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- If inspired by this work, please cite the corresponding papers (such as „**R. Pokorny** et al.: One-Dimensional Cold Cap Model for Melters with Bubblers, *Journal of the American Ceramic Society*, **98**, 2015, p.3112-3118.“, and others)

Cold cap modelling in waste vitrification

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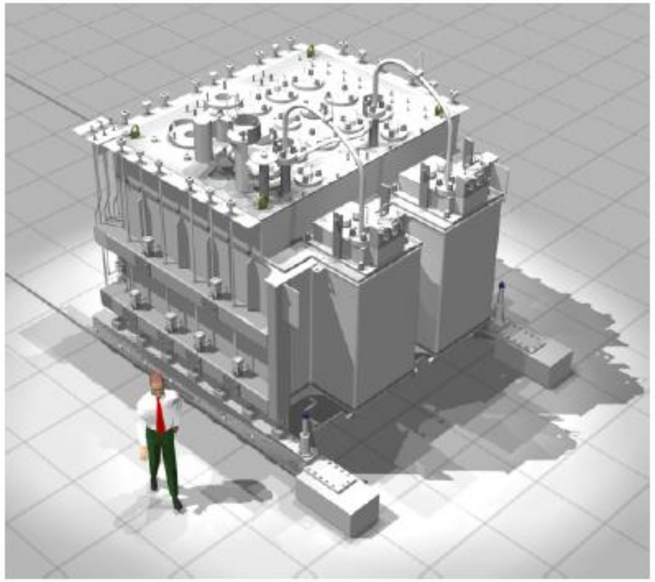

Joint ICTP-IAEA International School on Nuclear Waste Vitrification

September 23-27, 2019
Trieste, Italy

UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

About the Cold Top Melting

Cold cap in Commercial Electric Furnace

- All-electric cold top melter
  - ☐ Process developed decades ago
- Pyrex/Simax glass
  - ☐ Boro-silicate
- 15 m^2, 80 cm deep
- Hills formed by gas accumulating under cold top
  - ☐ Eventually break, forming „vent holes“

Cold cap in Commercial Electric Furnace

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Advantages

- Specialty products/smaller capacities (<~75 t/day)
  - ❑ Heat losses from fossil fuel furnace are high for small scales
- Reduced capital cost and furnace space requirements
- Significantly increased energy efficiency
- Better quality and more homogenous glass
- Very low direct emissions

Negatives

- High operating (energy) cost – currently not economically viable for very large-scale glass production
  - ❑ Some technical issues also present (low production rate)
- Reduced campaign length
  - ❑ But comparatively low rebuild costs
- Associated environmental implications of electricity generation

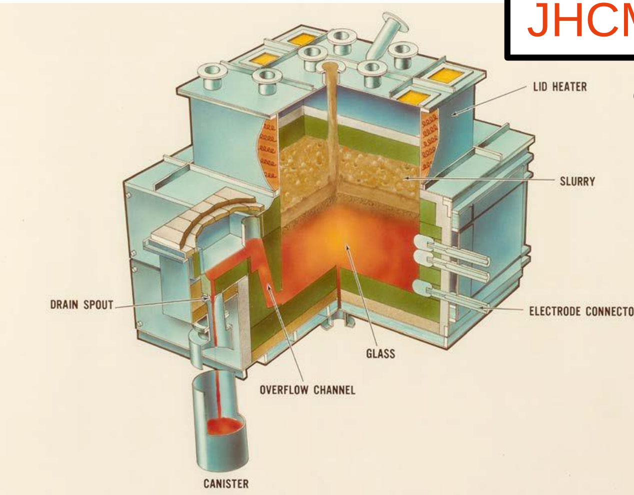
Electric cold top furnace

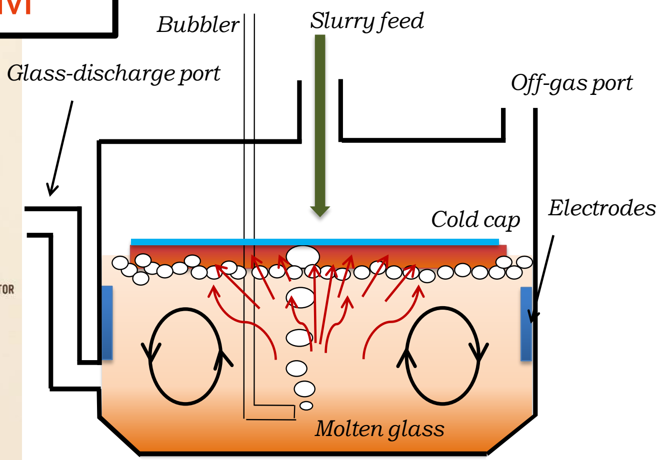
Gas-fired furnace

Waste Melter Design

- Electric melters – no emissions from the burning of fossil fuel
- At Hanford in USA, the waste is vitrified in cold top Joule-heated melters.
  - ☐ Large-scale production
  - ☐ Heat dissipates in the whole volume
- Other vitrification melter technologies are available
  - Hot-walled induction melter (HWIM)
    - Low frequency induction of the metal shell
    - Usually stirred
    - Low capacity
  - Cold Crucible melter
    - Direct induction of the glass melt
    - Usually stirred
    - Low capacity

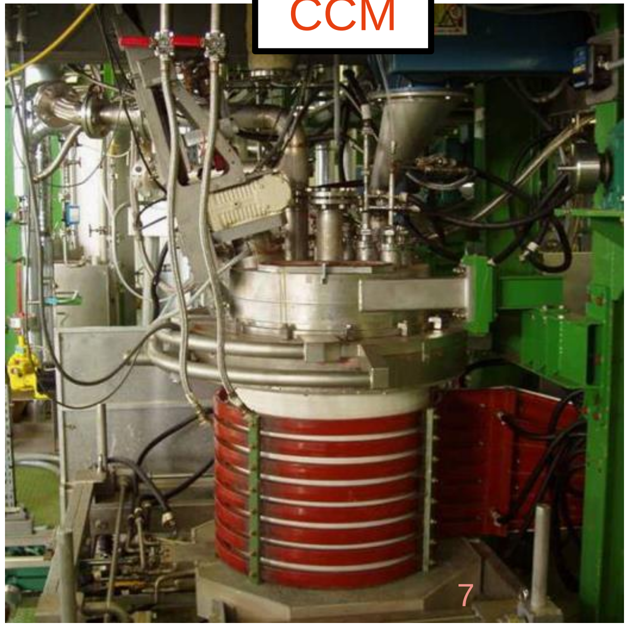
JHCM





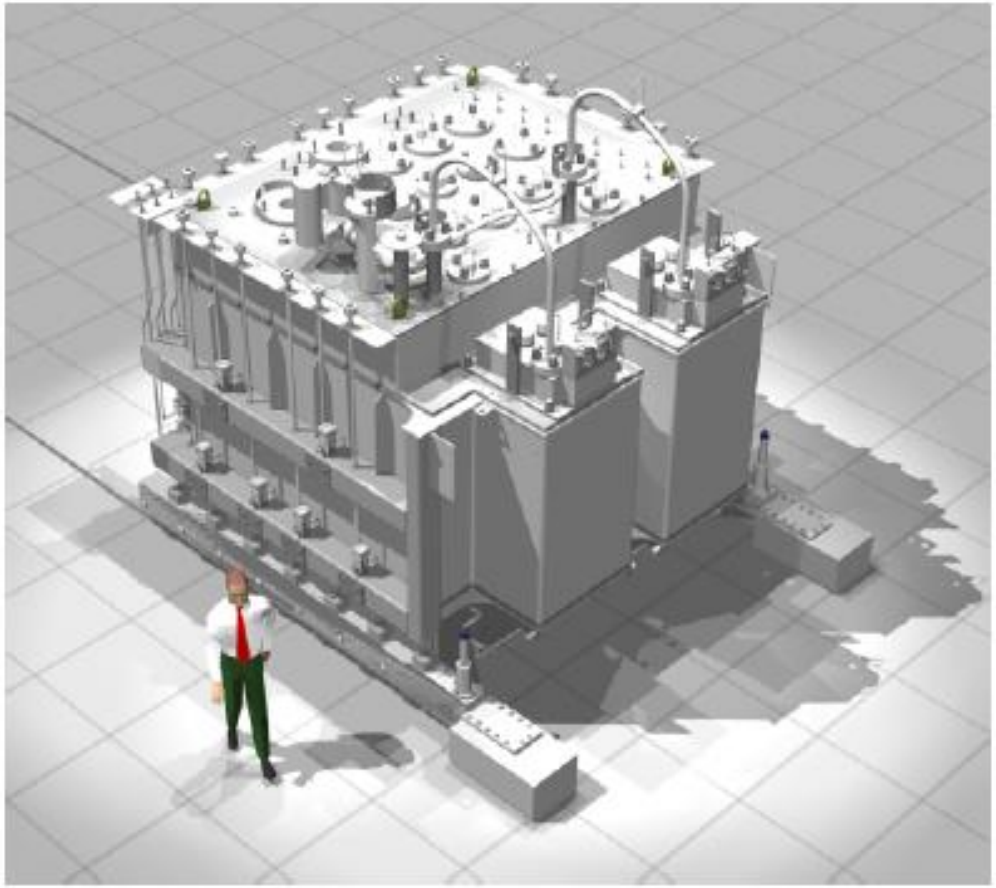
HWIM

CCM



Joule-heated melter for HLW glass

- Scaled drawing of HLW glass melter at Waste Treatment and immobilization plant



- Actual melter

Mathematical modeling in glass melting

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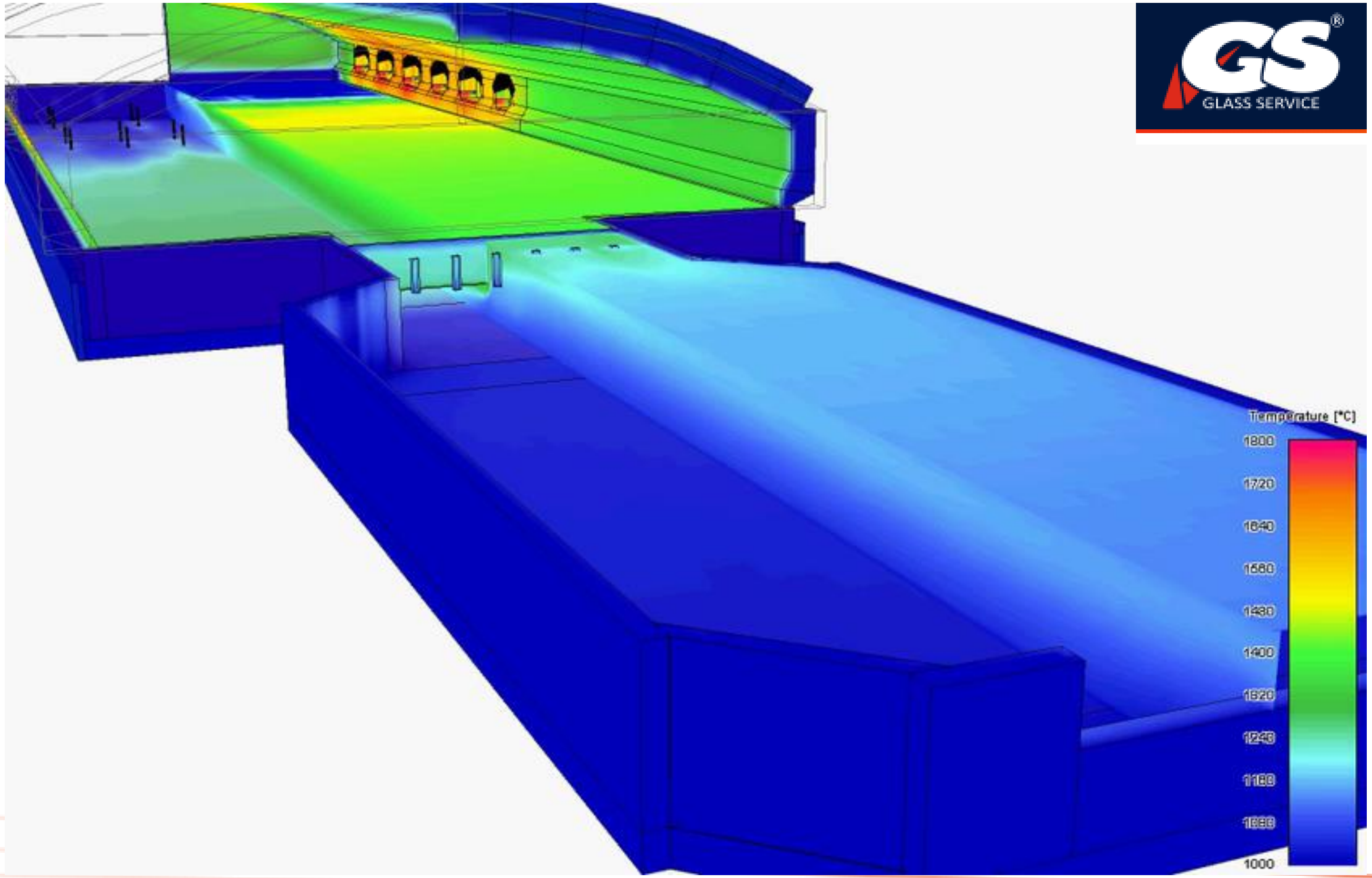
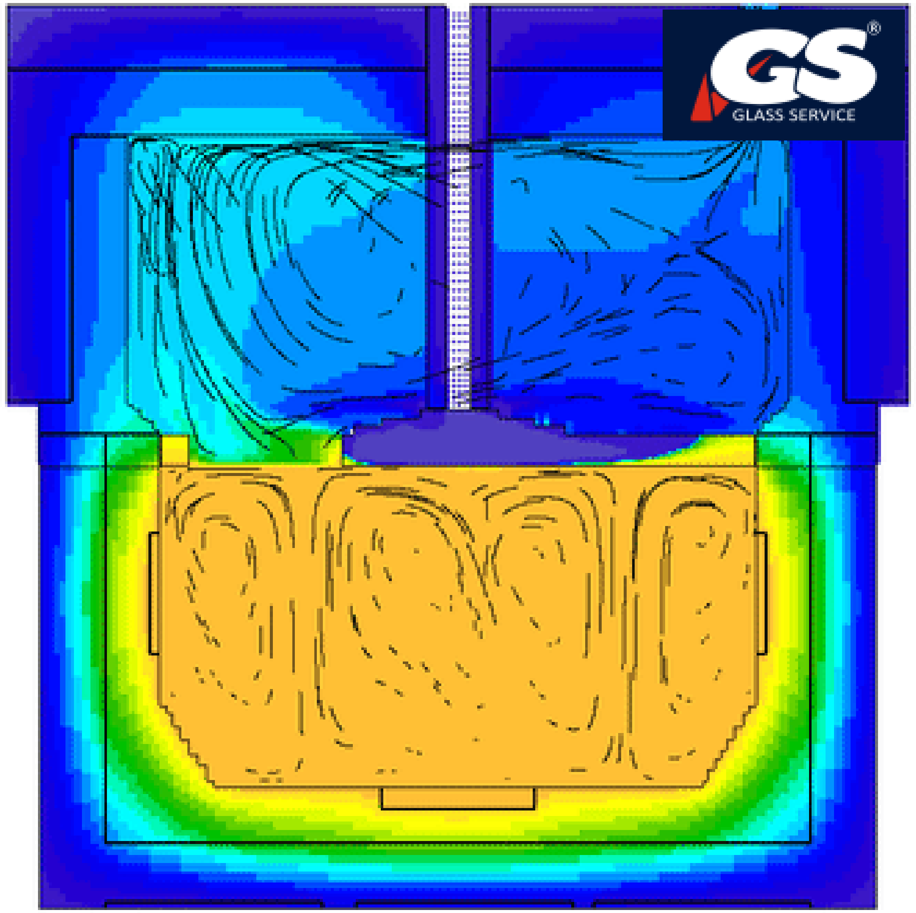
- Today, practically all new furnaces (or rebuilds) are simulated by CFD

Mathematical modeling in glass melting

- Today, practically all new furnaces (or rebuilds) are simulated by CFD





CFD models architecture (Glass Service)

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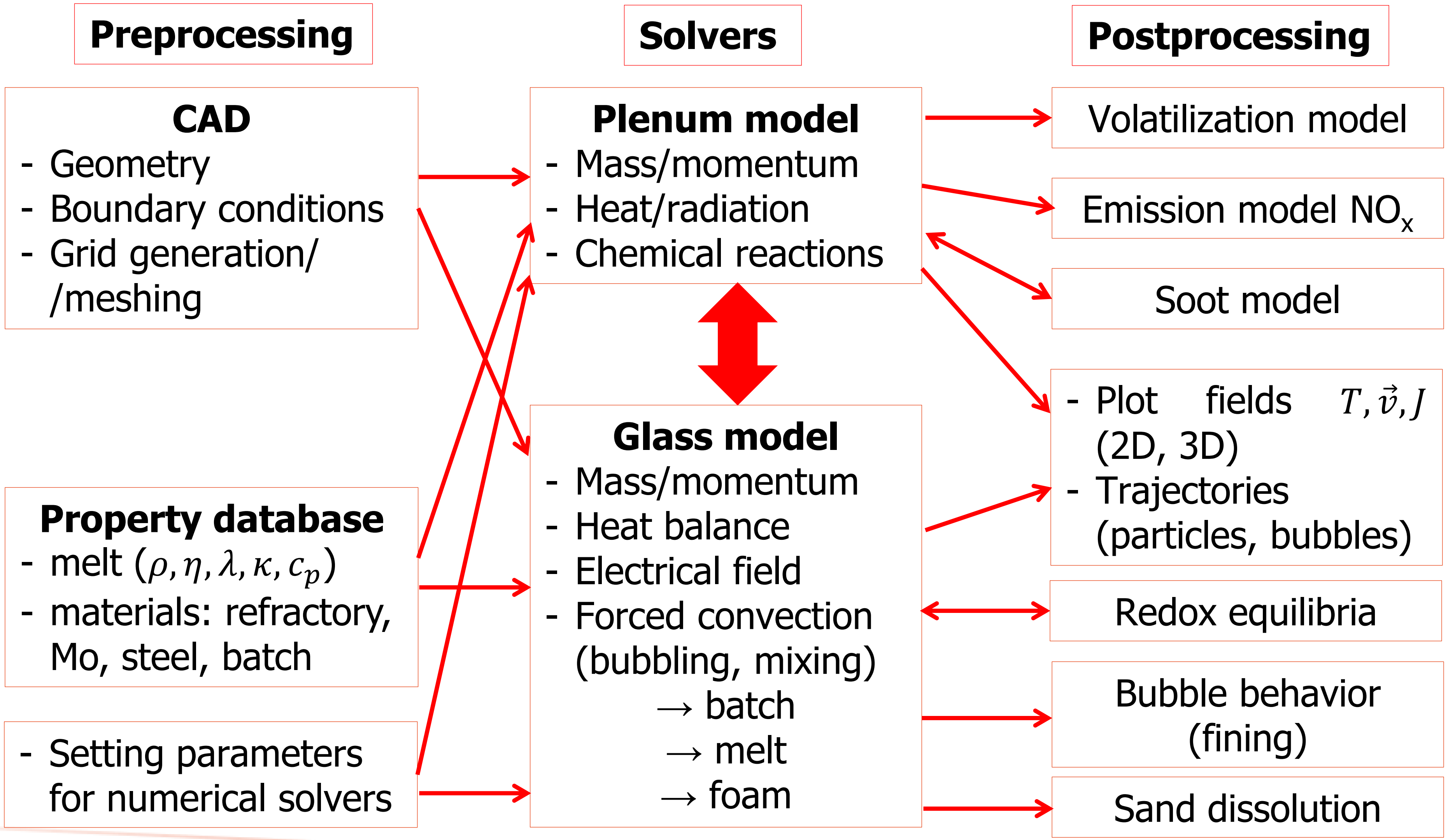


Preprocessing

Solvers

Postprocessing

CAD
- Geometry
- Boundary conditions
- Grid generation/ /meshing

Property database
- melt ($\rho, \eta, \lambda, \kappa, c_p$)
- materials: refractory, Mo, steel, batch

- Setting parameters for numerical solvers

Plenum model
- Mass/momentum
- Heat/radiation
- Chemical reactions

Glass model
- Mass/momentum
- Heat balance
- Electrical field
- Forced convection (bubbling, mixing)
  - → batch
  - → melt
  - → foam

Volatilization model

Emission model NO_x

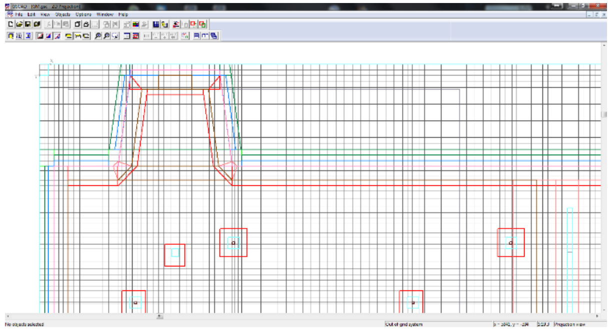
Soot model

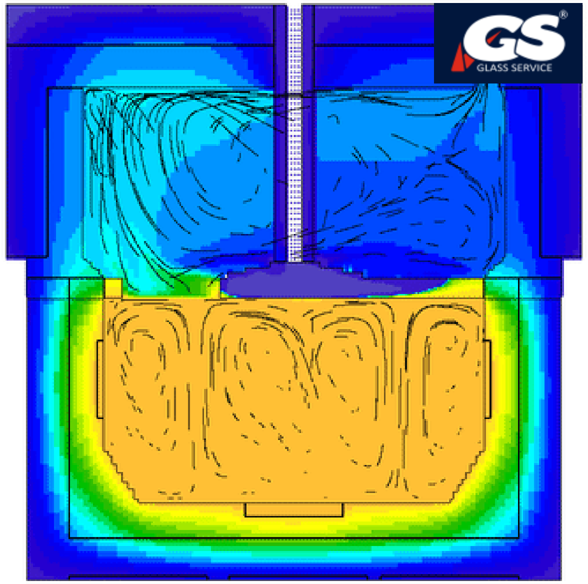
- Plot fields $T, \vec{v}, J$ (2D, 3D)
- Trajectories (particles, bubbles)

Redox equilibria

Bubble behavior (fining)

Sand dissolution





GS model – 77 % cold cap coverage

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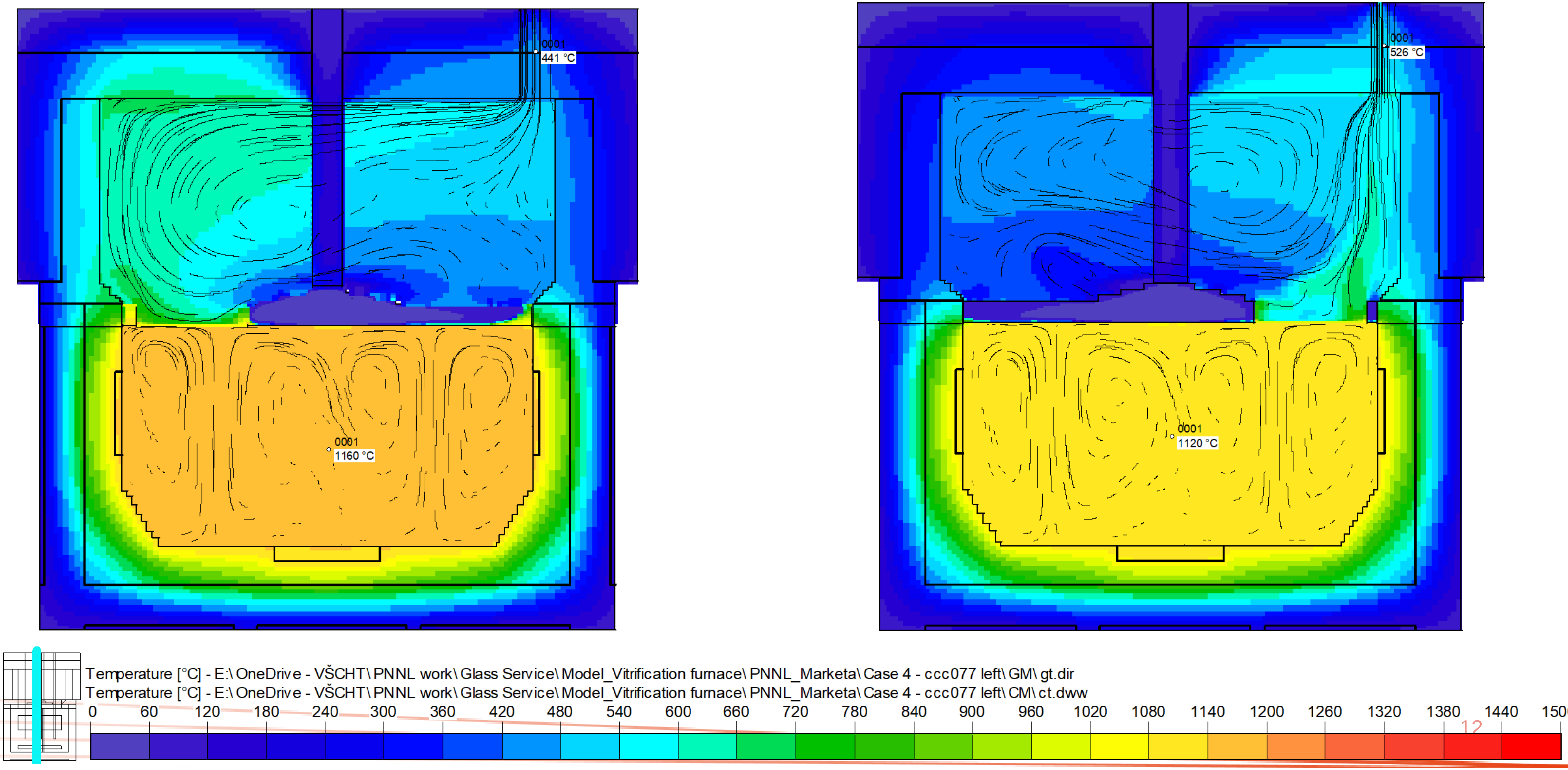

