-level waste feed (HLW AI-19)



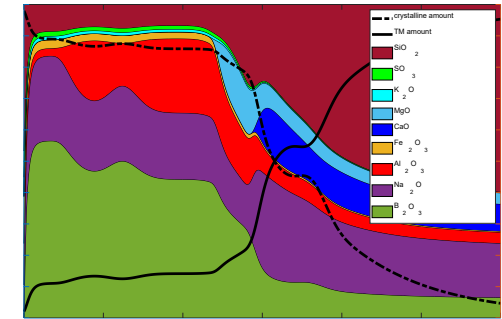
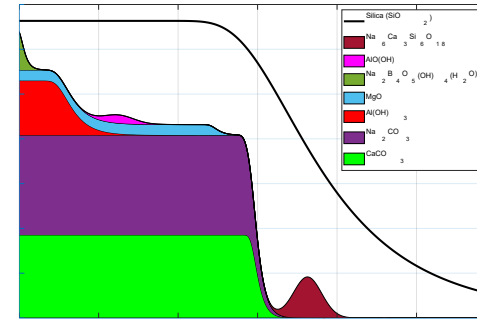
Soda-lime-silica batch (container)



Low activity waste feed (LAW AN-105)



Insulation fiber glass batch



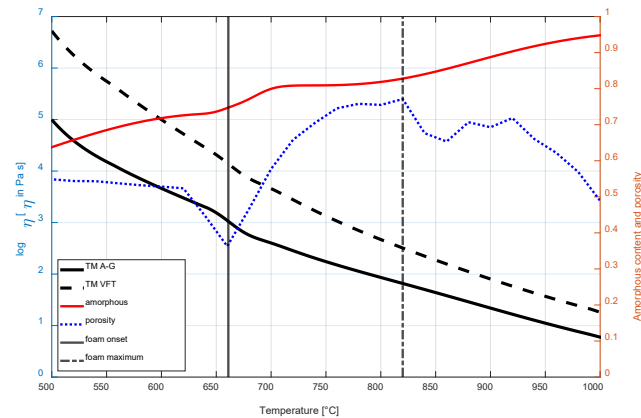
Other feeds and batches



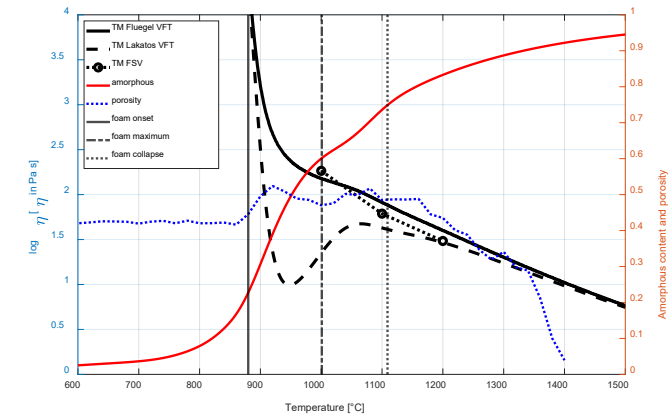
UCT PRAGUE

- Viscosity of transient melt – measured (points) and calculated using viscosity-composition models (black lines)

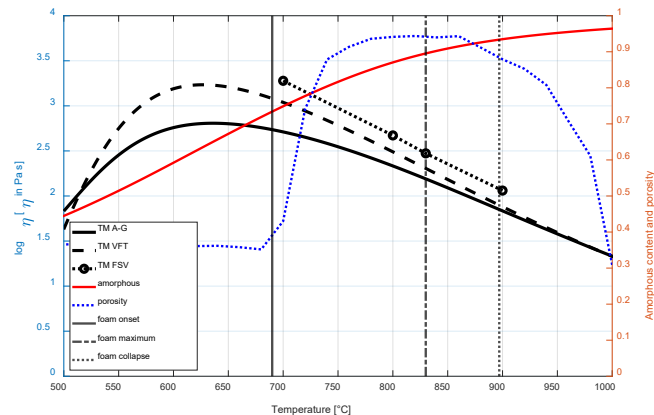
High-alumina High-level waste feed (HLW AI-19)