Mathematical modeling in glass melting

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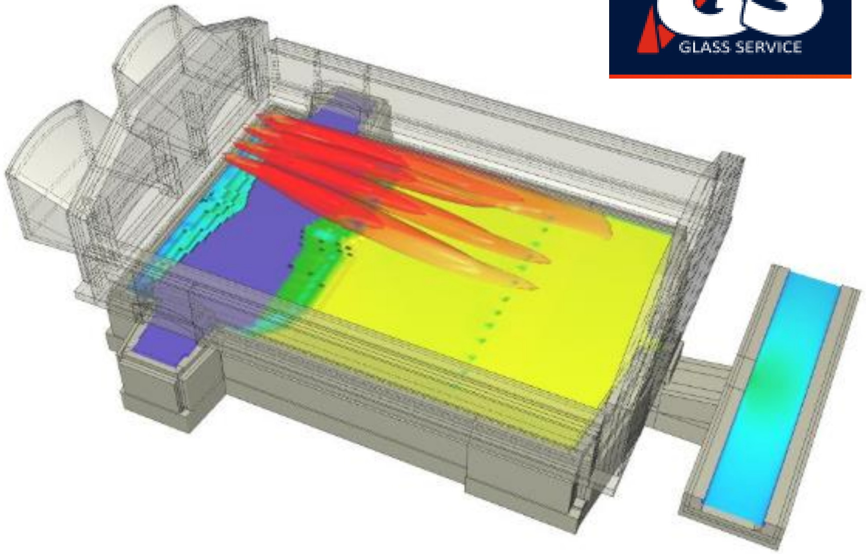
- Today, practically all new furnaces (or rebuilds) are simulated by CFD
- Main issues for successful glass making are:
  - (i) energy economy
  - (ii) product quality
  - (iii) environmental pollution
  - (iv) **production rate**
  - Mathematical models successfully deal with the first three issues, but generally fail to estimate the **production rate**

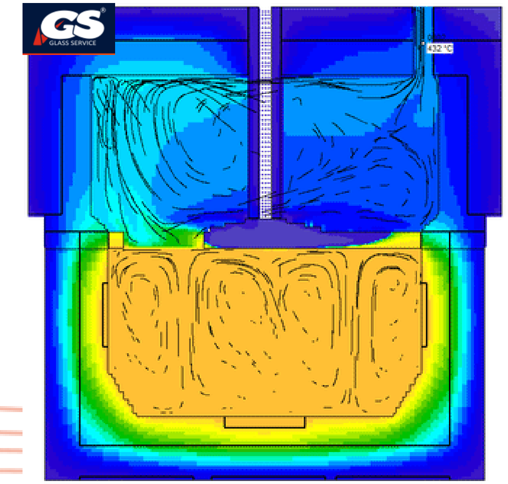


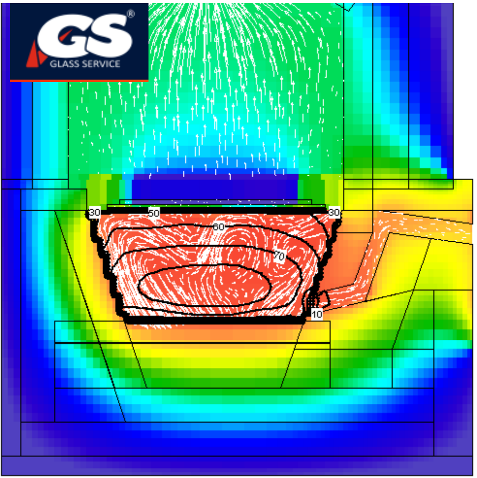
Regenerative end-port furnace for producing container glass

- Yet production rate is a primary factor in competitive commercial market (of low profit margins) as well as for the efficiency of nuclear waste vitrification
  - Rate of melting directly influences the lifecycle of the cleanup process
  - Resurgence of electric melting?

Modeling the batch-to-glass conversion

- Heat transfer from glass to batch – one of the least understood problem in glass melting
- Only with a realistic batch melting model, the melting rate can be predicted as a *function of feed properties* and *melter operating conditions*.
  - Electrode power, off-gas temperature, spinel settling, RTD, plant upsets, online control,...
- Current mathematical models oversimplify the *reaction layer*
  - This might be reasonable when investigating phenomena in molten glass
    - However, batch melting affects melter performance and the glass quality through its impact on the temperature underneath the batch, intensity of recirculation, and on the batch blanket dimensions (especially important for cold top electric melting)
  - Not OK, if you expect to process hundreds od feed compositions





Analogous situation?

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Analogous situation?


Photo Credit/Crédit photographique: Dan Crosbie

Modeling the batch-to-glass conversion

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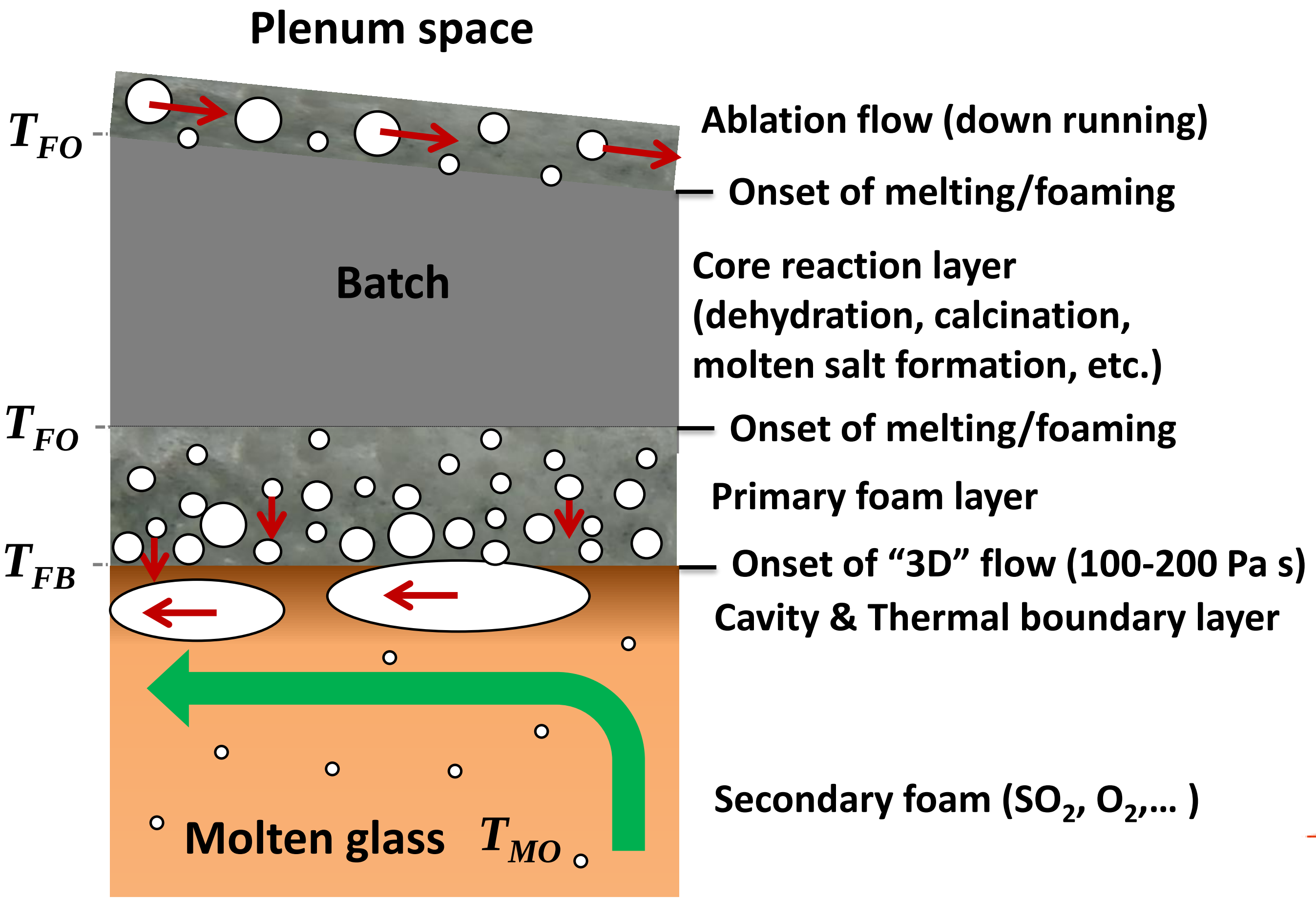
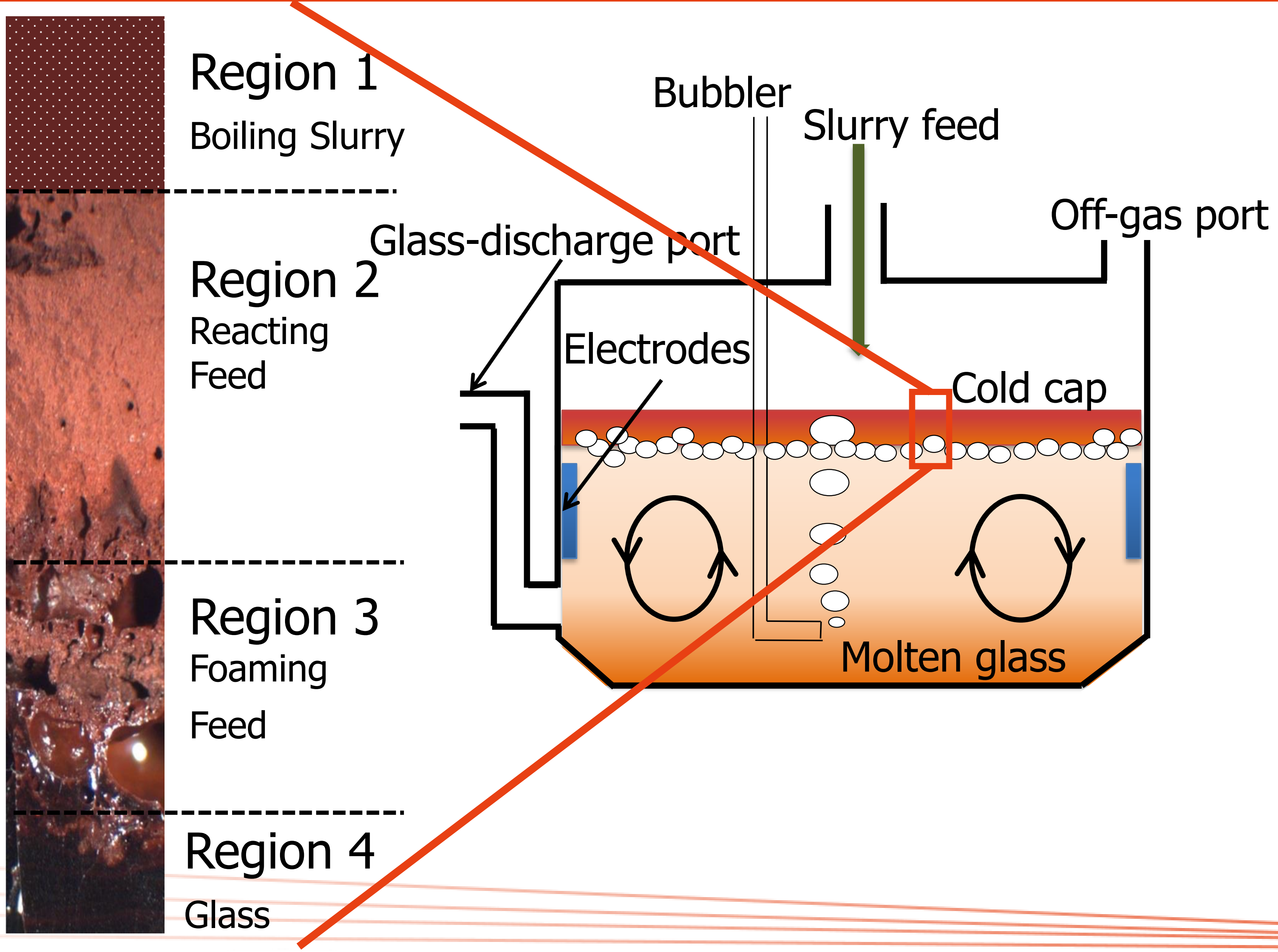
- Many complex phenomena occur in the batch layer
  - Water evaporation, gas evolution, melting of salts, borate melt formation, reactions between melt & salts & solids, precipitation of intermediate crystalline phases, growth and collapse of primary foam, dissolution of residual solids, …
- Various scales
  - Molecular scale: reaction kinetics
  - Micro-scale: sand dissolution
  - Meso-scale: foam growth and collapse
  - Macro-scale: blanket behavior



HLW Cold Cap and How is it Created?



Region 1

Boiling Slurry

Region 2

Reacting Feed

Region 3

Foaming Feed

Region 4

Glass

Bubbler

Slurry feed

Off-gas port

Glass-discharge port

Electrodes

Cold cap

Molten glass

- ▶ Conversion of waste to glass requires that the waste be mixed with glass forming additives making an aqueous slurry.
- ▶ The slurry is fed into a joule heated melter.
- ▶ In the melter the slurry turns into a cold cap that floats on molten glass.
- ▶ The conversion from chemicals to glass occurs in the cold cap.

HLW Cold Cap and How is it Created?

Region 1

Boiling Slurry

~100°C

Region 2

Reacting Feed

~750°C

Region 3

Foaming Feed

~900-1000°C

Region 4

Glass

~1150°C

- ► Evaporation of water
- ► Dehydration of feed (T < ~400°C)
  - $Fe(OH)_3$, hydrated sodium borate, and gibbsite dehydrated
- ► Evolution of CO_2 and NOx gases (~250°C < T < ~700°C)
- ► Formation of early-glass forming (borate) phases (~400°C < T < ~750°C)
- ► Feed shrank above 700°C
- ► Melt connected above ~750°C
- ► Emergence of borosilicate melt (T > ~750°C)
  - Dissolution of quartz
  - Formation and dissolution of intermediate silicates
- ► Expansion and collapse of foam (~800°C < T < ~1000°C)
- ► Formation of continuous melt
  - Dissolution of residual solids (mainly silica, possibly spinel)

HLW Cold Cap and How is it Created?

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Region 1

Boiling Slurry

~100°C

- ► Evaporation of water

Region 2

Reacting Feed

- ► Dehydration of feed (T < ~400°C)
  - Fe(OH)$_3$, hydrated sodium borate, and gibbsite dehydrated
- ► Evolution of CO$_2$ and NOx gases (~250°C < T < ~700°C)

~400°C < T

K. Xu, P. Hrma, J. Rice, M. J. Schweiger, B. J. Riley, J. V. Crum , “Melter Feed Reactions at T ≤ 700° C for Nuclear Waste Vitrification,” *J. Amer. Ceram. Soc*. 98, 3105–3111 (2015).

~750°C

- ► Melt connected above ~750°C

Region 3

Foaming Feed

- ► Emergence of borosilicate melt (T > ~750°C)
  - Dissolution of quartz
  - Formation and dissolution of intermediate silicates

~900-1000°C

- ► Expansion and collapse of foam (~800°C < T < ~1000°C)

Region 4

Glass

~1150°C

- ► Formation of continuous melt
  - Dissolution of residual solids (mainly silica, possibly spinel)

Modeling the Cold cap

Modeling of batch melting

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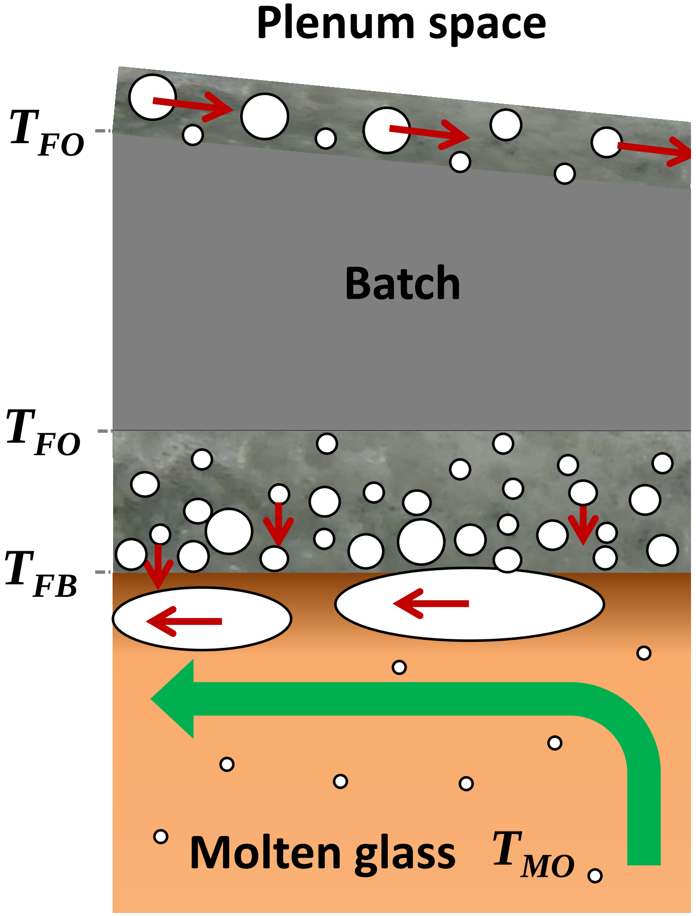
- Pointed out by Choudhary (Choudhary et al., Int. Journ. of Appl. Glass Sci., 2010. **1**(2), 2010, 188-214.) – two main approaches are usually used, according to the process they consider to be rate limiting:

Heat-transfer limited

- Do not consider reaction kinetics
- Conversion degree is predetermined using DSC or XRD
- The temperature profile and melting rate is determined by the thermal properties of the batch



Batch-kinetics limited

- Melting rate determined by the kinetics of the "terminal batch-to-glass conversion process"
- Several processes can be considered – dissolution of solids, foam evolution and collapse
- Usually defined by a single kinetic equation

Heat transfer in the batch blanket

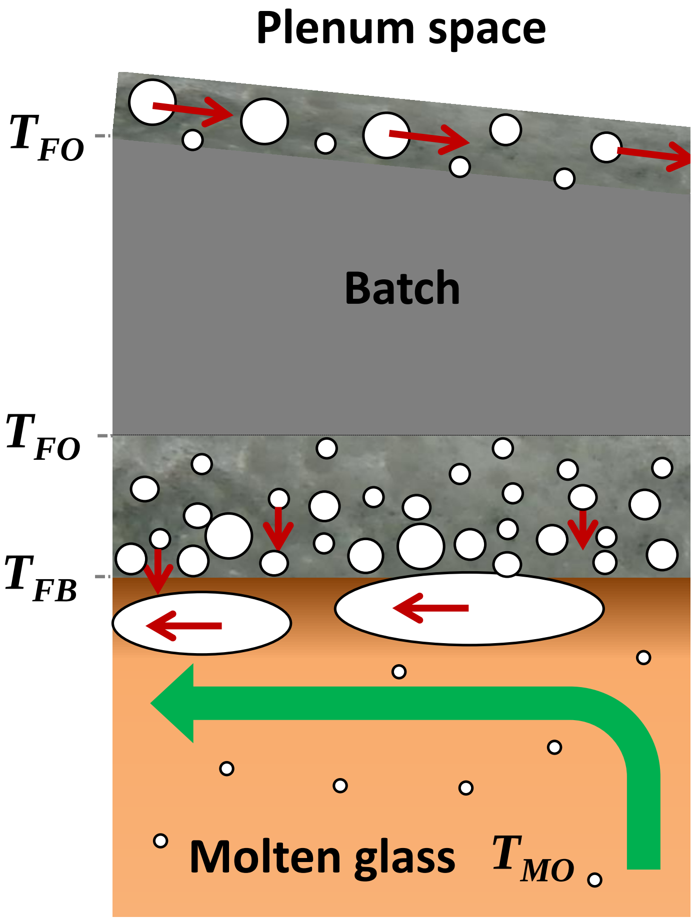
Heat transfer in batch blanket

- Batch usually considered as single continuous phase

$$\frac{\partial}{\partial t}(\rho_B c_B T) = \frac{\partial}{\partial z}\left(\lambda_B \frac{\partial T}{\partial z}\right) + H_{ch}$$

$$q_{\text{int}} = \lambda_B \frac{\partial T}{\partial z}\bigg|_{\text{interface}}$$

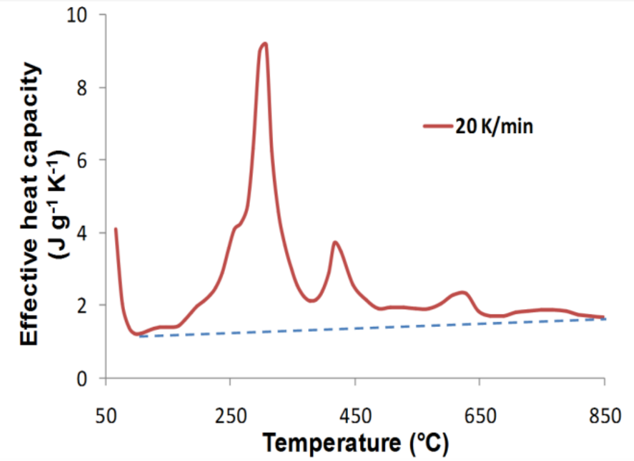
- q_{int} – usually determined by coupling with the CFD model (or in simpler cases using heat transfer coefficient)
- Models usually consider predetermined temperature at the interface
- The heat transfer models require a precise knowledge of material properties and conversion enthalpies



Cold cap modeling – Material properties

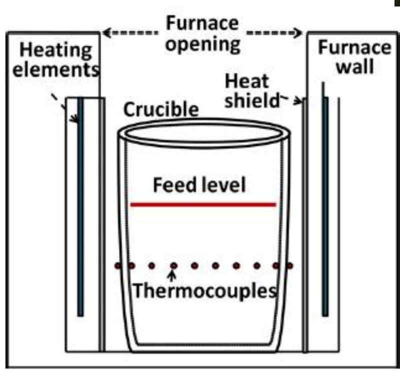
„Effective“ heat capacity

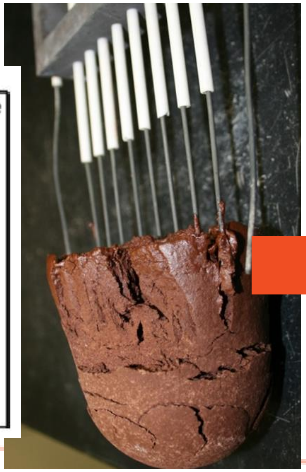
- Differential Scanning Calorimetry (DSC)
- Includes the reaction heat

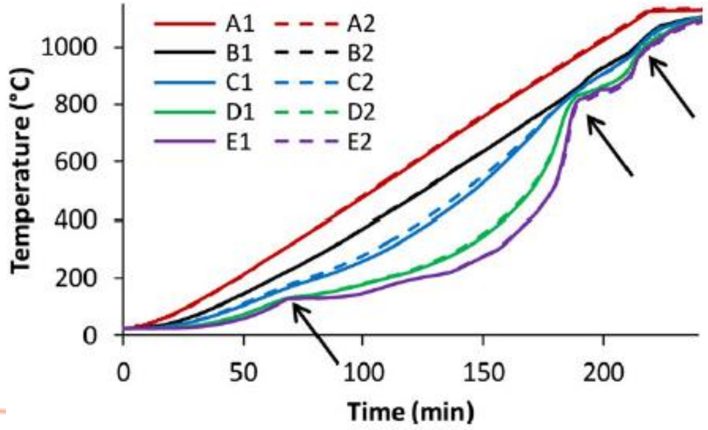


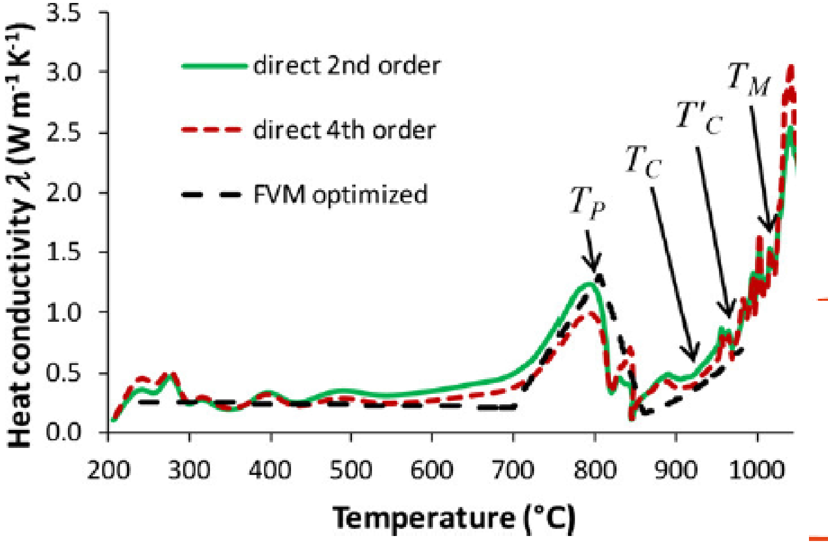
Feed heat conductivity

- calculated from temperature profiles in a heated feed



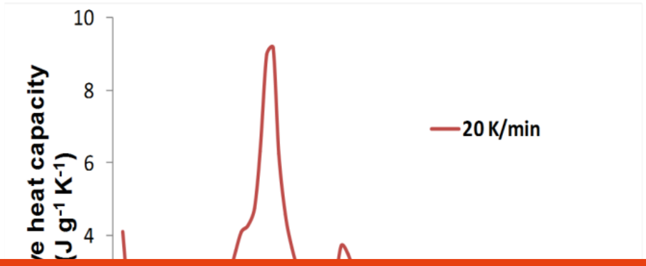






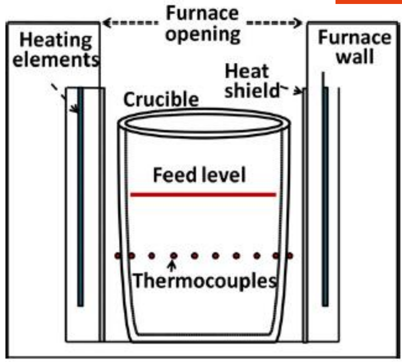
Cold cap modeling – Material properties

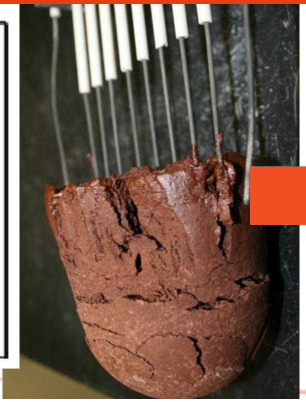
- **„Effective“ heat capacity**
  - Differential Scanning Calorimetry (DSC)
  - Includes the reaction heat

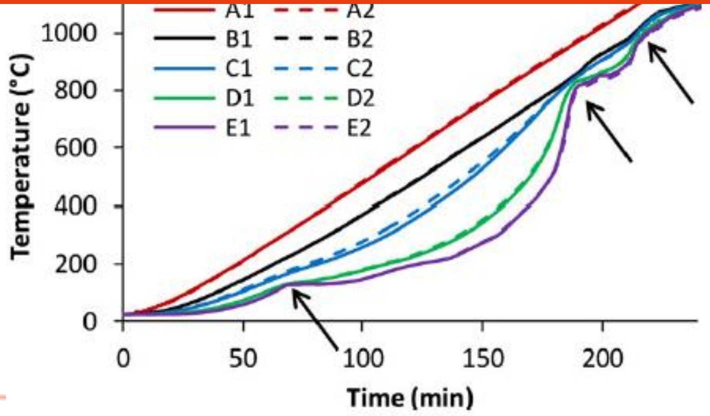


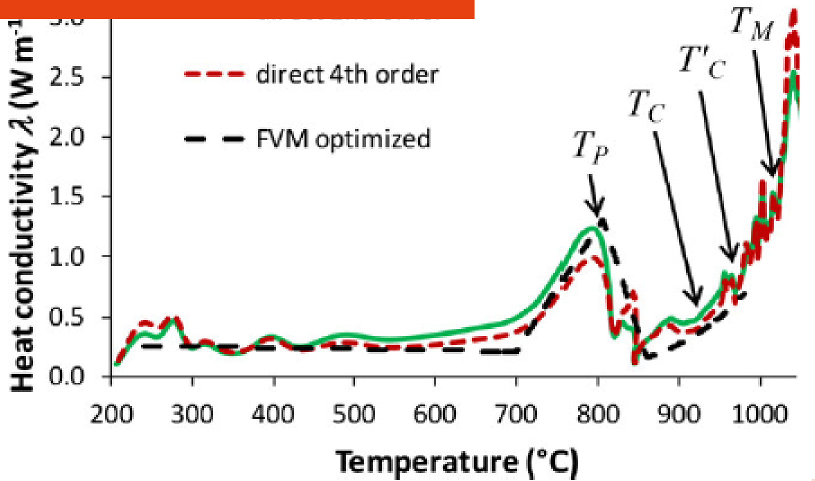
Problem – they depend on time-temperature history of the batch!