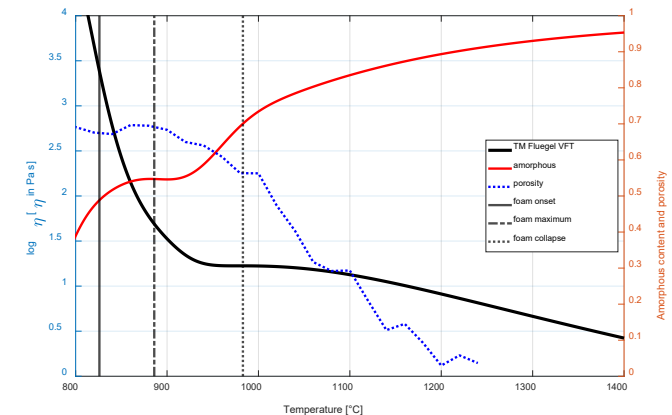
Soda-lime-silica batch (container)

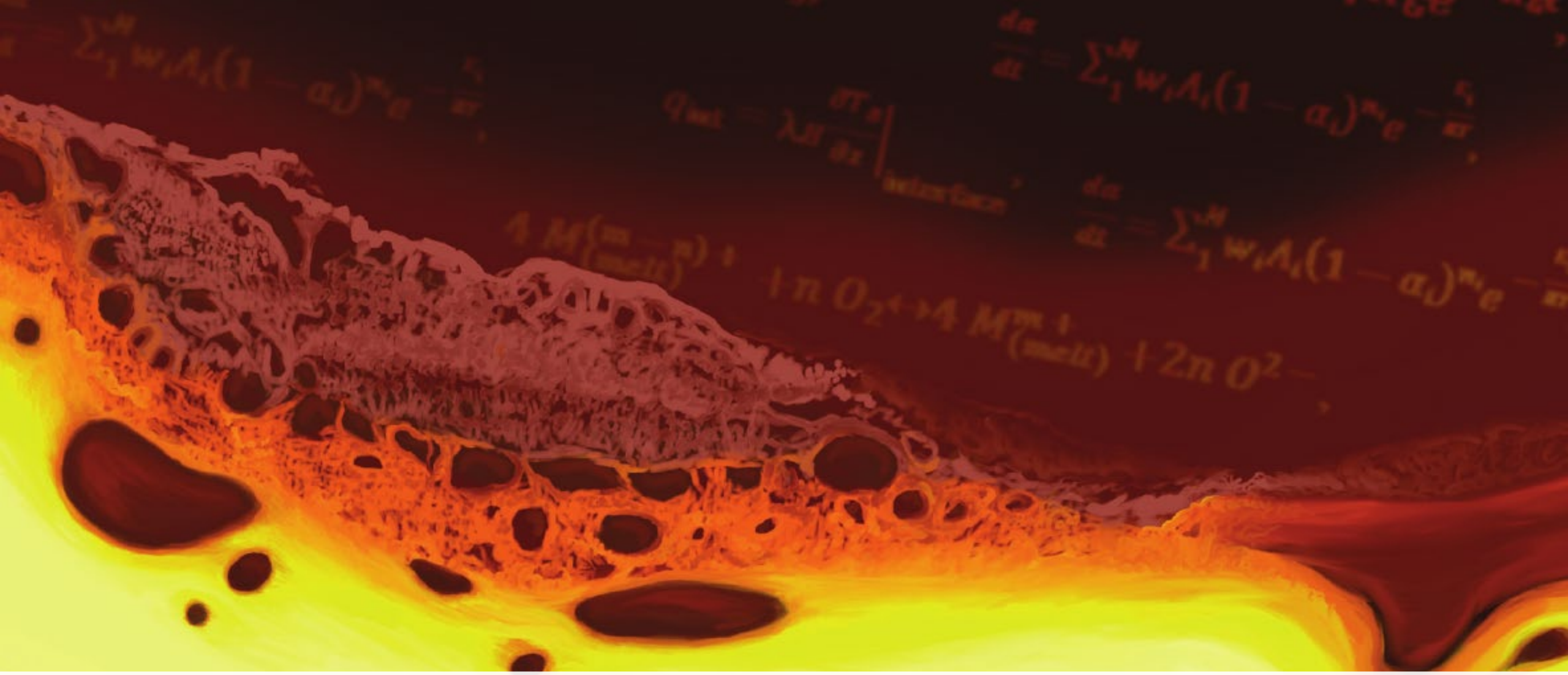


Low activity waste feed (LAW AN-105)



Insulation fiber glass batch





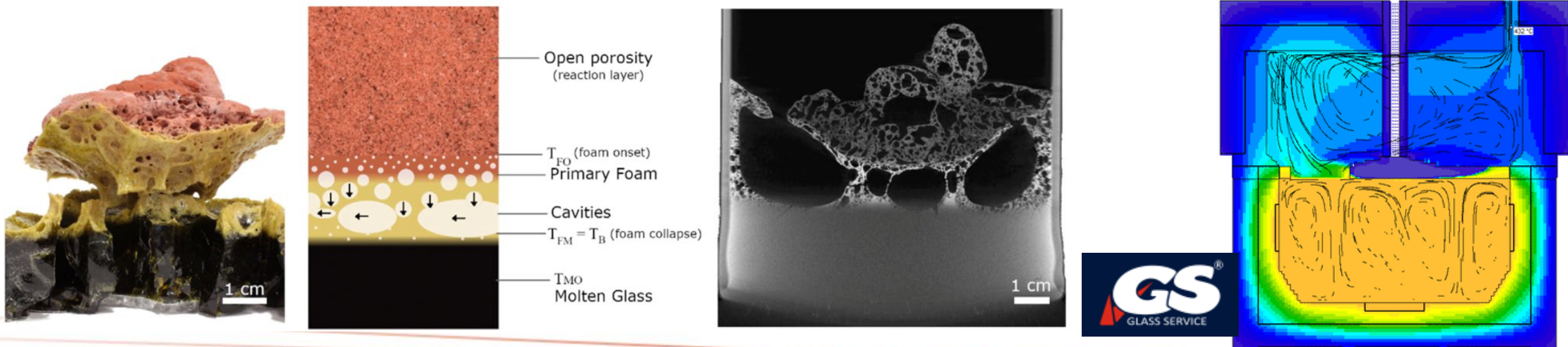
Summary

Conclusions



UCT PRAGUE

- ▶ Properties of batch layer (cold-cap) and molten glass determine the rate of melting
- ▶ Together with heat transfer, conversion kinetics should be considered when modeling batch melting
 - ▶ Increased heat flux to the batch typically increases foaming and shifts it to higher temperatures, decreasing the heat transfer driving force
- ▶ Decreasing the temperature of plenum space has detrimental effect on the foam decay rate due to increase in glass-forming melt viscosity



Want to know more?



UCT PRAGUE



- ▶ Pokorný R., Hřma P., Lee S., Klouček J., Choudhary M., Kruger A. (2020): *Modeling batch melting: Roles of heat transfer and reaction kinetics*. Journal of the American Ceramic Society. 103, 701-718.
- ▶ Kunc J., Klouček J., Vernerová M., Cincibusová P., Ferkl P., George J.K., Hřma P., Kruger A.A., Pokorný R. (2024): *Viscosity of transient glass-forming melt and its relation to foaming during batch-to-glass conversion*. Materials Letters. 363, 136284. doi: 10.1016/j.matlet.2024.136284
- ▶ Marcial J., Luksic S., Klouček J., Vernerova M., Cutforth D., Varga T., Hřma P., Kruger A., Pokorný R. (2022): In-situ x-ray and visual observation of foam morphology and behavior at the batch-melt interface during melting of simulated waste glass. *Ceramics International*. 48, 7975-7985. doi: 10.1016/j.ceramint.2021.11.344

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Acknowledgement



UCT PRAGUE

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