- **Feed hea**
  - calcul

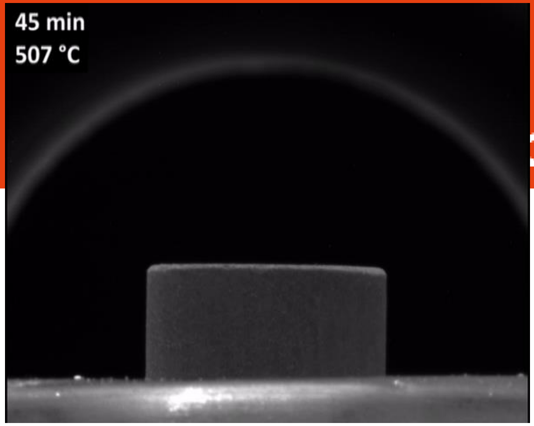


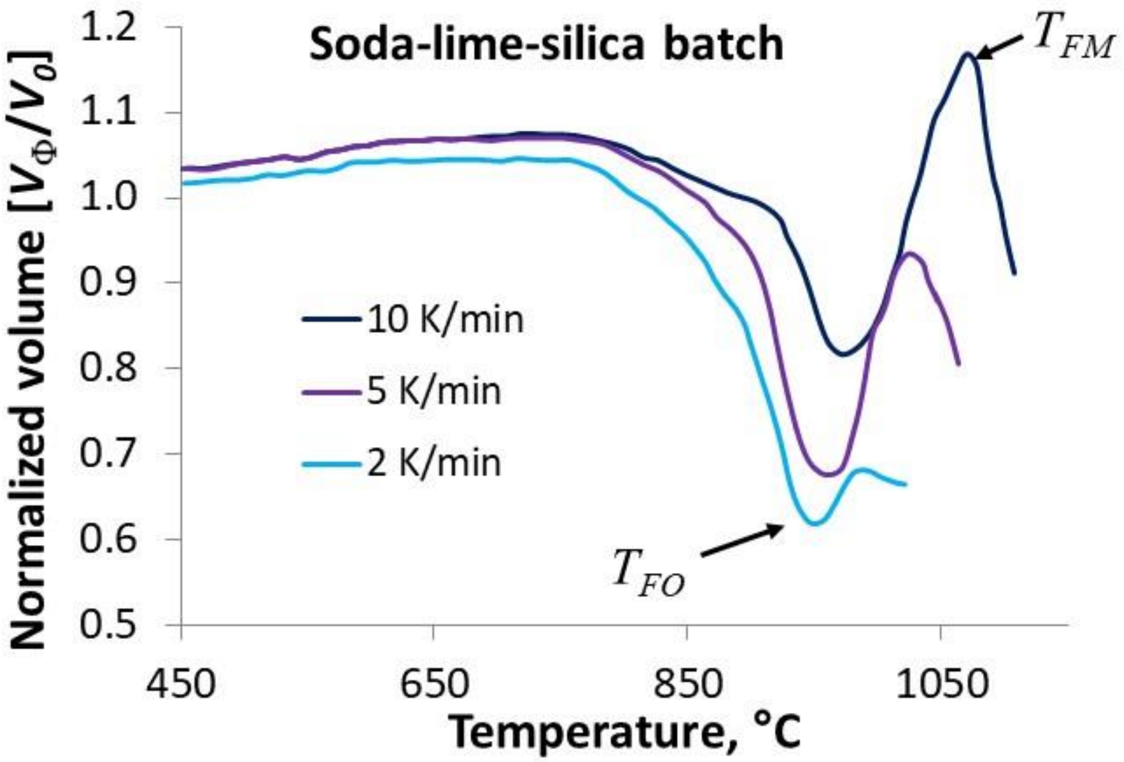




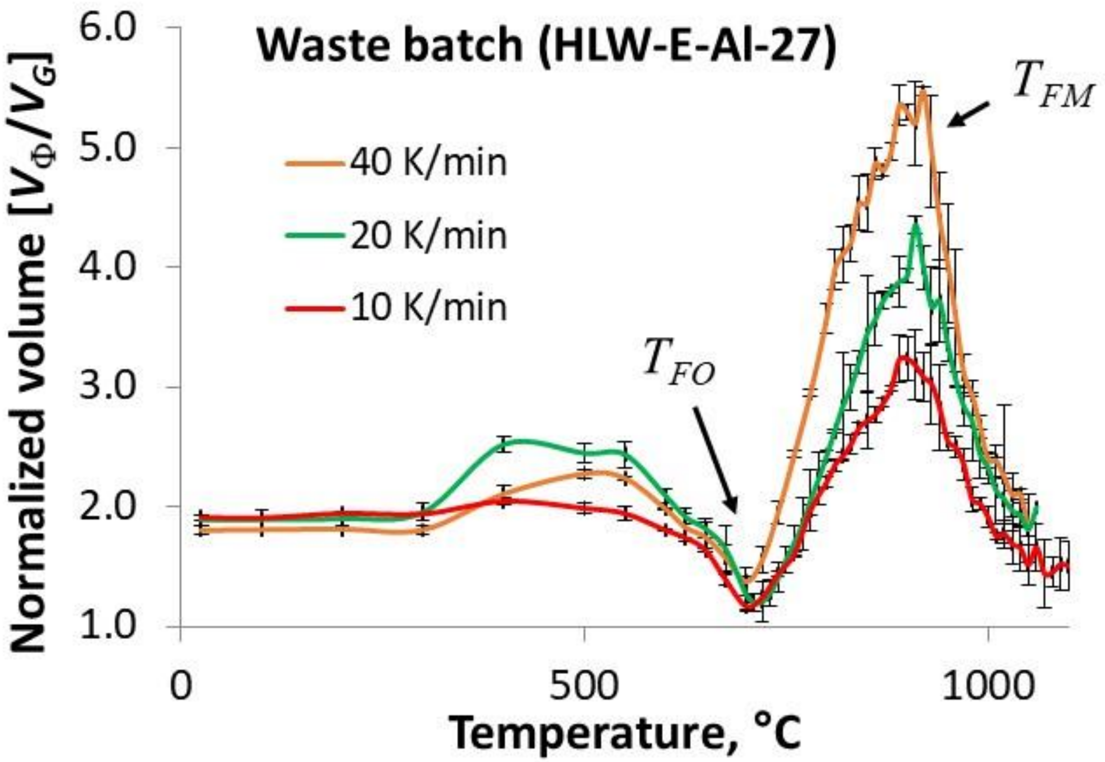


Effect of reaction kinetics





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



Lee, SM, Hrma, P, Pokorny, R, et al. Heat transfer from glass melt to cold cap: Effect of heating rate. Int J Appl Glass Sci. 2019; 00: 1– 13.

Effect of reaction kinetics on the batch

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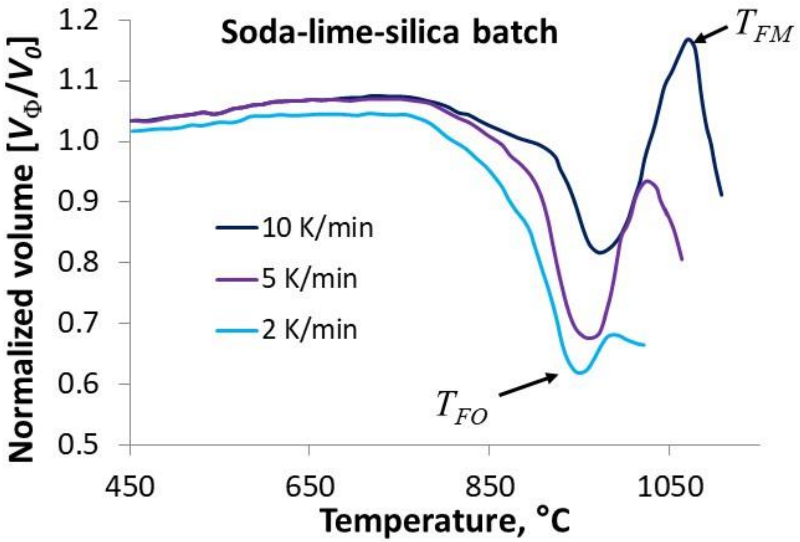
- ►Foam onset and foam maximum tends to increase with heating rate
  - ❑ Reaction kinetics shifts conversion extent to higher temperatures in response to faster heating
- ►The response of foam collapse is more complex, as it depends on transient melt viscosity, porosity, dissolving solids, etc.
  - ❑ Nevertheless, the foam level is higher at any given temperature when rate of heating is faster
  - ❑ Temperature at which the conversion is complete increases
- ►Clearly, material properties are significantly affected (density, effective heat conductivity, …)



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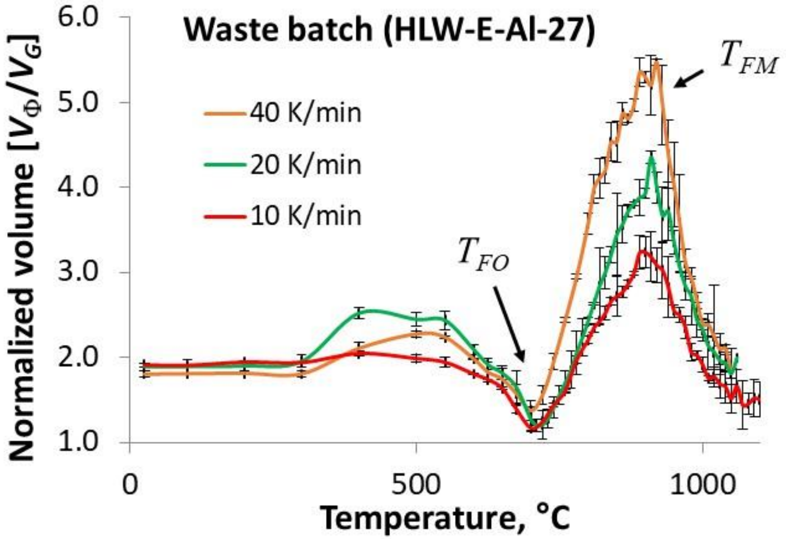
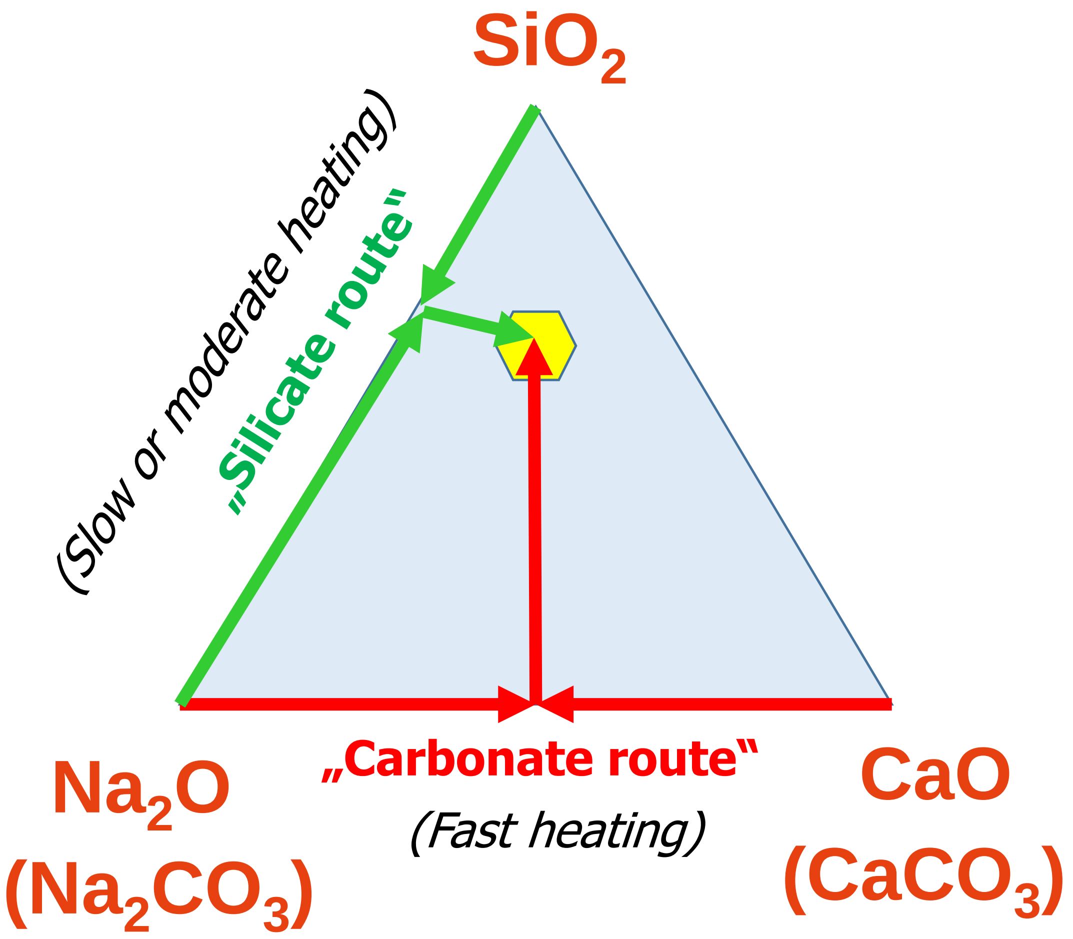


Lee, SM, Hrma, P, Pokorny, R, et al. Heat transfer from glass melt to cold cap: Effect of heating rate. Int J Appl Glass Sci. 2019; 00: 1– 13.

Effect of reaction kinetics on the batch

- The reaction pathway in soda-lime-silica glass depends on the rate of heating (prof. Conradt)
- At slower and moderate rates of heating, „silicate route“ dominates
  - ❑ the conversion of silica starts by the reaction between SiO_2 and Na_2CO_3, followed by the reaction of the produced sodium silicate with $CaCO_3$
- At fast heating rates, „carbonate route“ takes over
  - ❑ the early soda-lime melt reacts with SiO_2 forming Na_2O – CaO – SiO_2 melt
- Waste batches commonly contain >20 components!



Conradt, R., P. Suwannathada, and P. Pimkhaokham, Local Temperature Distribution and Primary Melt Formation in a Melting Batch Heap. Glastechnische Berichte, 1994. 67(5): p. 103-113.

Kinetics of batch-to-glass conversion

Heat transfer or kinetics?

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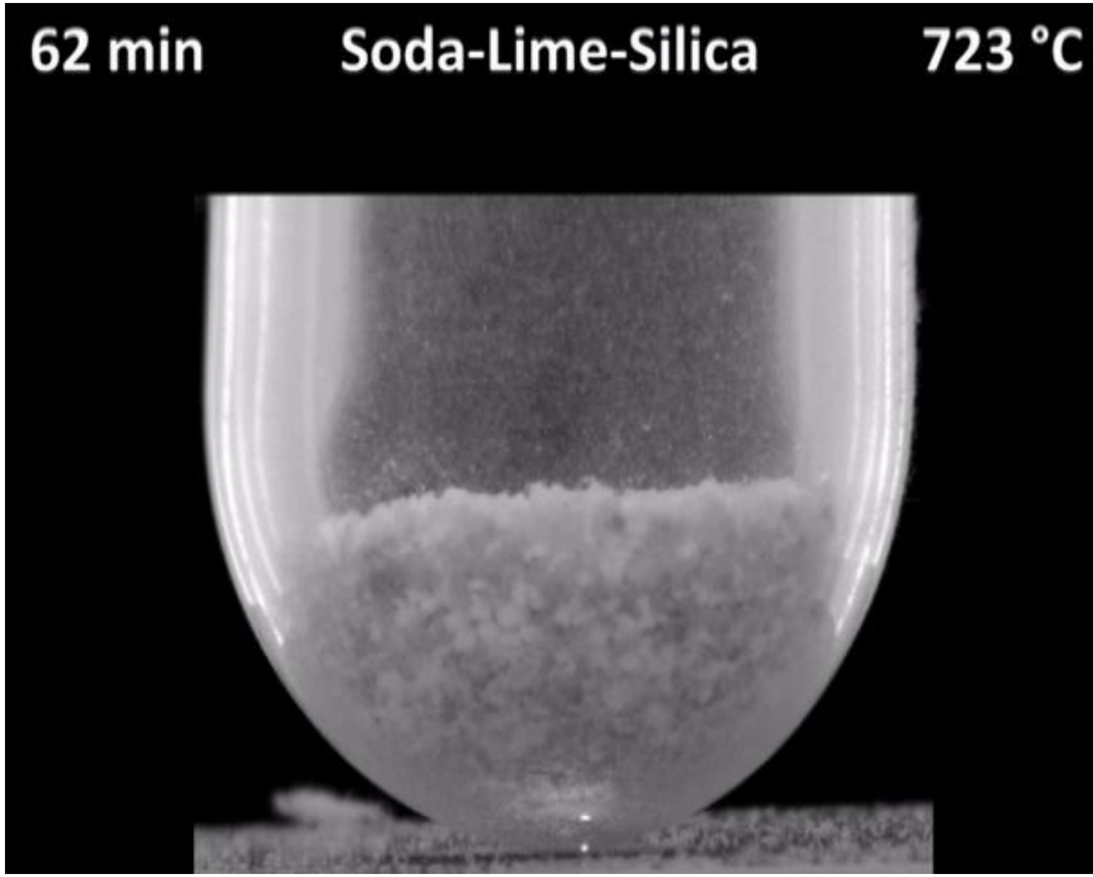
- From a lecture by professor R. Conradt:

„…conversion kinetics plays a role mostly on lab-scale, on industry-scale, it is the heat transfer to batch, not the reaction kinetics…“

- True in most cases, but kinetics affects the batch properties (porosity, conductivity, etc.)
  - ☐ How these properties depend on thermal history/kinetics?

- In some cases, heat transfer is not the limiting factor

- Kinetic approaches provide a good alternative/ supplement



Kinetics of conversion

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- Reaction kinetics
  - ❑ *„…reaction kinetics is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction….“*
  - ❑ Typically, reaction rates are expressed via reaction order, constants, etc.
- In theory, kinetic models cannot stand alone without a proper heat transfer model – they are temperature dependent
  - ❑ The heat balance provides the temperature/velocity profiles for the kinetic equation, which in turn gives the conversion degree

$$\frac{\partial}{\partial t}(\rho_B c_B T) = \frac{\partial}{\partial z}\left(\lambda_B \frac{\partial T}{\partial z}\right) + H_{ch}$$

$$\frac{d\alpha}{dt} = f(time - temperature\ history) = f(\alpha, T)$$

Kinetics of conversion

UCT PRAGUE

- Reaction kinetics
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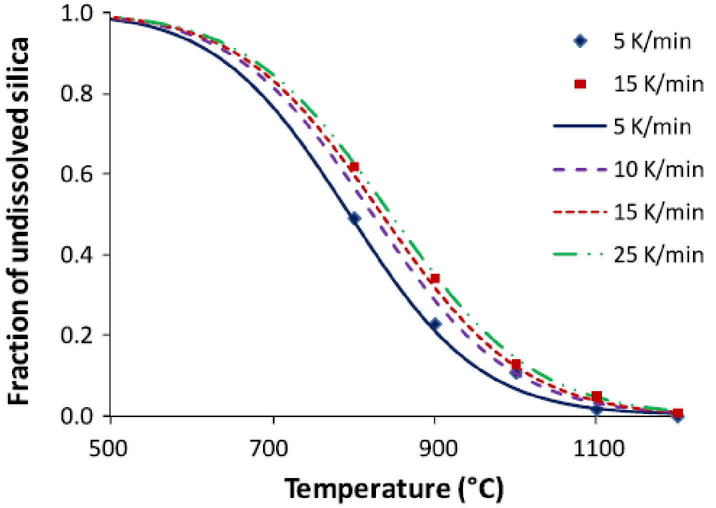
- In theory, kinetic models cannot stand alone without a proper heat transfer model – they are temperature dependent
  - ☐ The heat balance provides the temperature/velocity profiles for the kinetic equation, which in turn gives the conversion degree
- "Terminal batch-to-glass conversion process"?

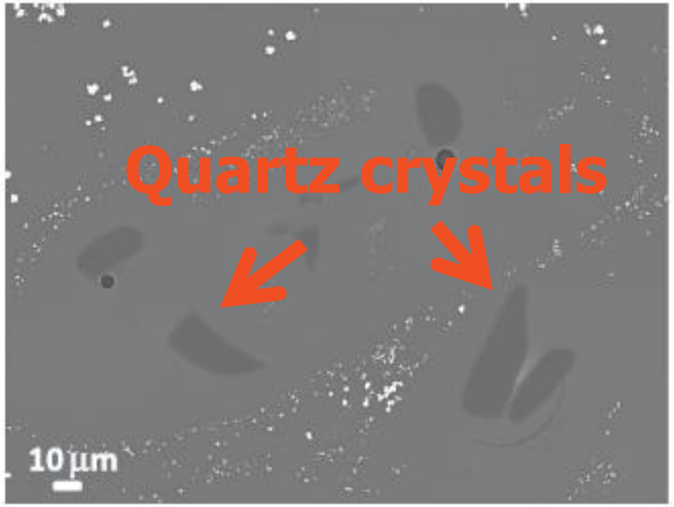
$$\frac{d\alpha}{dt} = f(time - temperature\ history) = f(\alpha, T)$$

Kinetics of silica dissolution

- ► Quartz – diffusion controlled dissolution
  - ☐ $j = \rho_G h(x_{SG} - x_{SB})$
  - ☐ The mass transfer coefficient h depends on numerous factors (presence of bubbles, overlap of concentration boundary layers of neighboring grains, temperature, …)



- ► Kinetic equation for silica dissolution:
  - ☐ $$\frac{d\alpha}{dt} = A(1-\alpha)^n \exp\left(-\frac{B}{T}\right)$$
  - ☐ Pre-exponential factor might depend on time-temperature history:
    - ☐ $A = f(t,T)$



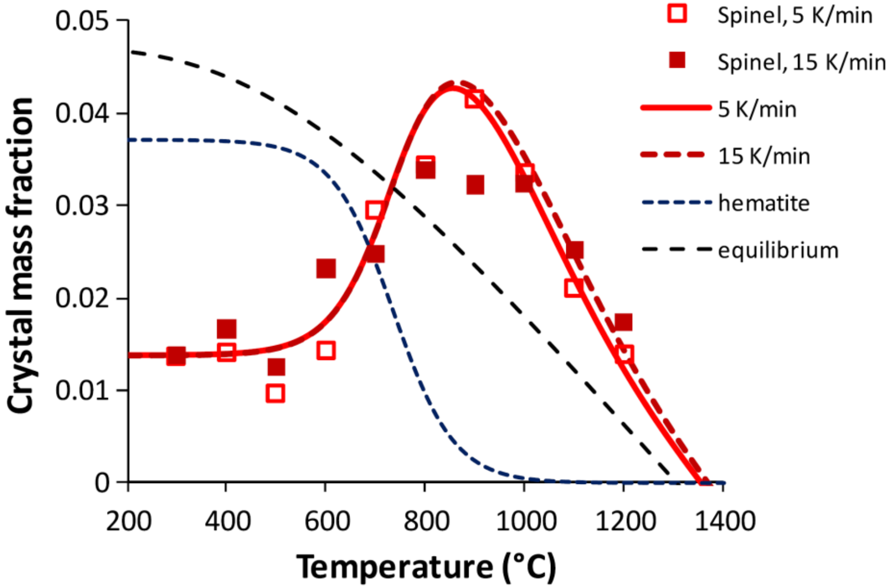
R. Pokorny et al. / Journal of Nuclear Materials 443 (2013) 230–235

Kinetics of spinel dissolution

- Kinetic equation for spinel growth and dissolution:
  - ☐ $$\frac{dc_s}{dt} = -p\frac{dc_H}{dt} + 2k_0(c_{s0} - c_s)exp(-B/T)$$

Spinel growth from hematite

Spinel dissolution (Hixon-Crowell equation)



R. Pokorny et al. / Journal of Nuclear Materials 443 (2013) 230–235

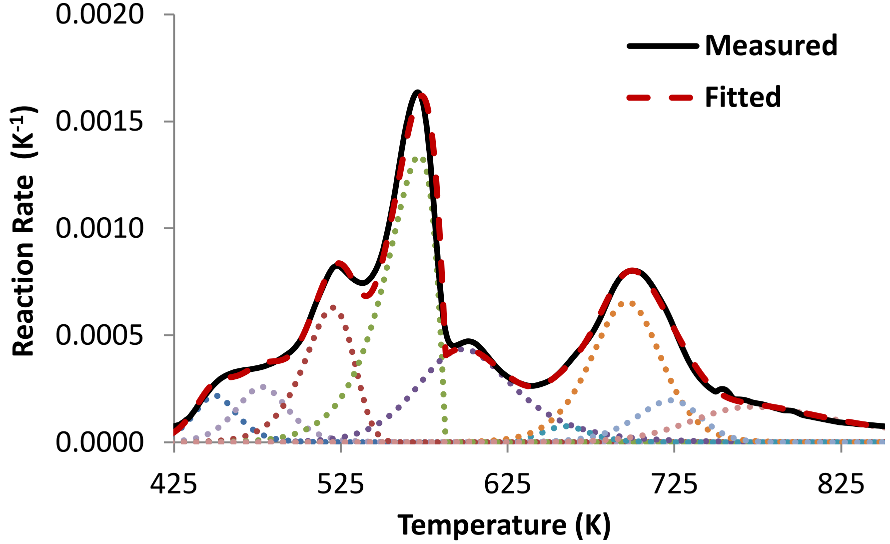
- Useful for stirred melters that mix the batch directly into the melt – such as in French induction heated melters
  - k_0 as a function of melt convection (Sherwood number)

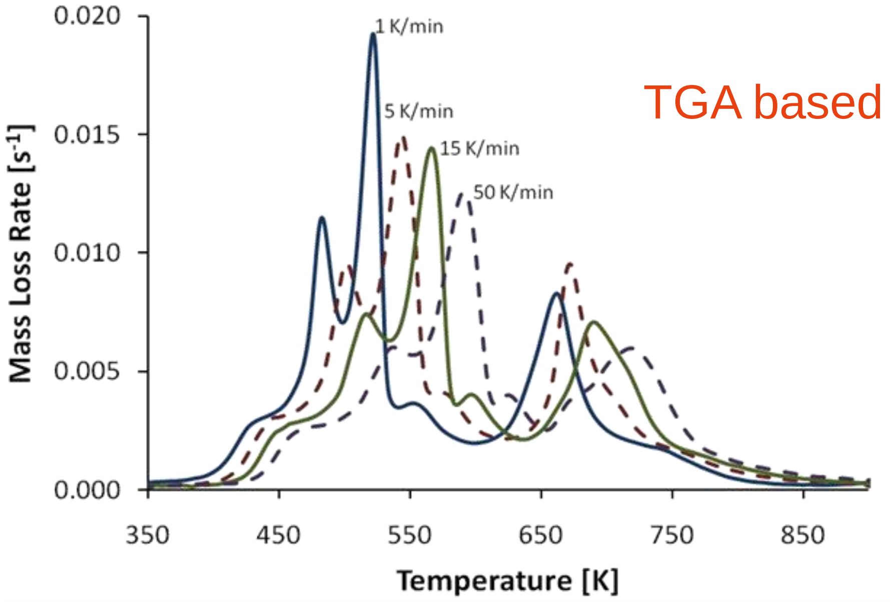
Kinetics of batch conversion (TGA, DSC)

UCT PRAGUE

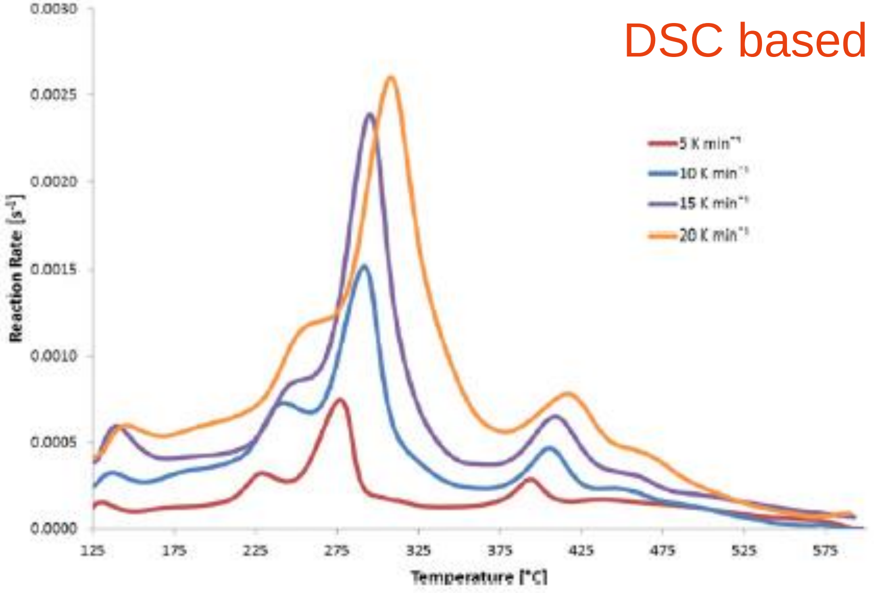
- ▶ Gas evolving reactions (i.e, TGA based kinetics)
- ▶ Reaction heat based kinetics (i.e, DSC based kinetics)

$$\frac{d\alpha}{dt} = \sum_{1}^{N} w_i A_i (1-\alpha_i)^{n_i} e^{-\frac{E_i}{RT}}$$





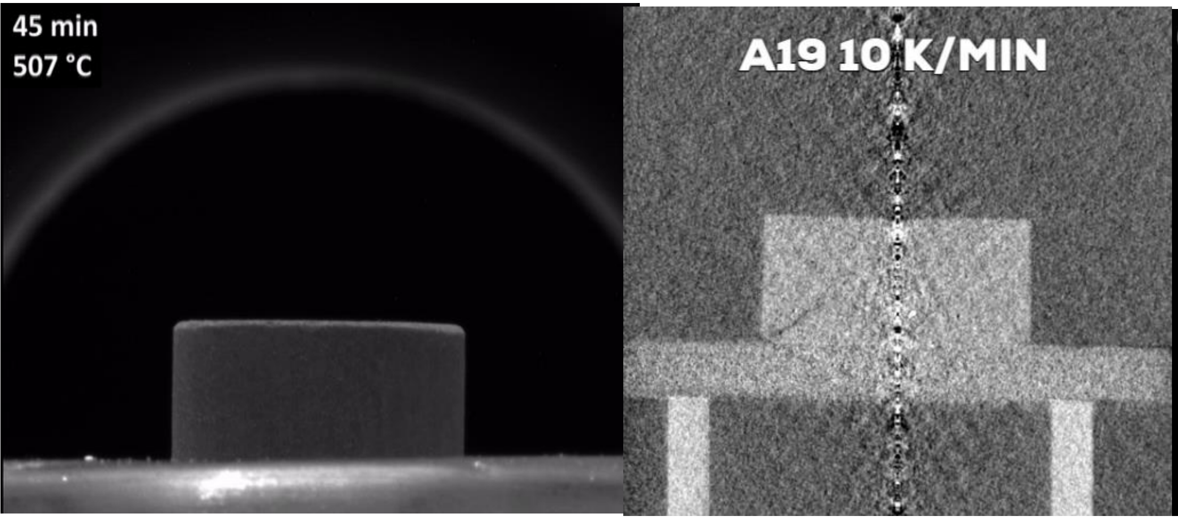
TGA based



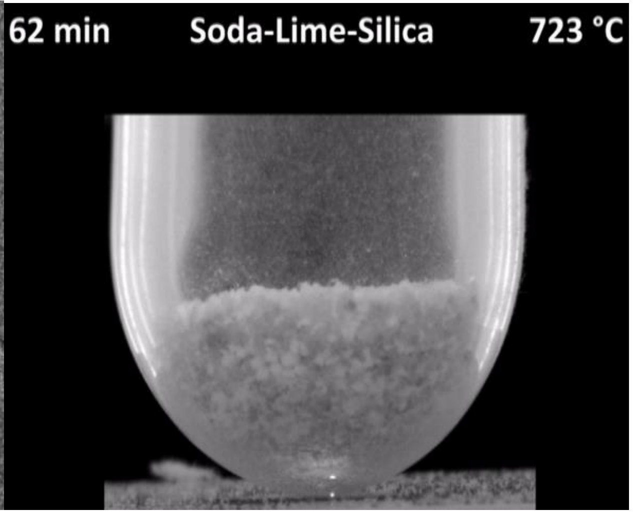
DSC based

Kinetics of foam evolution and collapse

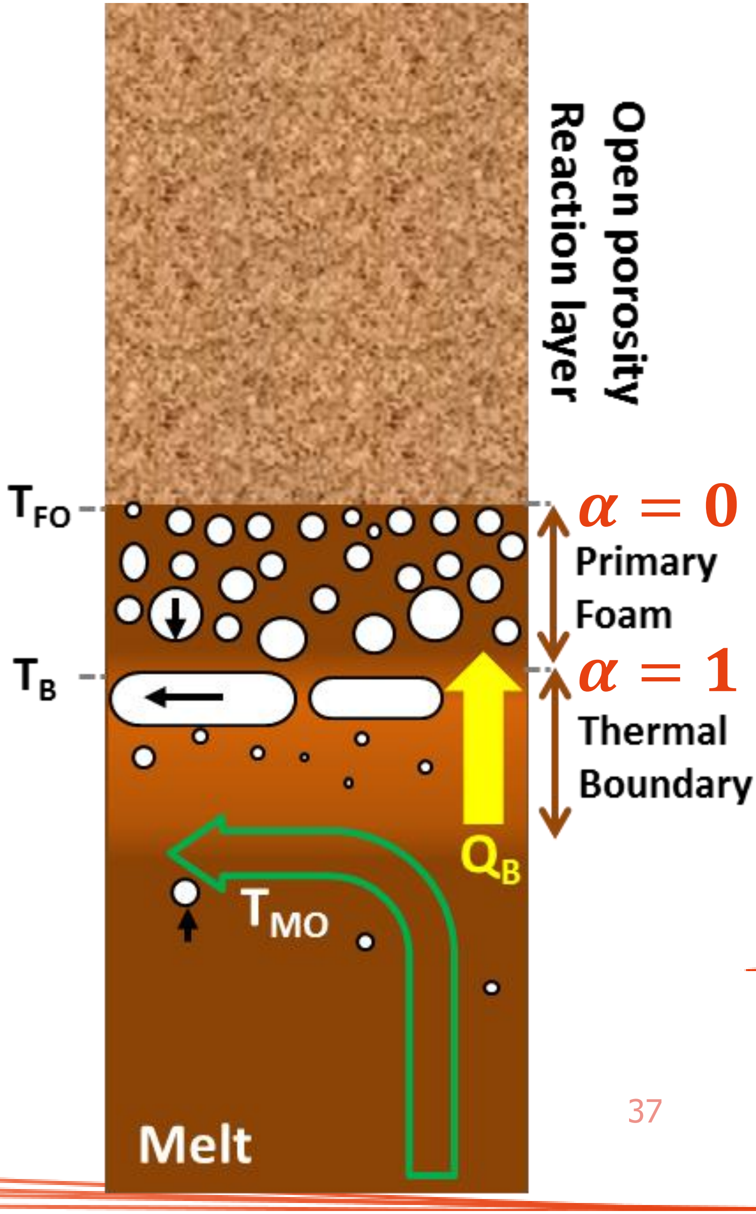
- While most gases evolve at low temperatures and escape through open porosity, residual gas evolving reactions create primary foam



Nuclear Waste Feed A19



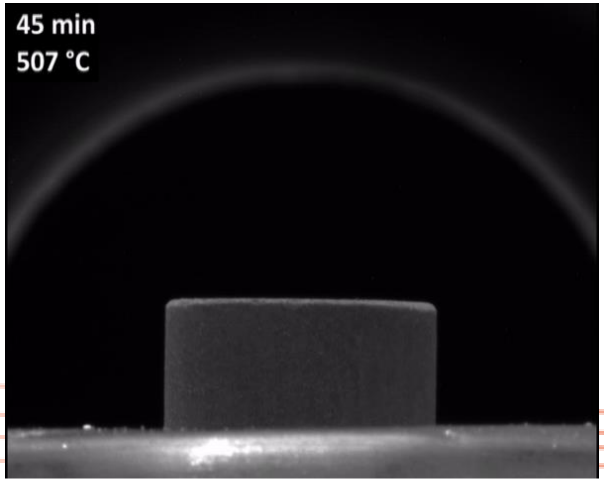
Commercial Soda-Lime-Silica

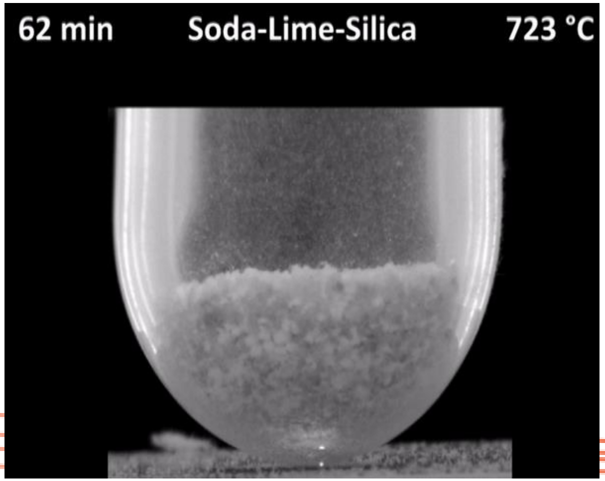


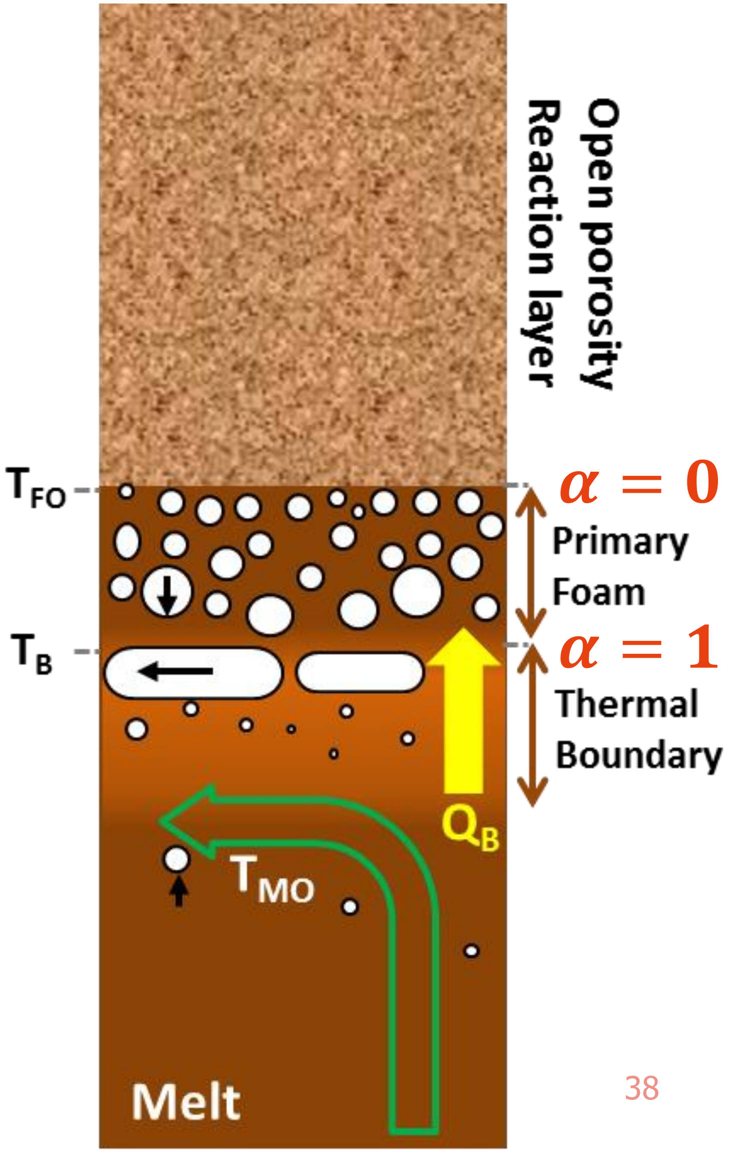
Kinetics of primary foam

- ►We can assume that the conversion finishes (α = 1) at cold cap bottom, when the feed (foam) collapses and bubbles are released.

- ►By measuring the foam evolution and collapse at different heating rates, we obtain a kinetic relationship, providing bottom temperature T_B as a function of time-temperature history the feed experienced in the reaction layer

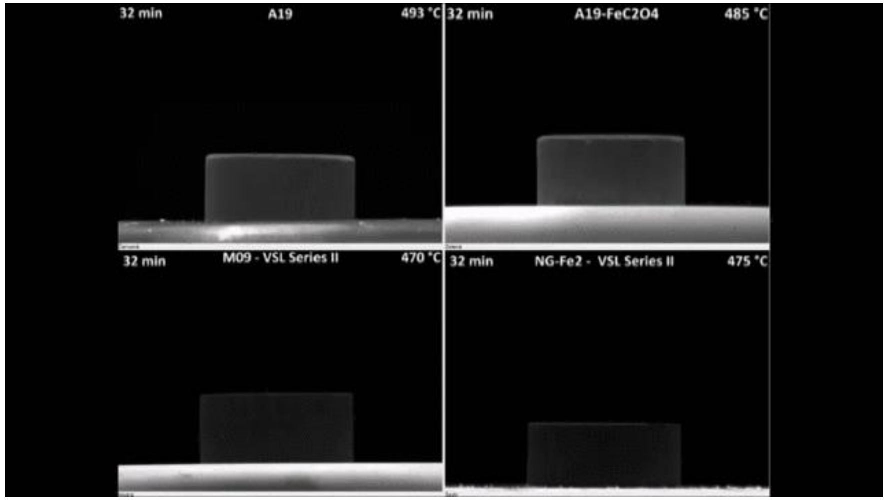


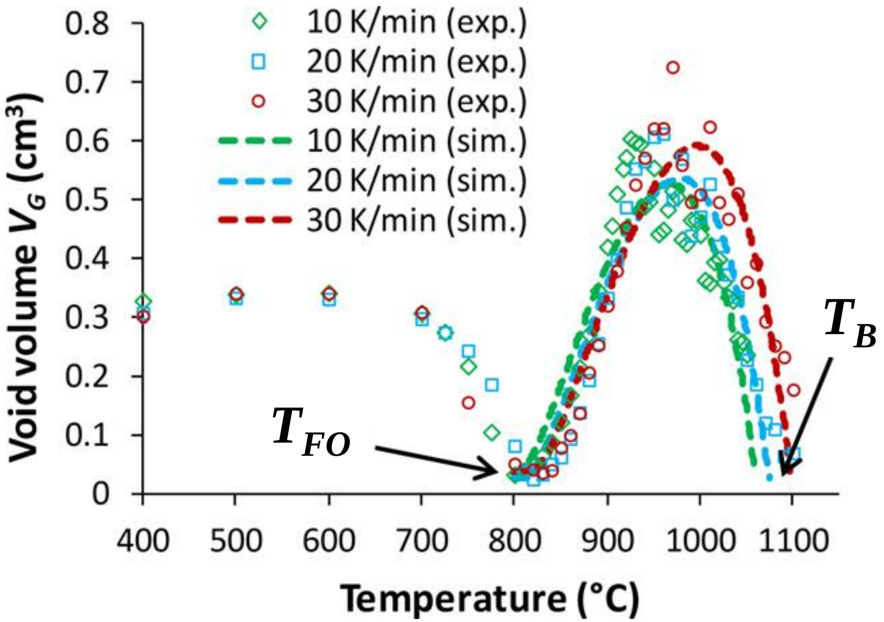




Kinetics of foam evolution and collapse

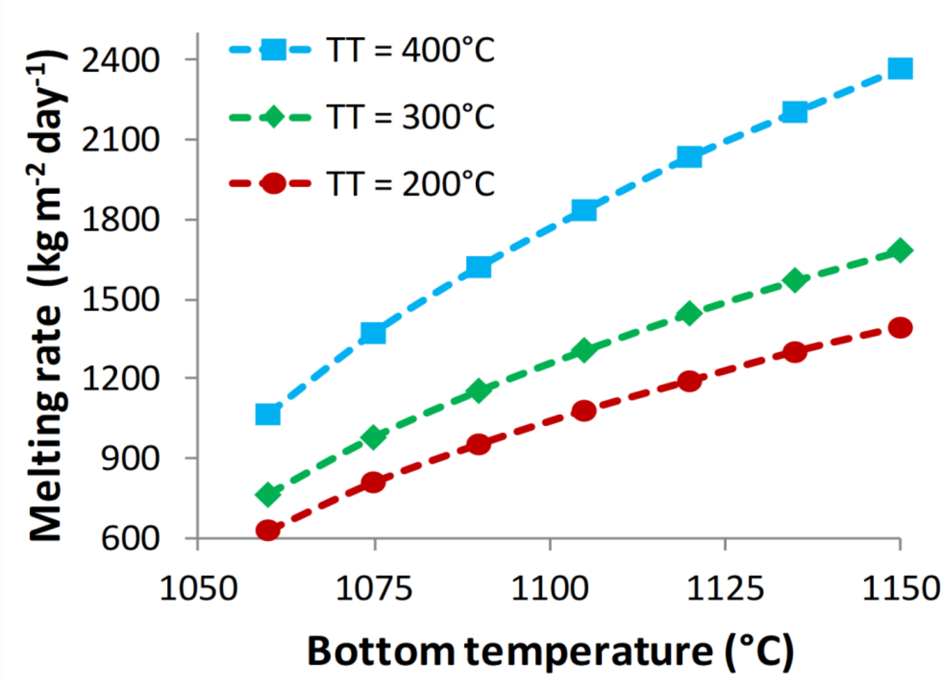
- ►Detailed mathematical description of foam evolution and decay is not yet developed
- ►Experimental data can be sufficiently represented by empirical or semi-empirical equations for foam growth and foam collapse rates:
  - ❑ Foam volume: $$\frac{dV_G}{dt} = R_G - R_C$$
  - ❑ Foam growth: $$R_G = b_G \arctan\left[\frac{T - T_1}{T_2}\right]$$
  - ❑ Foam collapse: $$R_C = b_C e^{-\frac{B_C}{T}}$$

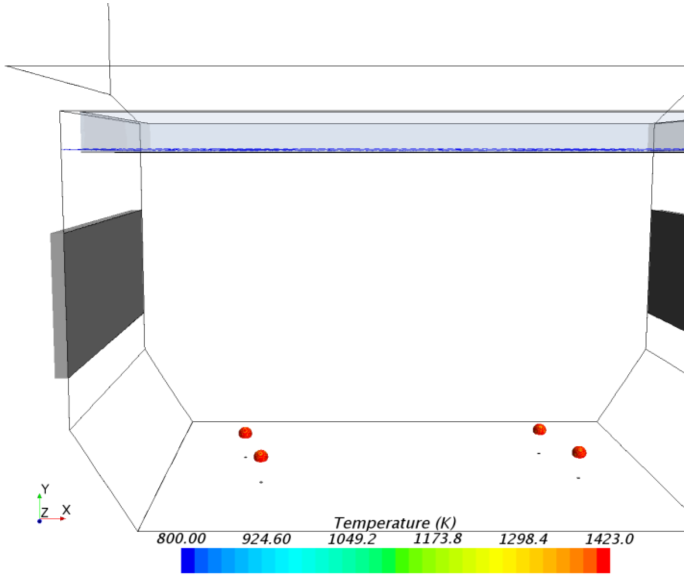


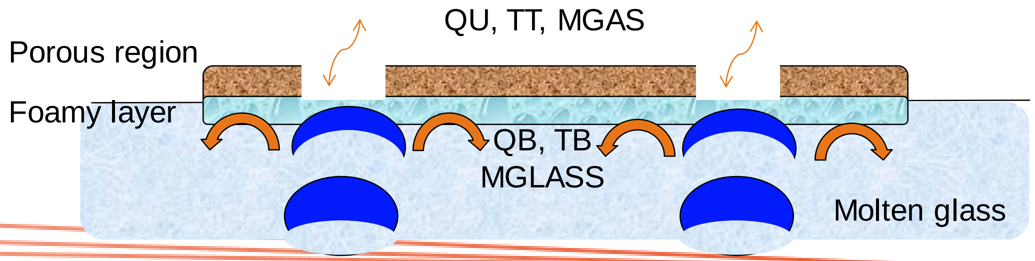


Boundary conditions

- The cold cap model computes the *melting rate* as a function of the *bottom temperature*, T_B, and the *top surface temperature* (T_T) (or alternatively heat flux to the top surface Q_{plenum}).
  - ☐ The boundary conditions are obtained by coupling the cold cap model with the CFD model of the melter or using heat transfer coefficients.

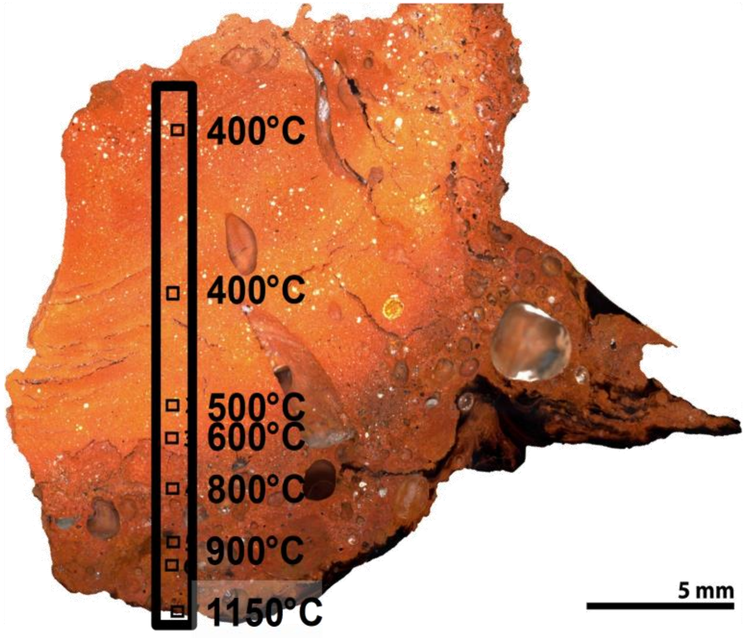


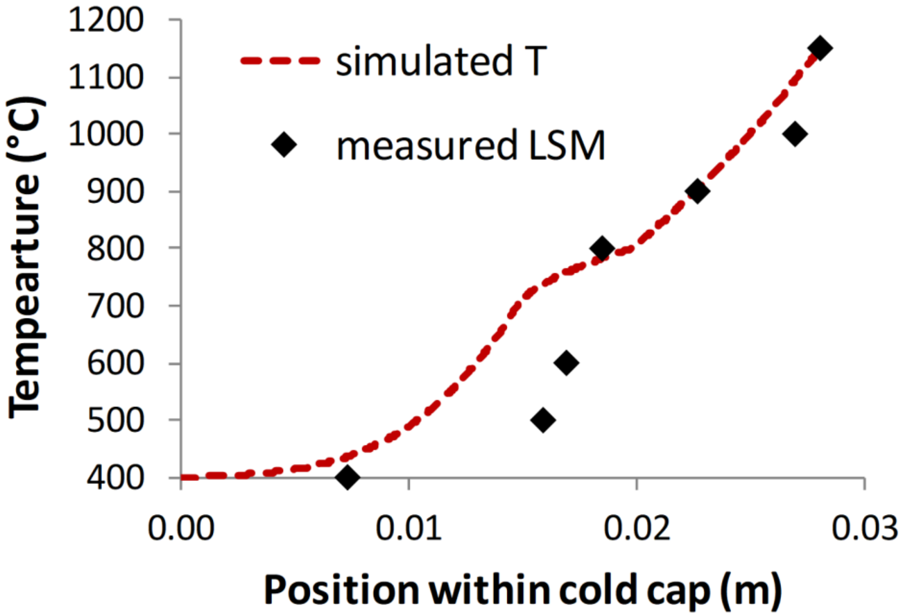




Comparison with LSM data

- ▶The model also computes the temperature distribution within the cold cap.
- ▶The simulated temperature profile is in satisfactory agreement with the profile obtained for a cold cap generated in the laboratory-scale melter (LSM).



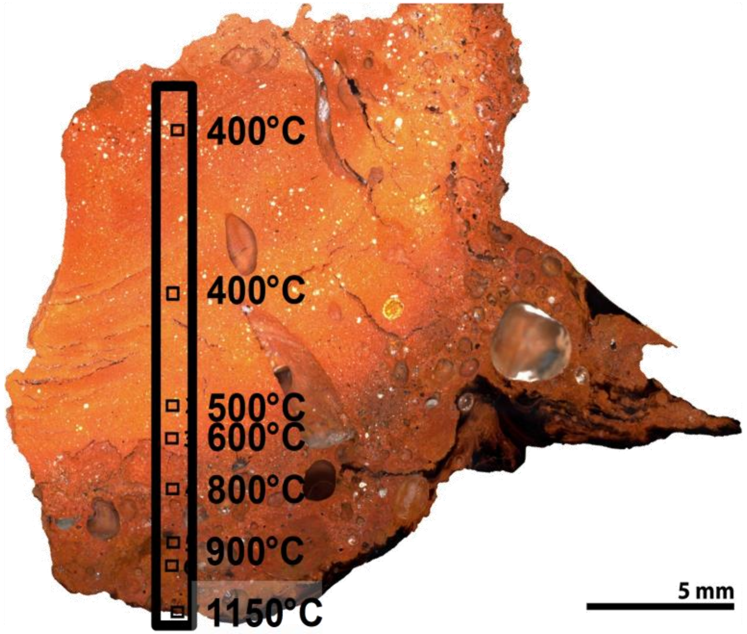


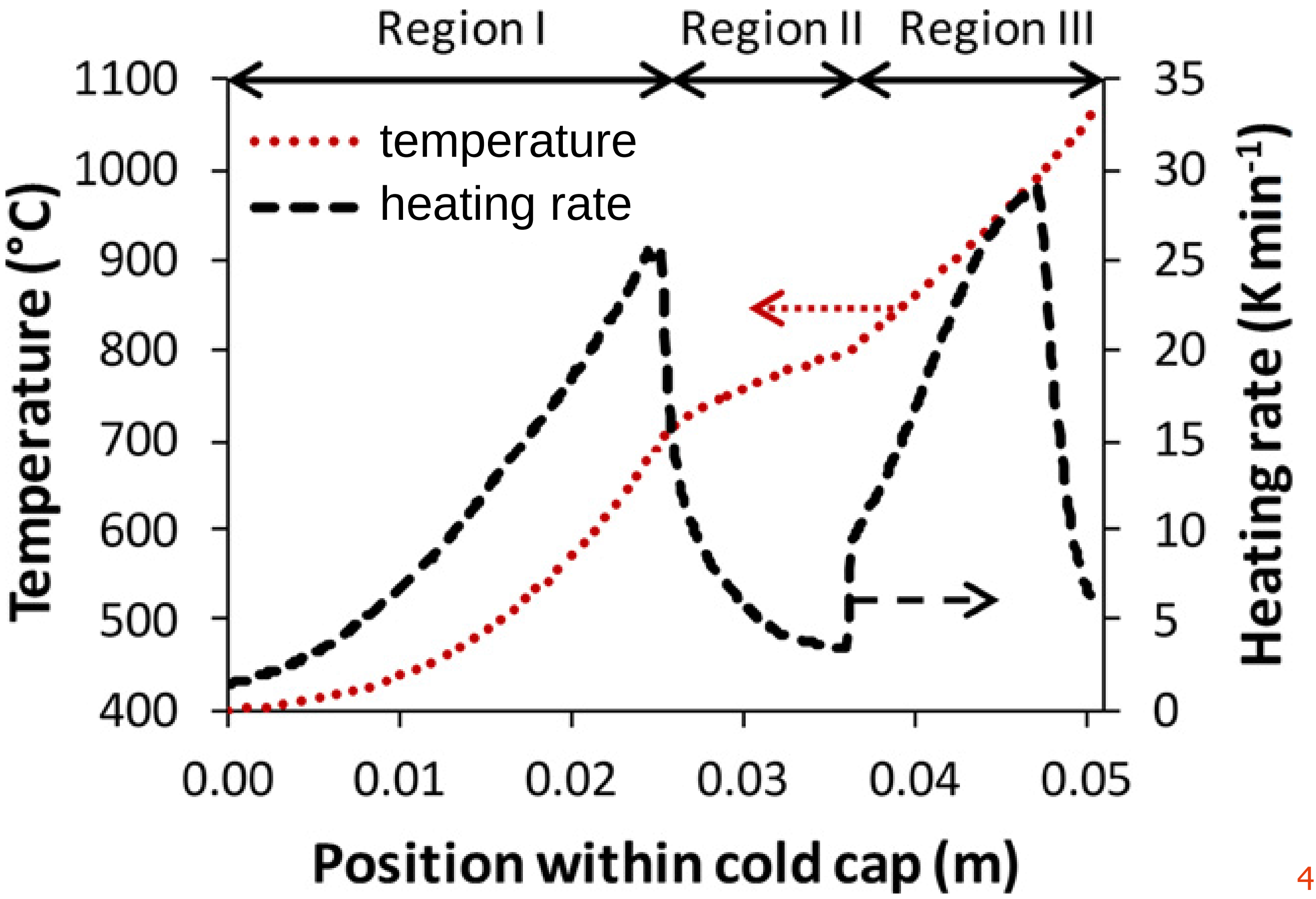
__R. Pokorny__ et al.: One-Dimensional Cold Cap Model for Melters with Bubblers, Journal of the American Ceramic Society, __98__, 2015, p.3112-3118.

__D. Dixon__ et al.: Temperature Distribution within a Cold Cap during Nuclear Waste Vitrification, Environmental Science & Technology, 49, 2015, p.8856-8863.

Model results preview

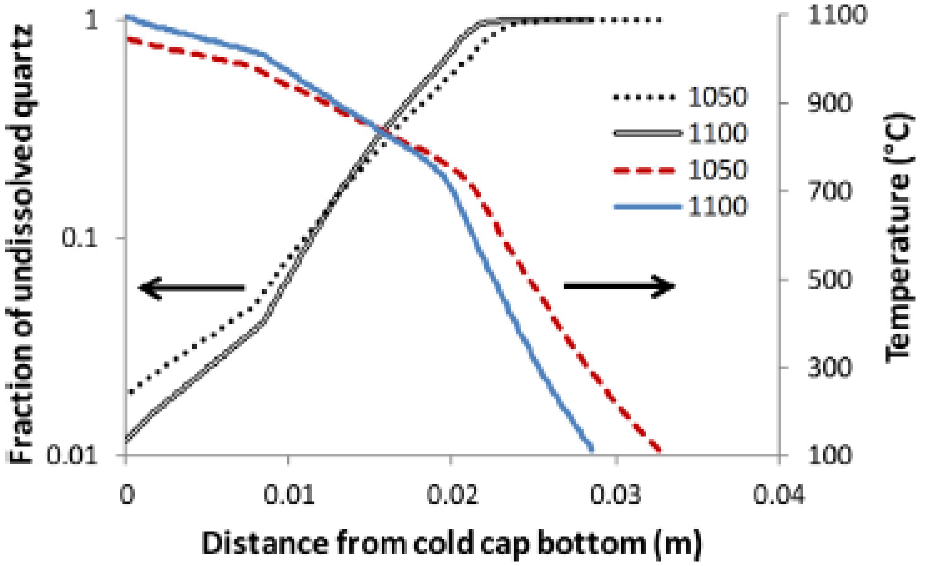
- Feed properties in the cold cap
  - ❑ Temperature and heating rate profiles

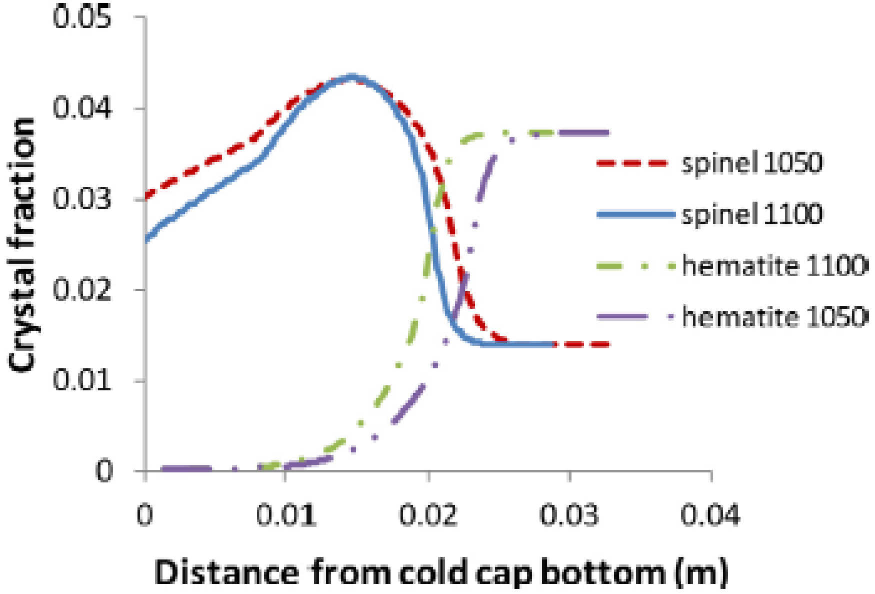


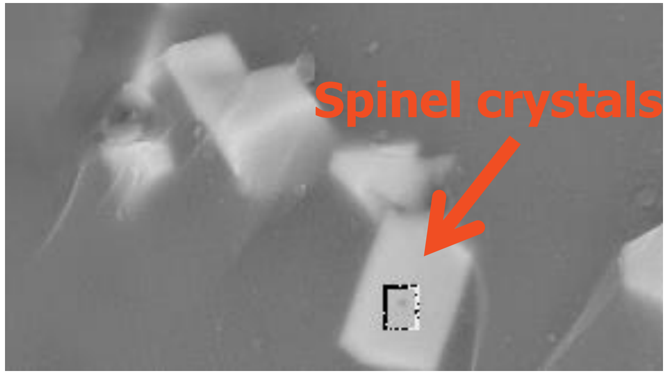


Model results preview

- Concentration of solid *silica*, *hematite*, and *spinel*







Pokorny et al, Journal of Nuclear Materials 443 (2013) 230–235

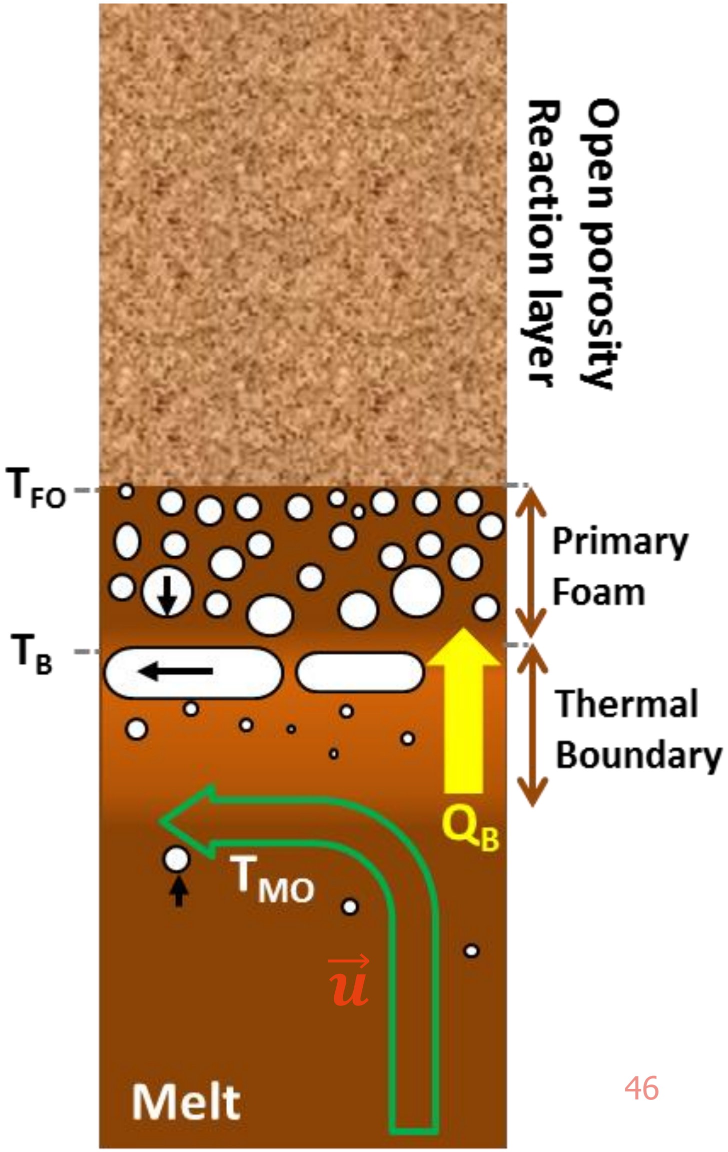
Heat transfer from melt to cold cap

Convection heat transfer – Analogy?

Convection heat transfer

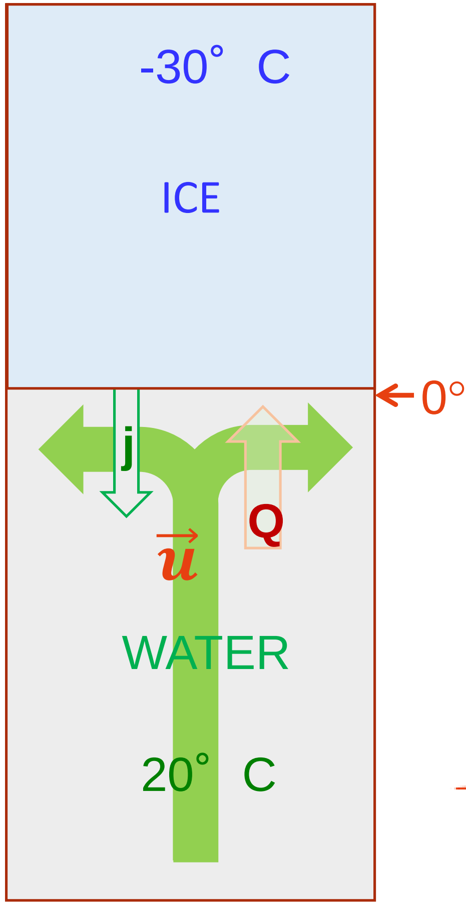
What about glass batch on hot melt?

- Melt under the cold cap contains dissolving solids, gas bubbles ascending from the melt and large bubbles/cavities from primary foam collapsing at cold cap bottom.
- Inhomogeneities and nonuniformities affect density, viscosity, and heat conductivity. Fast moving cavities cause turbulence.
- Radiation heat transfer can play a role



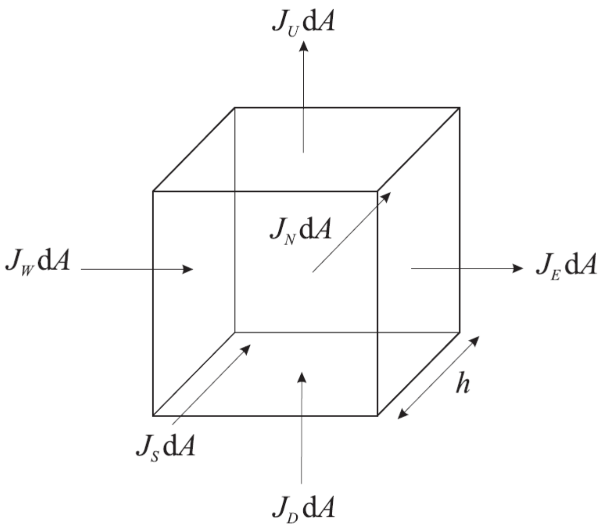
Heat transfer from melt

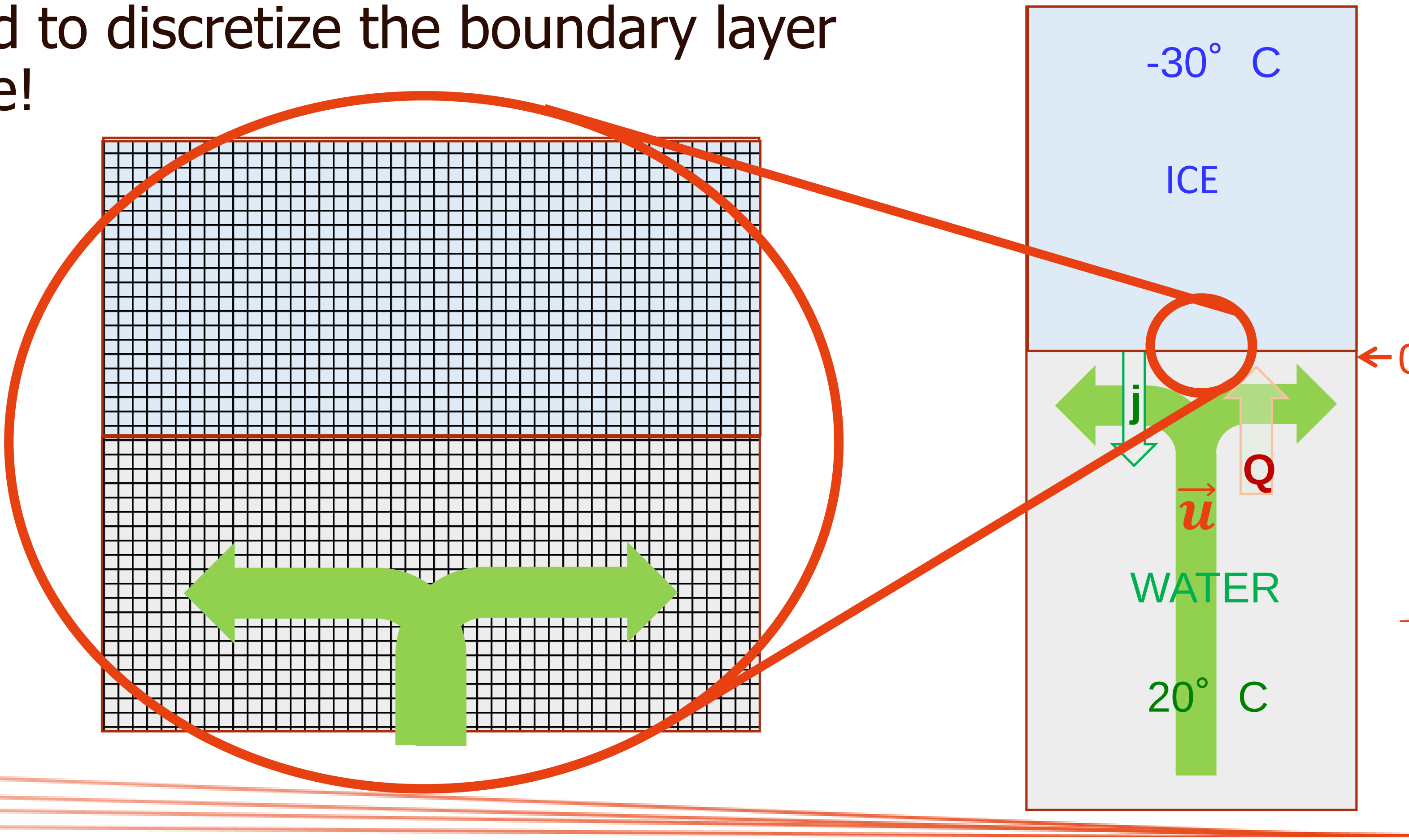
- Analogy – melting of an ice cube (cold ice on warm water)
  - Melting rate depends on heat the heat flux (*Q*)
  - ***j* = *Q*/ *H***, where *H* is the melting heat.
- The heat flux depends on the heat transfer across the interface depends on
  - Convection in molten glass and molten glass properties
  - „Melting temperature"
- Solution possible! (both numerical and analytical)



Convection heat transfer – CFD

- Numerical solution –
  - ❑ Finite volume method
  - ❑ Finite element method
- Sufficient resolution is needed to discretize the boundary layer developed near the interphase!





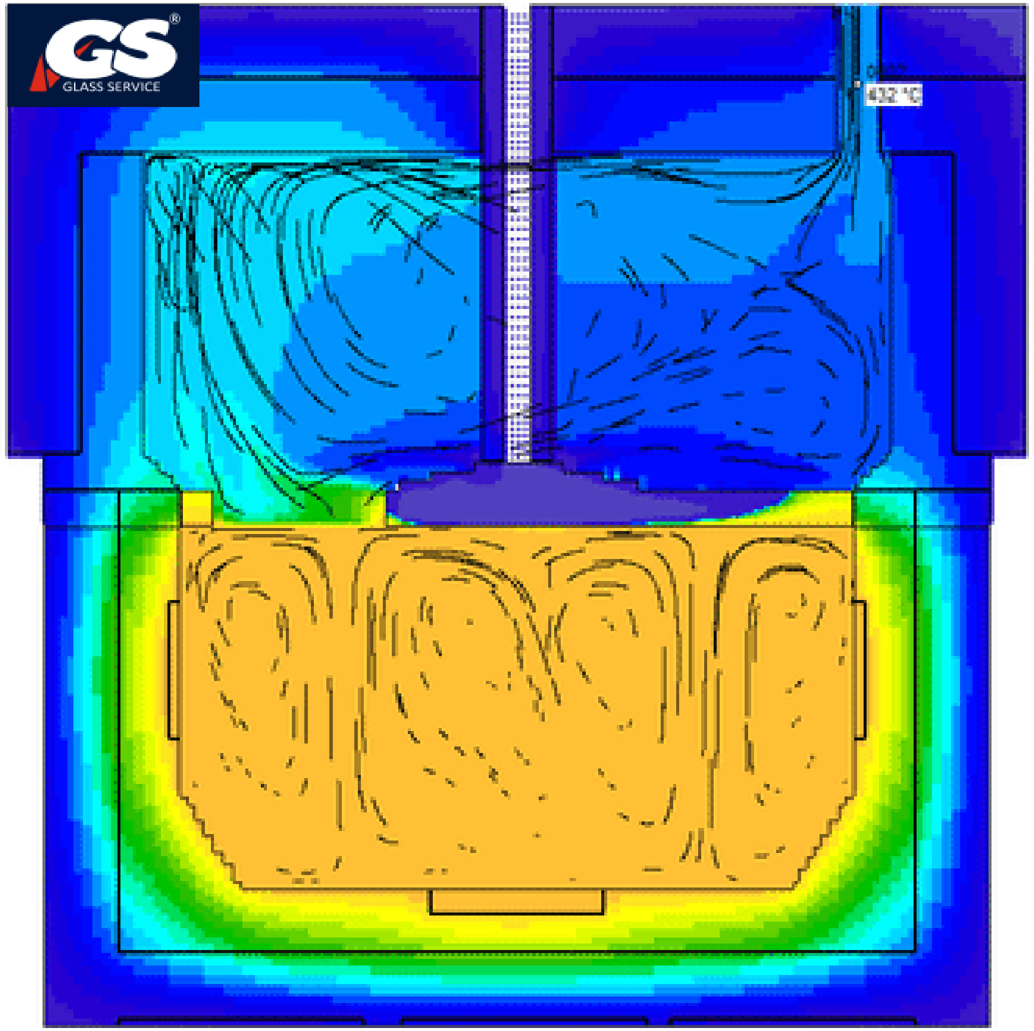
CFD modeling – thermal boundary layer

- Coupling heat & mass balances at the interface between batch and melt/combustion space

$$\lambda_B \frac{\partial T_B}{\partial z}\bigg|_{\text{interface}} = \lambda_{G/C} \frac{\partial T_{G/C}}{\partial z}\bigg|_{\text{interface}}$$

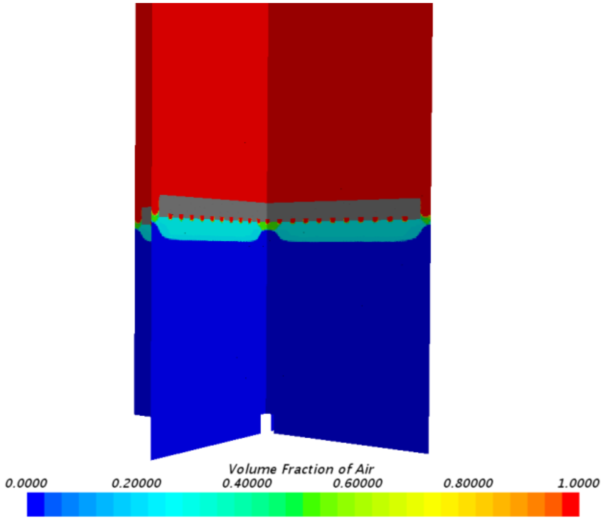
$$T_B\big|_{\text{interface}} = T_{C/G}\big|_{\text{interface}}$$

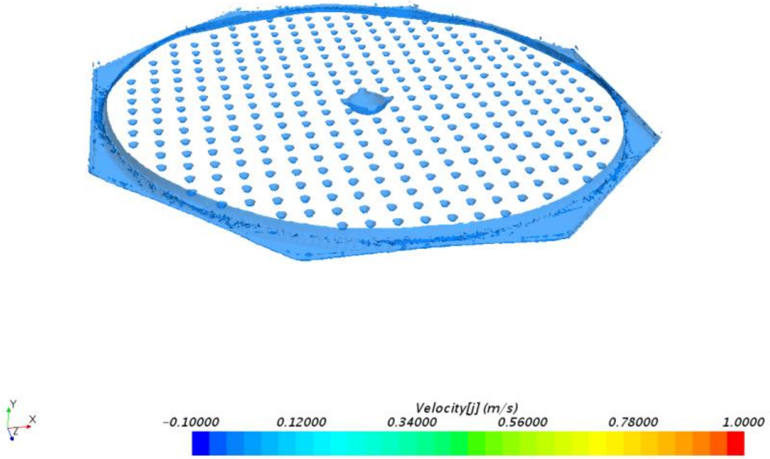
- Generally, CFD models use grids that are too coarse to properly resolve the complicated cases of mass and heat transfer that occurs in the boundary layers near the interfaces with the batch
  - ☐ Especially true for the batch/melt interface, where primary foam bubbles coalesce and collapse into cavities

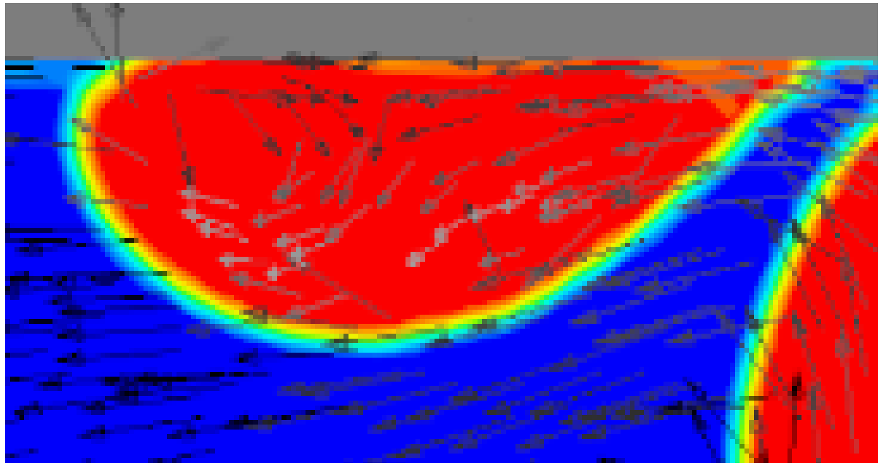


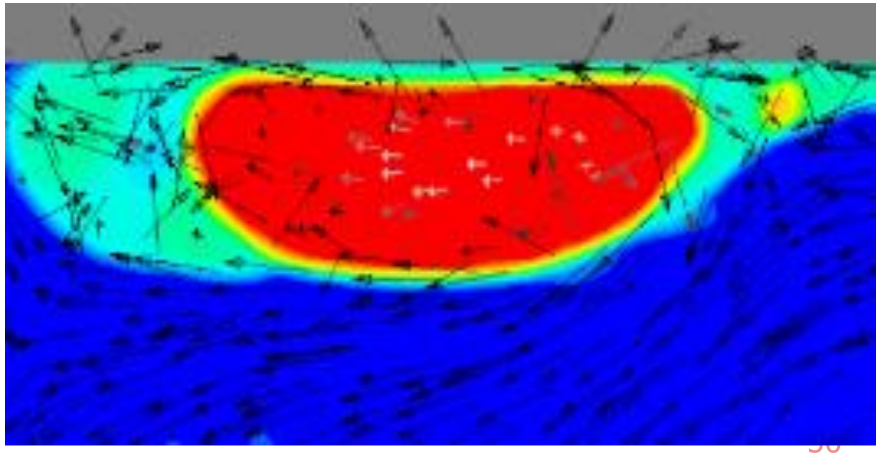
CFD modeling – thermal boundary layer

- Resolving the phenomena in boundary layer using CFD





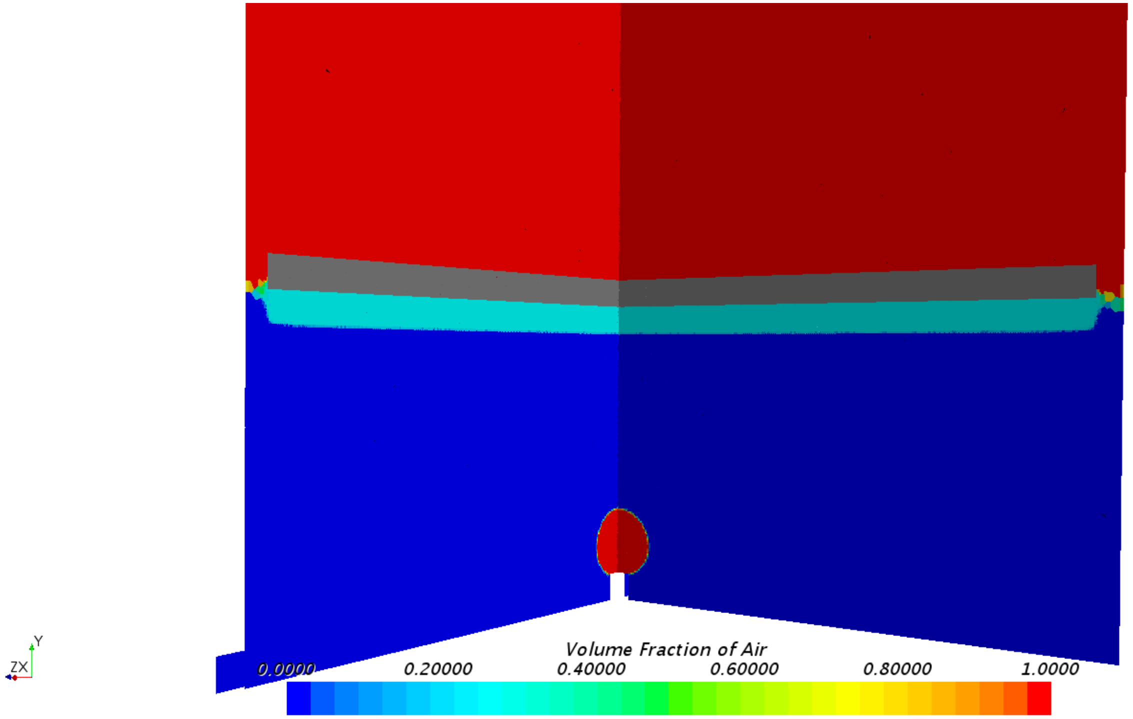




Abboud, A.W., et al., *Numerical Experiments of the Cavity Layer underneath the Cold Cap in a Waste Glass Melter*. Submitted, 2019.

CFD modeling – thermal boundary layer

- Resolving phenomena in the boundary layer using CFD



Abboud, A.W., et al., *Numerical Experiments of the Cavity Layer underneath the Cold Cap in a Waste Glass Melter.* Submitted, 2019.

Convection heat transfer – Analytical

- Convection heat transfer is expressed as

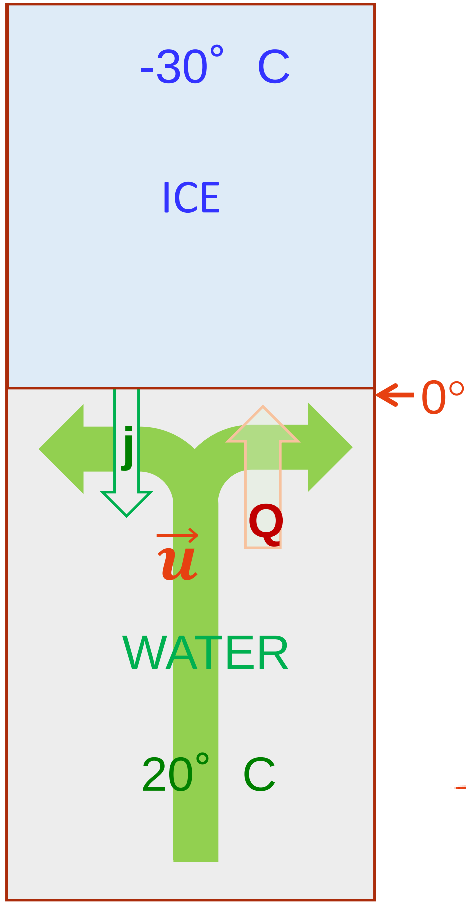
$$Q = h(T_{liquid\ bulk} - T_{Melting})$$

Q is the heat flux [W m^{-2}]

h is the heat transfer coefficient [W m^{-2}K^{-1}]

$T_{liquid\ bulk}$ is the bulk liquid temperature [K]

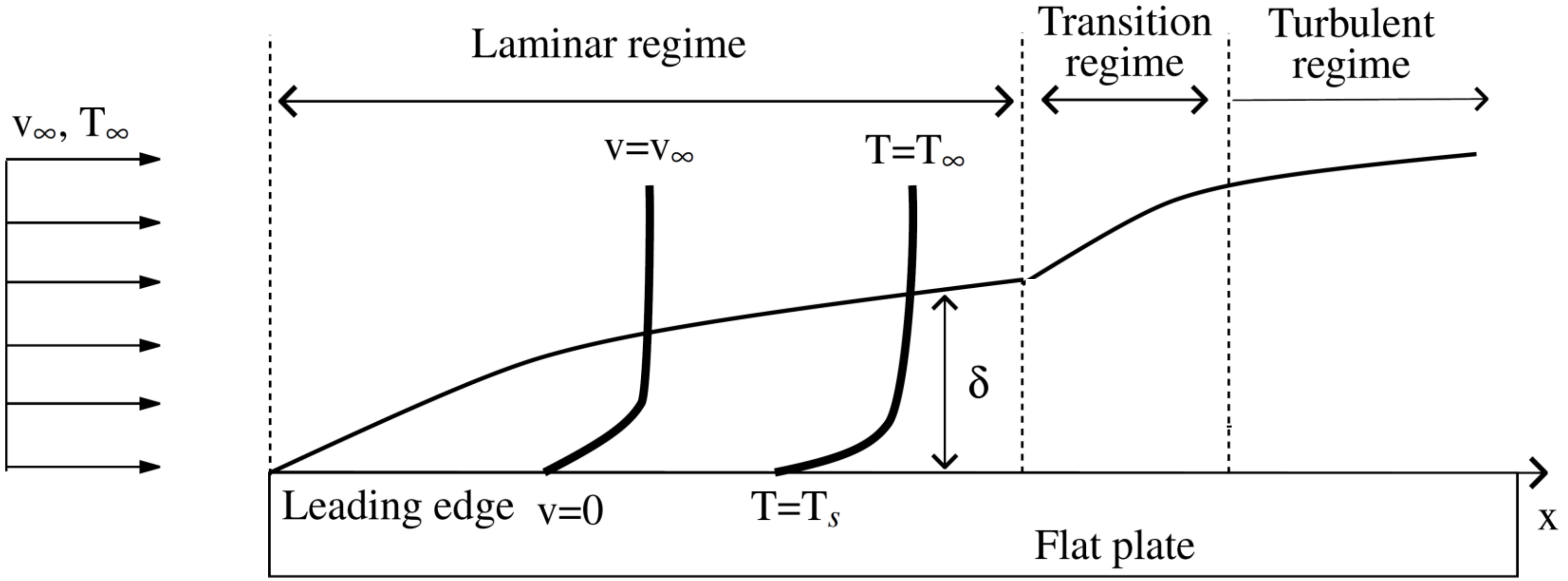
$T_{Melting}$ is the melting/interface temperature [K]

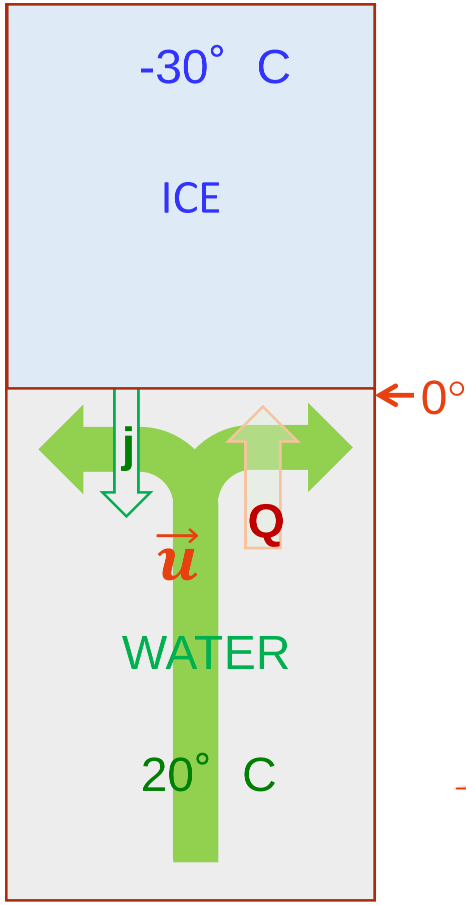


- The heat transfer coefficient depends on the fluid properties and the fluid flow velocity (type – laminar/turbulent)
  - ☐ How to calculate it?

Convection heat transfer

- Boundary layer theory
  - ☐ Convection heat transfer over flat plate





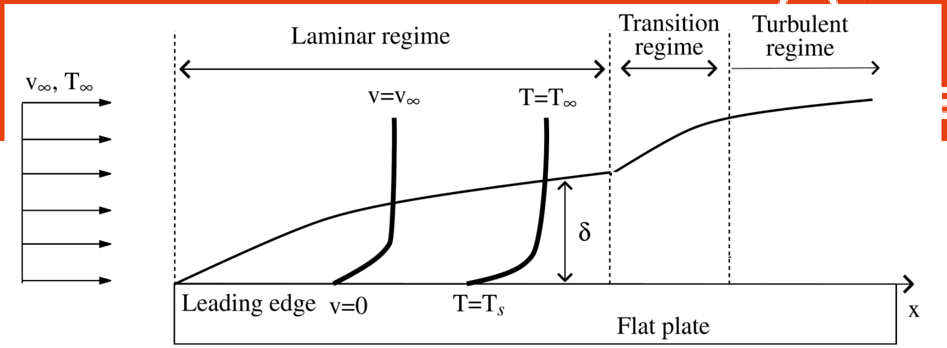
v is the velocity

T is the temperature

δ is the boundary layer thickness

x is the distance from leading edge

Convection heat transfer



- How to obtain the heat transfer coefficient?
  - ☐ non-dimensionalize the governing equations
- Nusselt number – obtained by solving the dimensionless governing equations for mass, momentum, and energy over flat plate, we get
  - ☐ ratio between convective and conductive heat transfer
  - ☐ represents the enhancement of heat transfer through a fluid as a result of convection relative to conduction across the same fluid layer

$$Nu = \frac{convective\ heat\ transfer}{conductive\ heat\ transfer} = \frac{hL}{\lambda}$$

h is the heat transfer coefficient

L is the characteristic length

λ is the thermal conductivity

- It was found that Nusselt number can be evaluated as

$$Nu = \frac{hL}{\lambda} = CRe^{a}Pr^{b}$$

C, a, b are constants

Re is the Reynolds number

Pr is the Prandtl number

Convection heat transfer

- Nusselt number $Nu = \frac{hL}{\lambda} = CRe^{a}Pr^{b}$

- Reynolds number – ratio between inertial and viscous forces

$$Re = \frac{inertial\ forces}{viscous\ forces} = \frac{uL}{\nu} = \frac{\rho uL}{\eta}$$

u is the velocity
L is the characteristic length
ν is the kinematic viscosity
ρ is the density
η is the dynamic viscosity

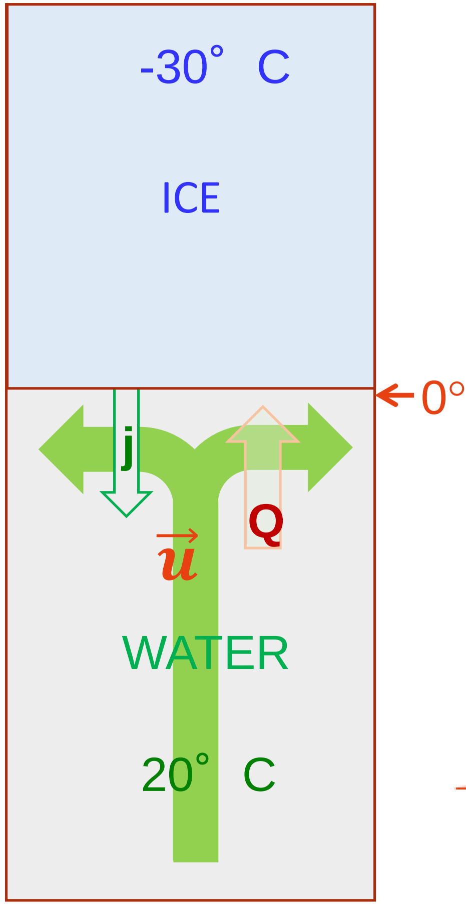
- Prandtl number

$$Pr = \frac{momentum\ diffusivity}{thermal\ diffusivity} = \frac{\nu}{\alpha} = \frac{\eta C_p}{\lambda}$$

ν is the kinematic viscosity
α is the thermal diffusivity
η is the dynamic viscosity
C_p is the heat capacity
λ is the thermal conductivity

- For example, for a laminar flow over flat plate, heat transfer and thus melting rate can be calculated!

$$Nu = \frac{hL}{\lambda} = 0.664Re^{1/2}Pr^{1/3}$$



Convection heat transfer

hL

- Nusse
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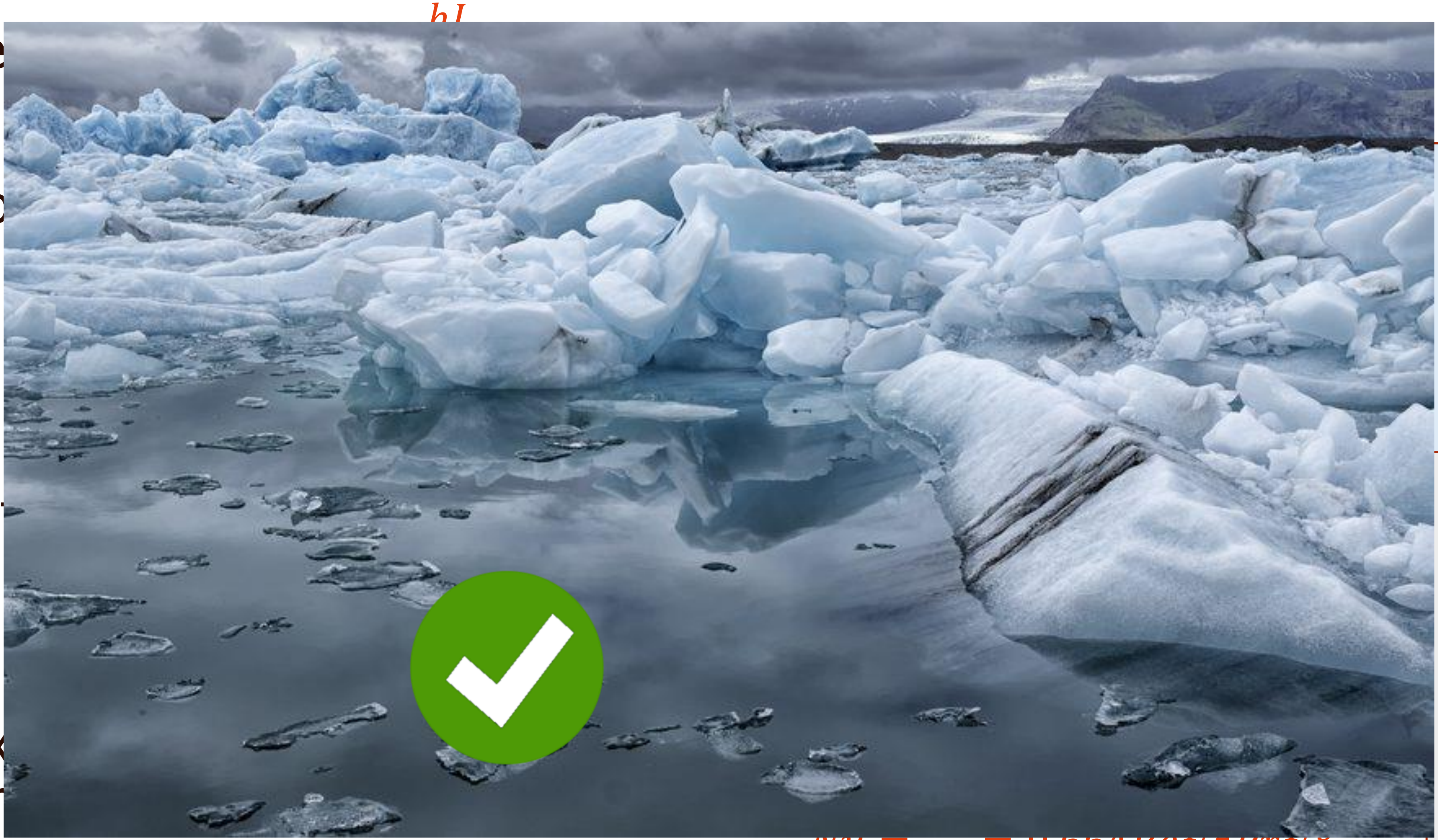
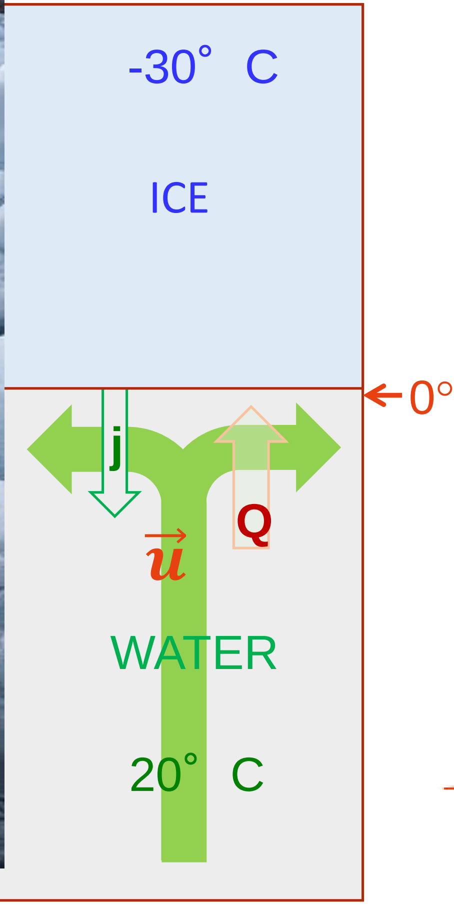




$$Nu = \frac{\quad}{\lambda} = 0.664Re^{1/2}Pr^{1/3}$$

Convection heat transfer

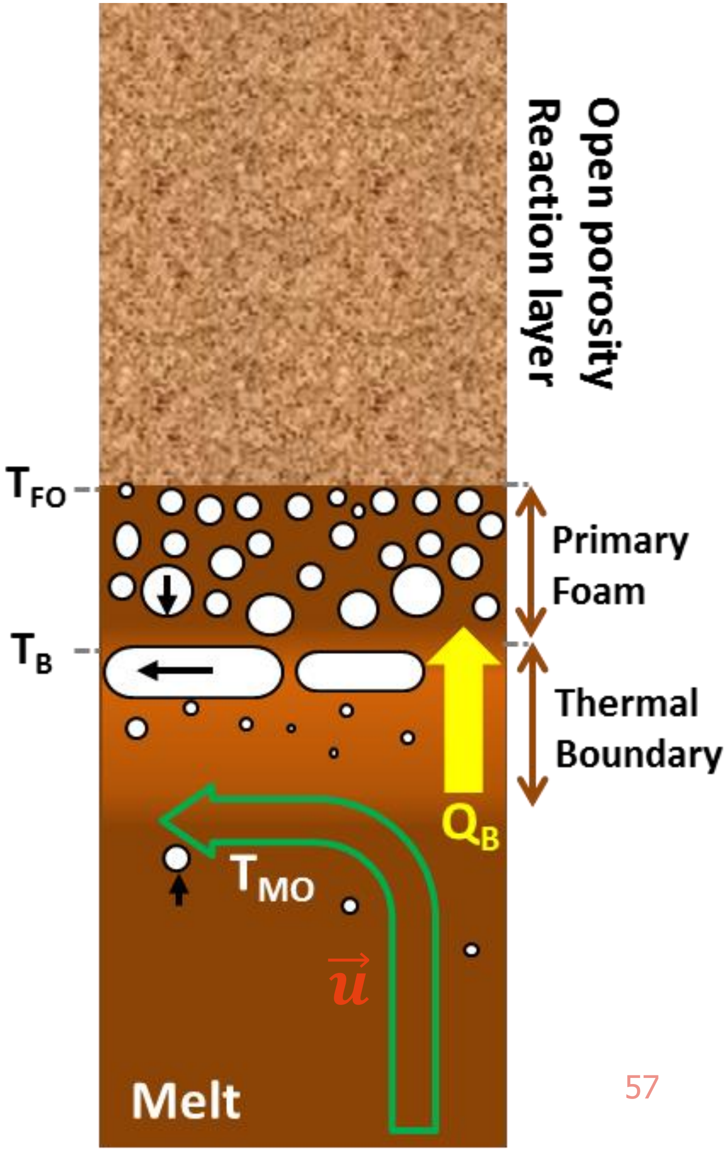
UCT PRAGUE

What about glass batch on hot melt?

- ►Challenge #1 – how can we obtain the interface temperature T_B (temperature at cold cap bottom)?

$$Q = j\Delta H = h(T_{MO} - T_B)$$

Q is the heat flux [W m^{-2}]
j is the melting rate [kg $m^{-2}s^{-1}$]
ΔH is the conversion heat [J kg^{-1}]
h is the heat transfer coefficient [W $m^{-2}K^{-1}$]
T_{MO} is the melter operating temperature [K]
T_B is the cold cap bottom temperature [K]



Convection heat transfer

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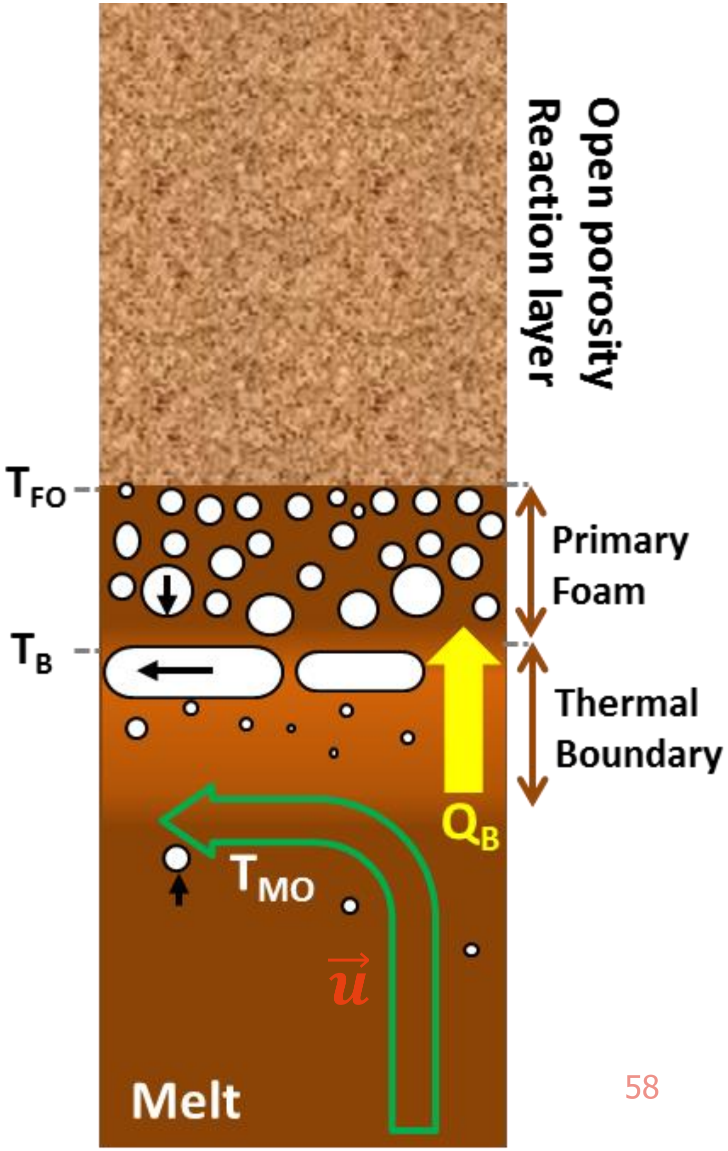
T_{MO} is the melter operating temperature [K]
T_B is the cold cap bottom temperature [K]

- Challenge #2 – flow pattern near cold cap is complex:
  - ☐ Several circulation cells may exist, possibly variable.
    - ○ the melt velocity under the cold cap varies
  - ☐ Moving cavities disturb the boundary layer
    - ○ Up to date CFD models do not have sufficient resolution to account for this
  - ☐ How to estimate h, when we do not know the exact values of coefficients C, a, b to calculate Nu?

$$Nu = \frac{hL}{\lambda} = CRe^aPr^b$$

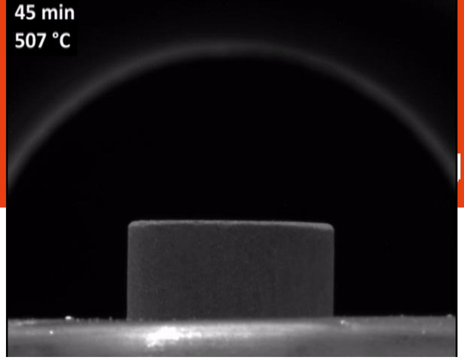


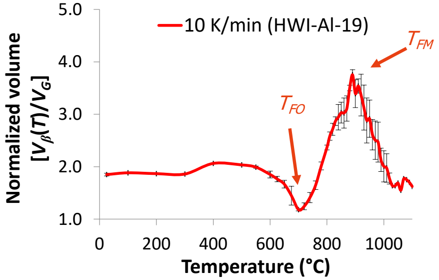
How to obtain cold cap bottom T?

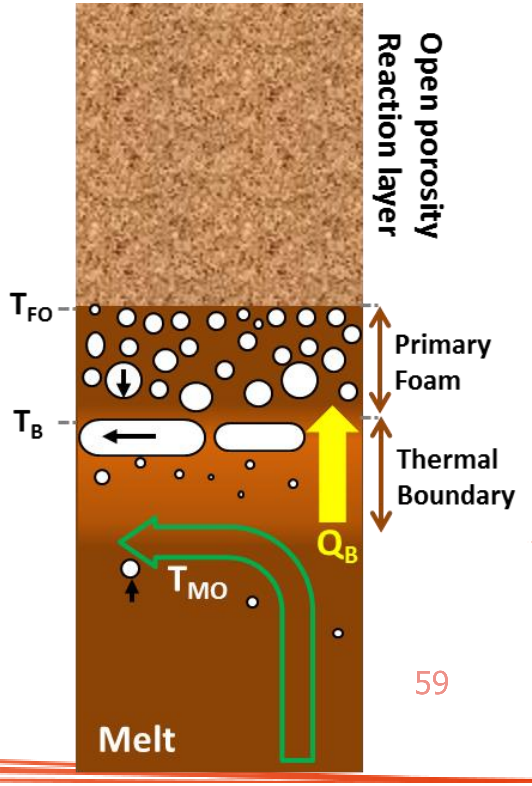
FEED EXPANSION TESTS (FET)

- ▶ During the feed expansion test (FET), the heated feed represents a feed particle in the cold cap as it moves down while being converted to molten glass
  - ❑ Virtually no gas is released from pellet during foam growth from HLW feeds – the interval between T_{FM} and T_{FO} represents the primary foam interval in the cold cap
  - ❑ The release of primary foam gas starts at T_{FM}
  - ❑ For most HLW feeds, the primary foam collapsing temperature under the cold cap (T_B) is the same as the primary foam collapsing temperature (T_{FM}) of the feed pellet.

$$T_B = T_{FM}$$







Convection heat transfer

What about glass batch on hot melt?

- ▶ Challenge #1 – how can we obtain the interface temperature T_B (temperature at cold cap bottom)?

Solved using FET

$$T_B = T_{FM}$$

$Q = j\Delta H$

-2]

m^{-2}s^{-1}]

eat [J kg^{-1}]

h is the heat transfer coefficient [W m^{-2}K^{-1}]

T_{MO} is the melter operating temperature [K]

T_B is the cold cap bottom temperature [K]

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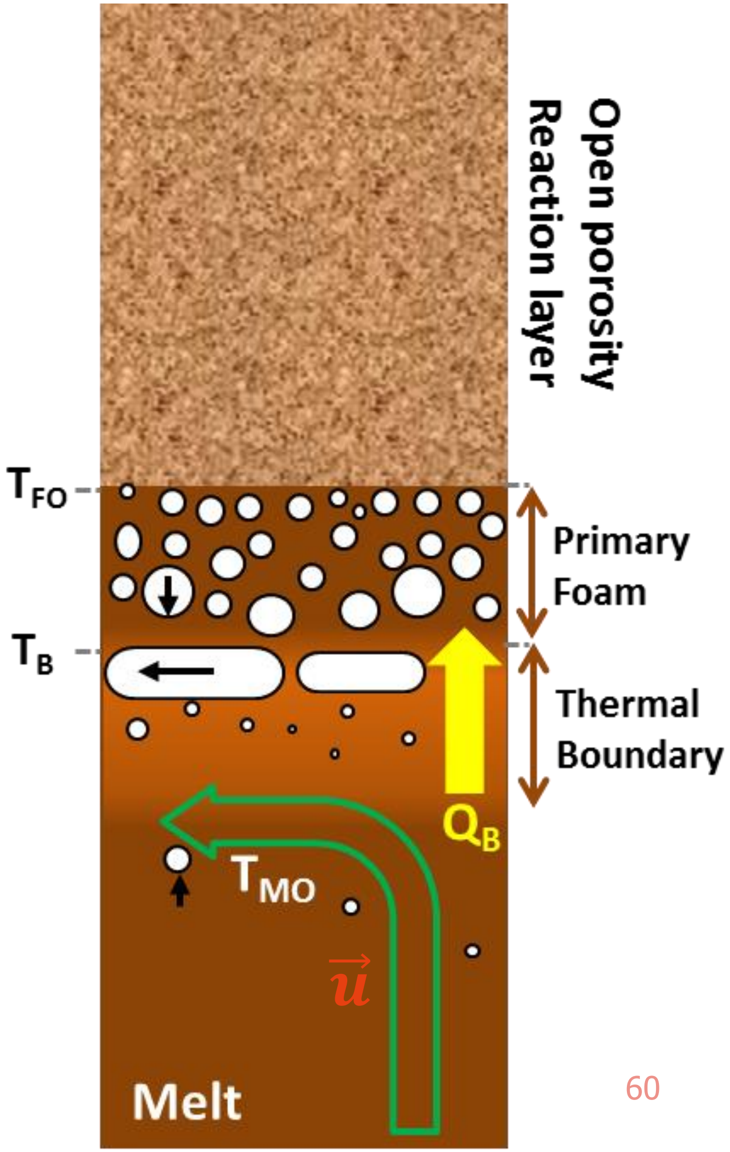
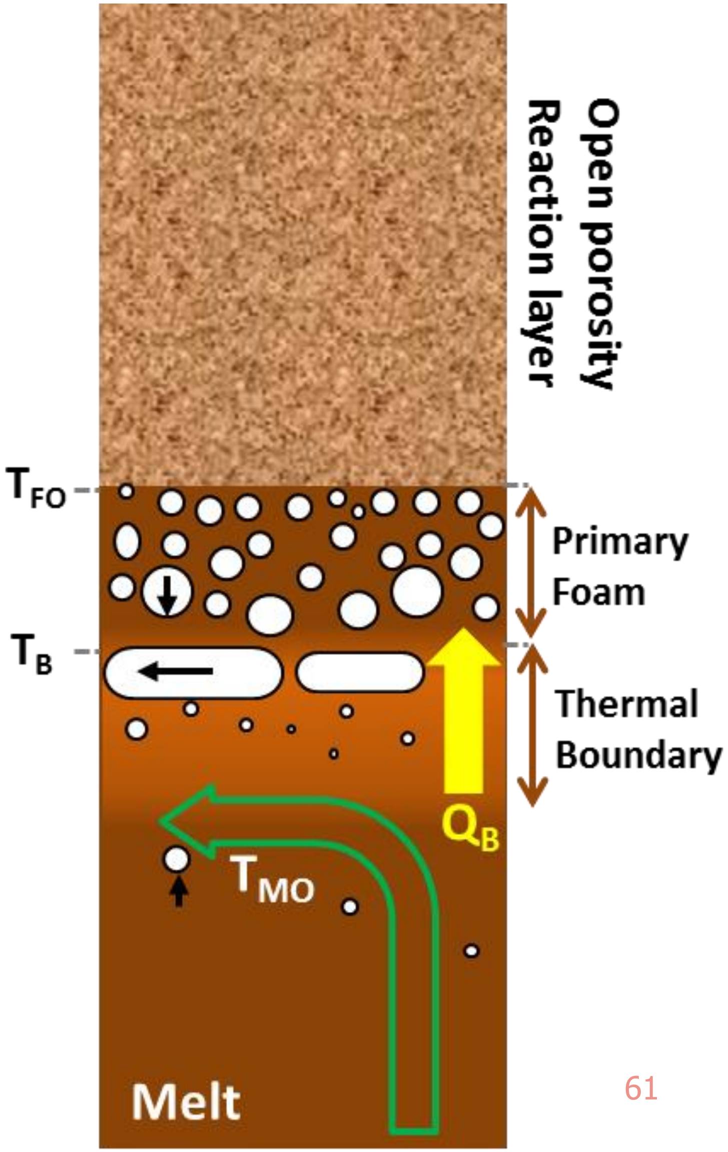


Melter data

UCT PRAGUE

- Using data measured by Vitreous State Laboratory (VSL) of the Catholic University of America
  - ☐ 250 melter runs with high-level waste (HLW) melter feeds
  - ☐ 290 melter runs with low-activity waste (LAW) melter feeds
  - ☐ DM100 melter, melting area 0.108 m^2, operated at T_{MO} = 1150, 1175, and 1200°C, and with rate of bubbling from 5.0 to 9.6 m h^{-1}
  - ☐ DM1200 melter, melting area 1.2 m^2, operated at T_{MO} = 1150 and 1175°C and uB from 5.5 to 6.3 m h^{-1}

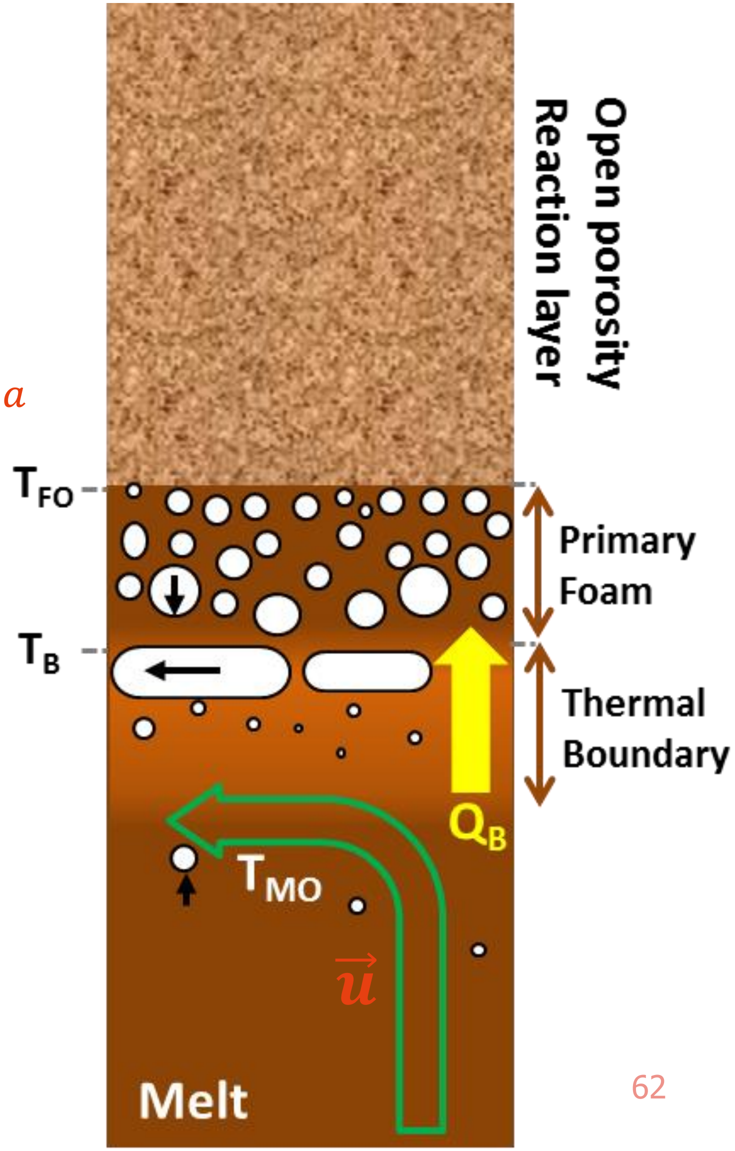


Melting rate correlation equation

Challenge #2 – how can we estimate the heat transfer coefficient *h*?

- ►Fitting the equation based on the boudnary layer theory to measured data

$$Nu = \frac{hL}{\lambda} = C Re^a Pr^b = C\left(\frac{\rho u L}{\eta}\right)^a \left(\frac{\eta C_p}{\lambda}\right)^b \Rightarrow h = C\rho^a L^{a-1}\lambda^{1-b} C_p^b \eta^{b-a} u^a$$



Melting rate correlation equation

Challenge #2 – how can we estimate the heat transfer coefficient *h*?

- Fitting the convection heat transfer equation based on the boudnary layer theory to measured data

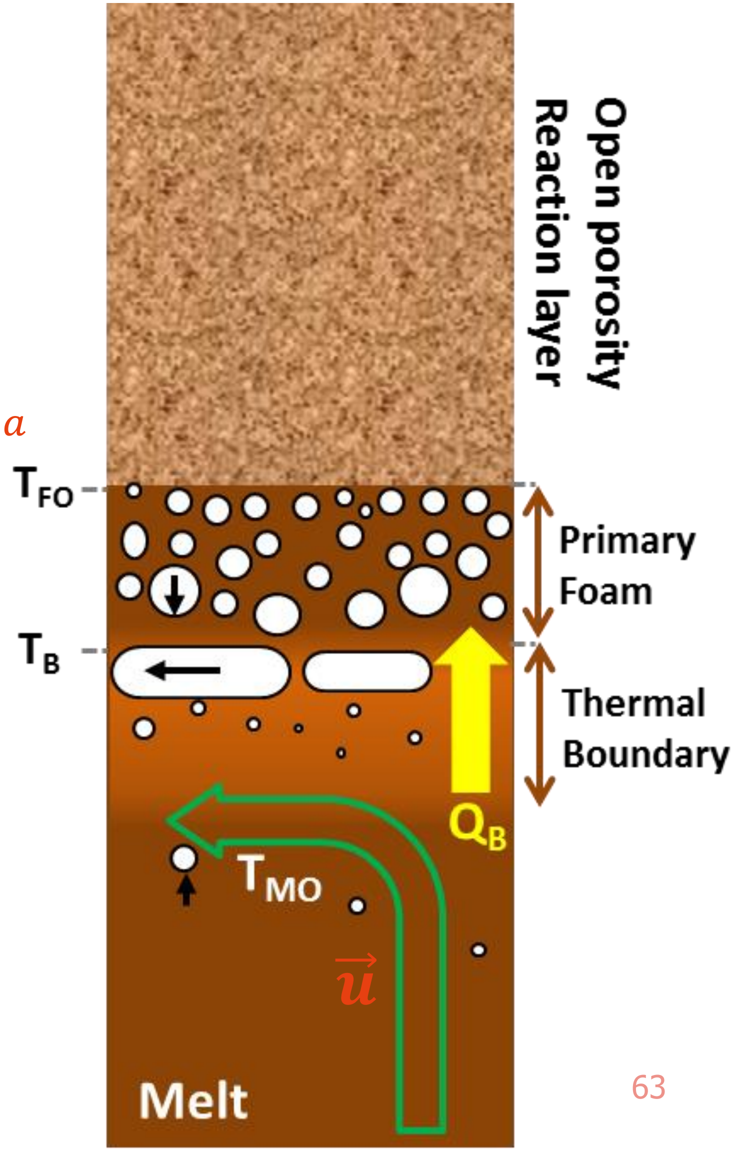
$$Nu = \frac{\xi L}{\lambda} = C Re^{a} Pr^{b} = C\left(\frac{\rho u L}{\eta}\right)^{a}\left(\frac{\eta C_p}{\lambda}\right)^{b} \Rightarrow \xi = C\rho^{a} L^{a-1}\lambda^{1-b} C_p^{b}\eta^{b-a}u^{a}$$

$$j = Q\Delta H^{-1} = \xi(T_{MO} - T_B)\Delta H^{-1} = \xi_0\left(1+\frac{u_B}{u_0}\right)^{\beta}\left(\frac{\eta_{MO}}{\eta_R}\right)^{-\alpha}(T_{MO} - T_B)\Delta H^{-1}$$

$$u = u_N\left(1+\frac{u_B}{u_0}\right)$$

$$\xi_0 = C\rho^{\beta} L^{\beta-1}\lambda^{1-\beta-\alpha} C_p^{b}\eta_R^{-\alpha}u_N^{\beta}$$

u_N is the gas bubbling rate/velocity
u_B is the hypothetical bulk velocity in a melter with no artificial bubbling
u_0 is the coefficient
η_R is the reference viscosity (1 Pa s)
$\alpha = a - b$, $\beta = a$ are coefficients
ξ_0 is the heat transfer coefficient to cold cap bottom for $\eta_{MO} = \eta_R$ (a reference value) and $u_B = 0$ [W m^{-2}K^{-1}]

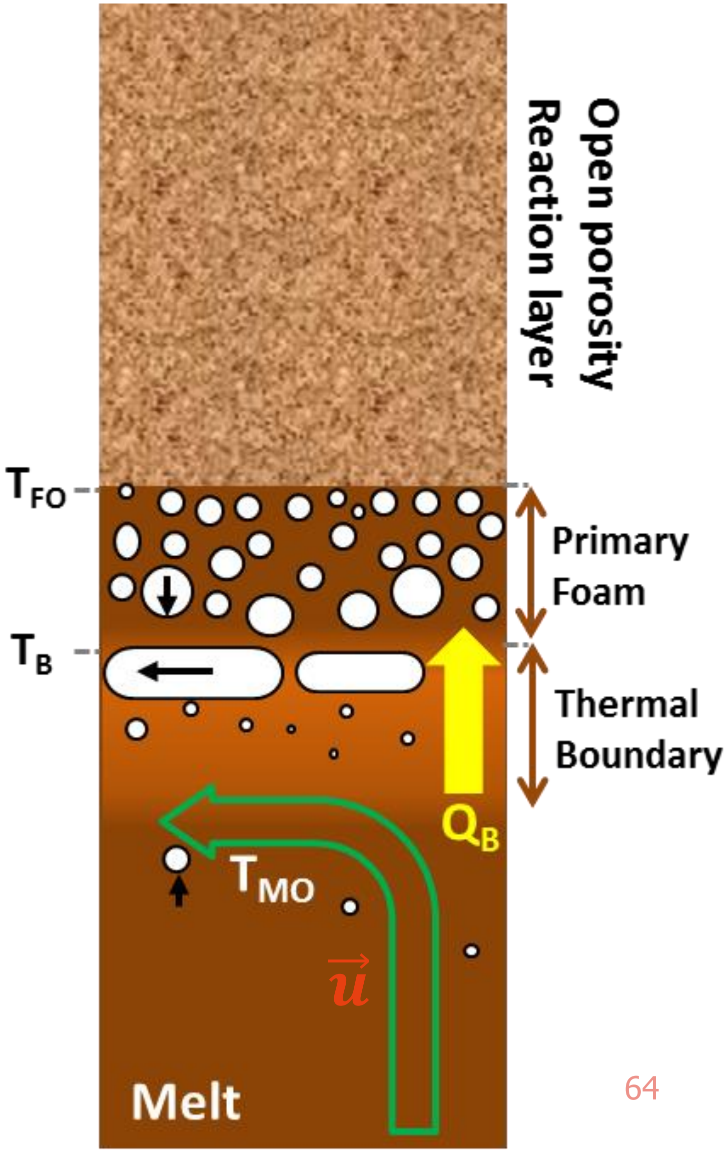


Melting rate correlation equation (MRC)

- The semiempirical Melting Rate Correlation (MRC) equation relates the melting rate as a function of the influential variables.
- The MRC:

$$j = \xi_0 \left(1+\frac{u_B}{u_0}\right)^{\beta}\left(\frac{\eta_{MO}}{\eta_R}\right)^{-\alpha}(T_{MO}-T_B)\Delta H^{-1}$$

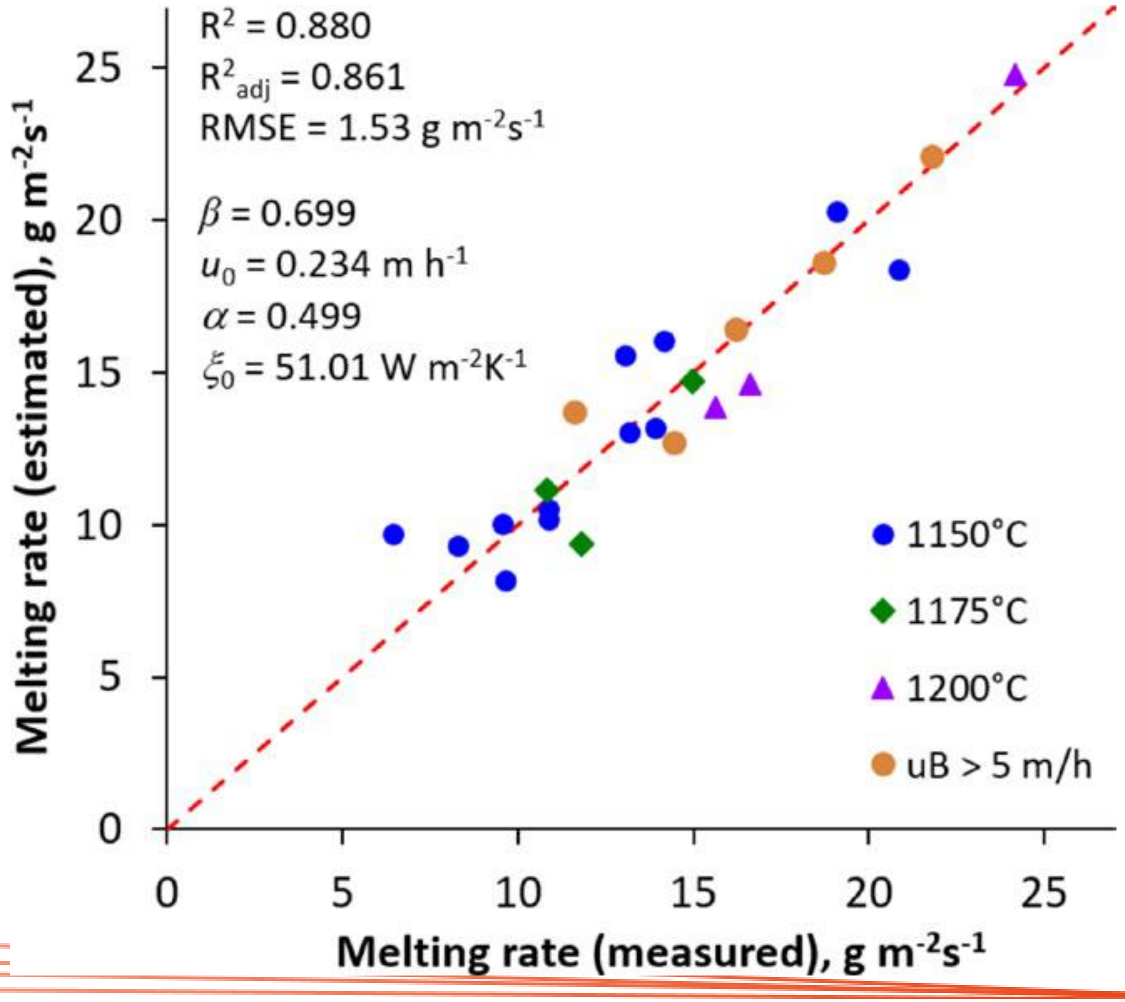
- The MRC contains two types of input data:
  - Melter processing data: melter operating temperature (***T_{MO}***) and gas bubbling rate (***u_B***)
  - Batch and melt properties: conversion heat per glass (***ΔH***), cold cap bottom temperature (***T_B***), and melt viscosity at T_{MO} (***η_{MO}***). The properties must be measured (***ΔH*** by calorimetry, ***η_{MO}*** by viscometer (we select ***η_R*** = 1 Pa s), and ***T_B*** by **feed expansion test**).
- ξ_0, α, β, and u_0 are determined by fitting the MRC equation to data



Fitting the MRC equation

- Estimated (j_E) versus measured (j_M) melting rates exhibit good agreement for **DM100 melter** data in the rage of 5 – 25 g m^{-2}s^{-1} (500 – 2100 kg m^{-2}d^{-1}) ⇒

$$j = \xi_0 \left(1+\frac{u_B}{u_0}\right)^{\beta}\left(\frac{\eta_{MO}}{\eta_R}\right)^{-\alpha}(T_{MO}-T_B)\Delta H^{-1}$$



- Fitting MRC equation to data allowed us to conclude that h_0 **was independent of the feed processed.**

ξ_0 = 51 W m^{-2}K^{-1}

Summary on Melting Rate Correlation

- **Melting rate correlation (MRC) equation** estimates the glass production rate of HLW glasses as a function of feed properties and melter operation parameters
  - ☐ the gas injection rate (u_B), melter operating temperature (T_{MO}), melt viscosity (η_{MO}), cold cap bottom temperature (T_B), and batch-to-melt conversion heat (ΔH).

- MRC application can help limit reduced-scale melter experiments to the most promising cases.

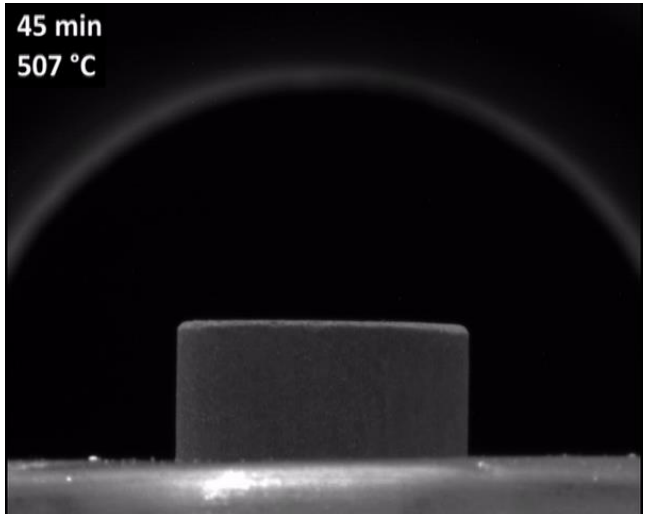
- More data will show MRC applicability limits for **excessively foaming** LAW feeds.

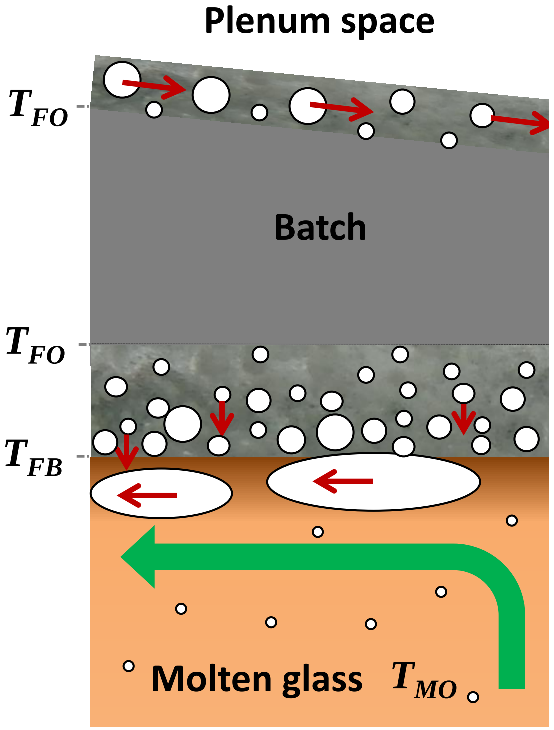
Where do we go from here?

Models for foaming & heat transfer

UCT PRAGUE

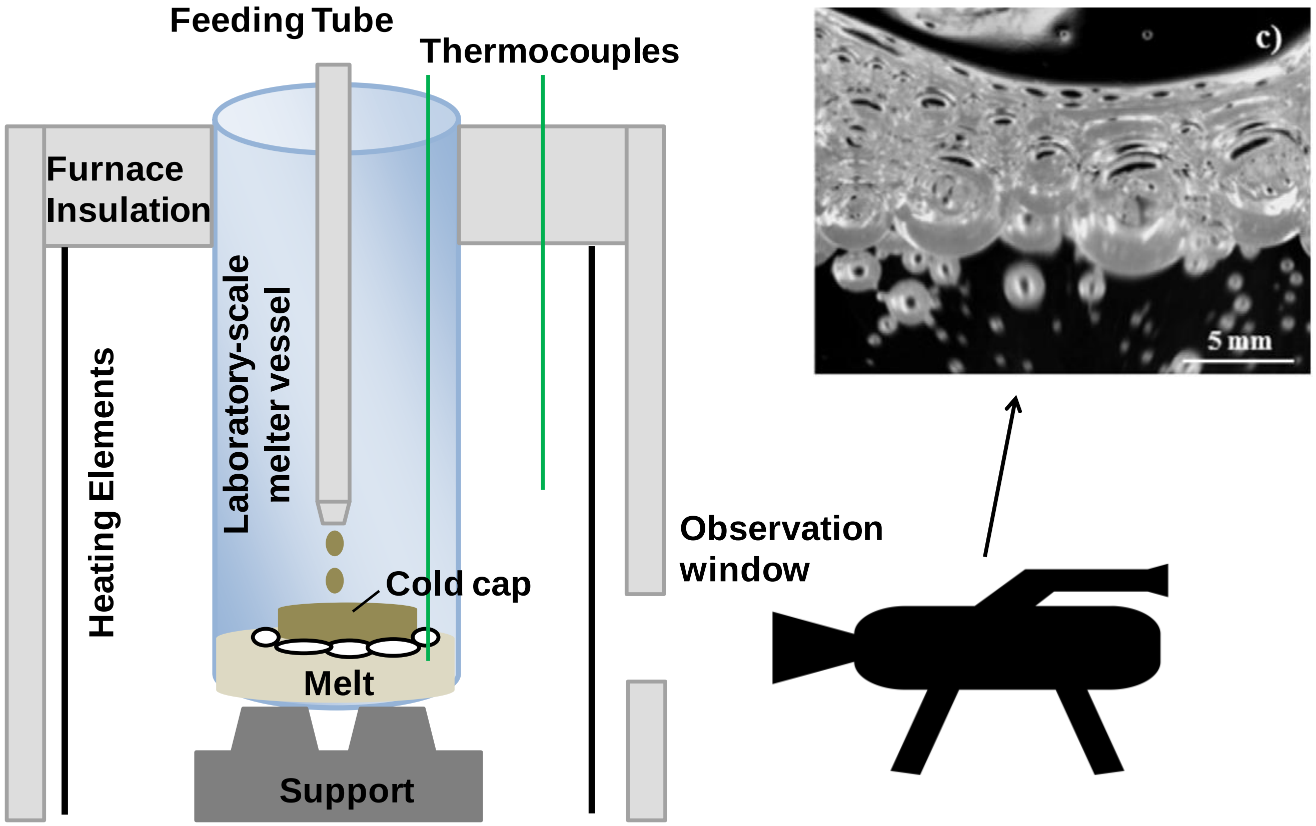
- Better understanding the formation and structure of the primary foam?





Models for foaming & heat transfer

- Better understanding the formation and structure of the primary foam?
  - ☐ Using in-situ optical observation and X-Ray methods



Models for foaming & heat transfer

- Better understanding the formation and structure of the primary foam?
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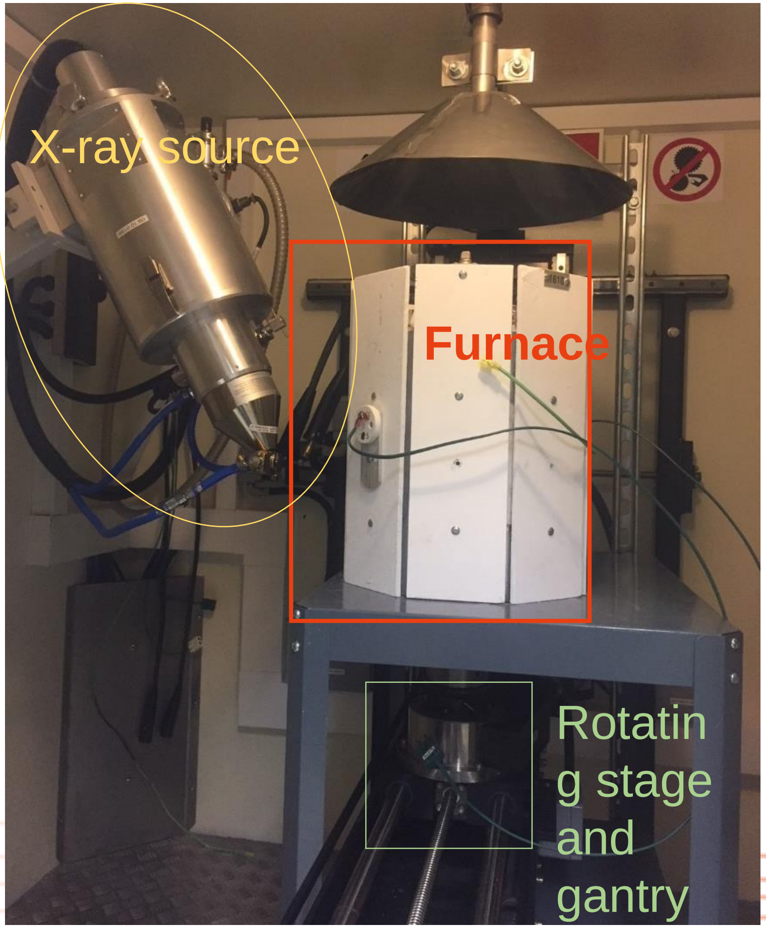
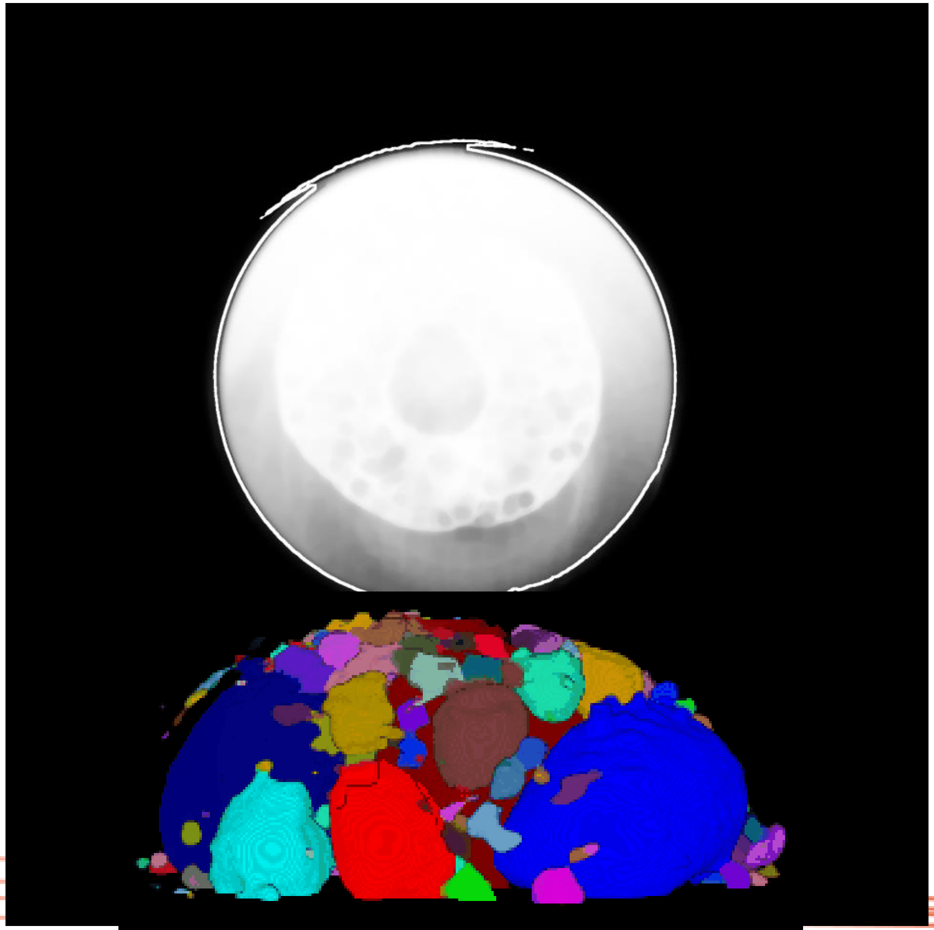
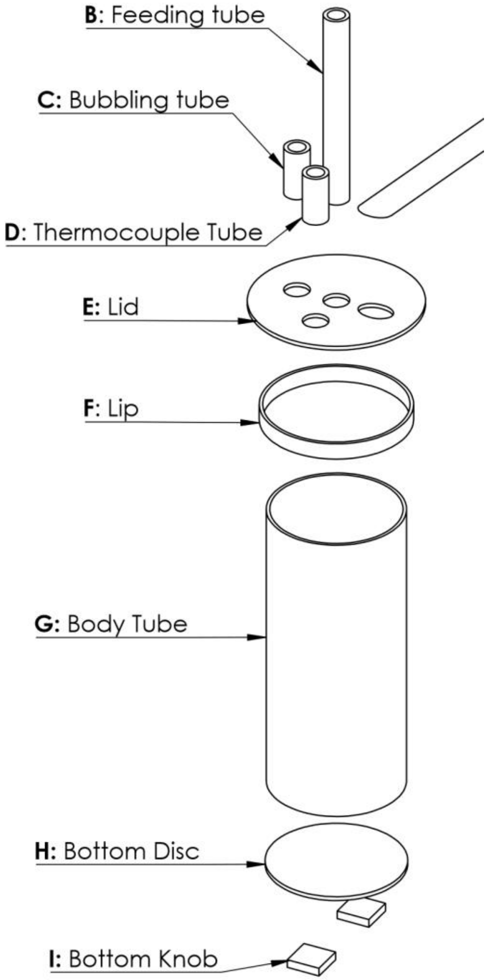






Models for foaming & heat transfer

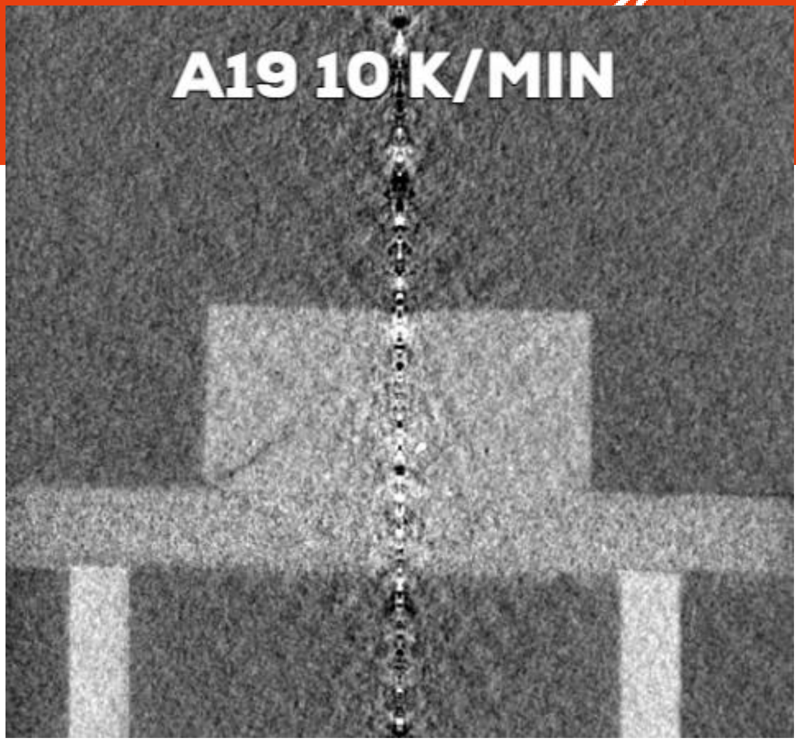
- How the foam layer affects the heat transfer?
  - Development of representative, but still applicable models of heat transfer in the foam

$$\lambda\frac{d^2T}{dx^2}+cj\frac{dT}{dx}-\rho\Delta H\frac{d\alpha}{dt}=0$$

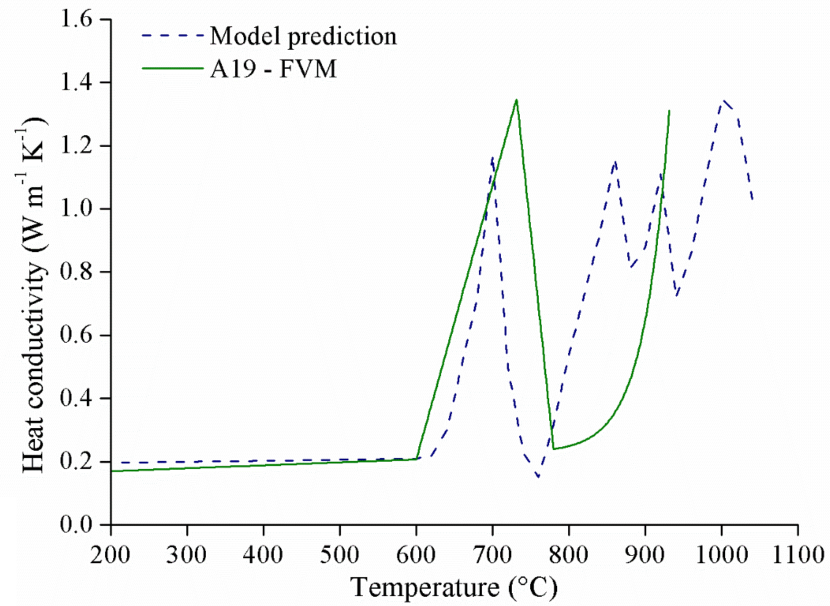
$$\Downarrow$$

$$\lambda(\boldsymbol{\alpha},\boldsymbol{t})\frac{d^2T}{dx^2}+cj\frac{dT}{dx}-\rho(\boldsymbol{\alpha},\boldsymbol{t})\Delta H\frac{d\alpha}{dt}=0$$

Heat conductivity as a function of batch structure



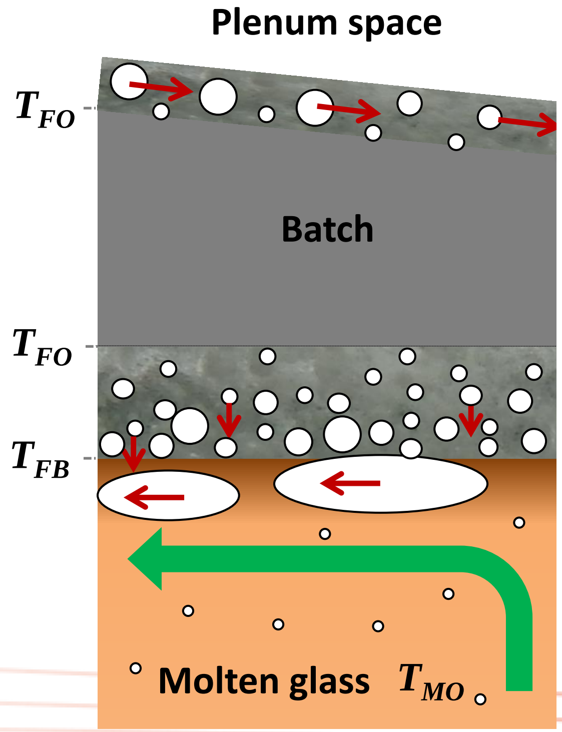
- Experimental determination of λ as a function of temperature history is hardly feasible
- Theoretical approach combined with measured morphology
  - ☐ Models of multi-phase heat transfer, including radiation, combined with porosity and pore (bubble) size distribution
- Although promising for the foam growth temperature region, not very useful once foam bubbles start to coalesce and/or collapse
  - ☐ Initial conductivity increase caused by *decreasing porosity* when feed sinters
  - ☐ Decrease caused by *increasing porosity* during foaming, but small pore size
  - ☐ Second increase caused by *growing bubbles* while porosity stays constant or decreases

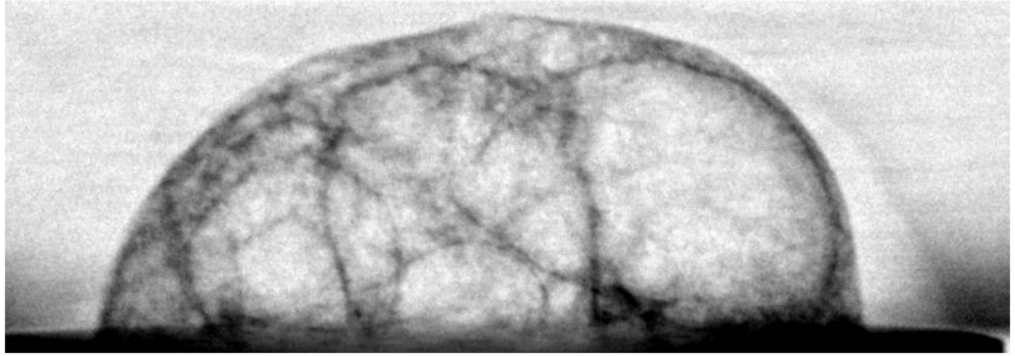


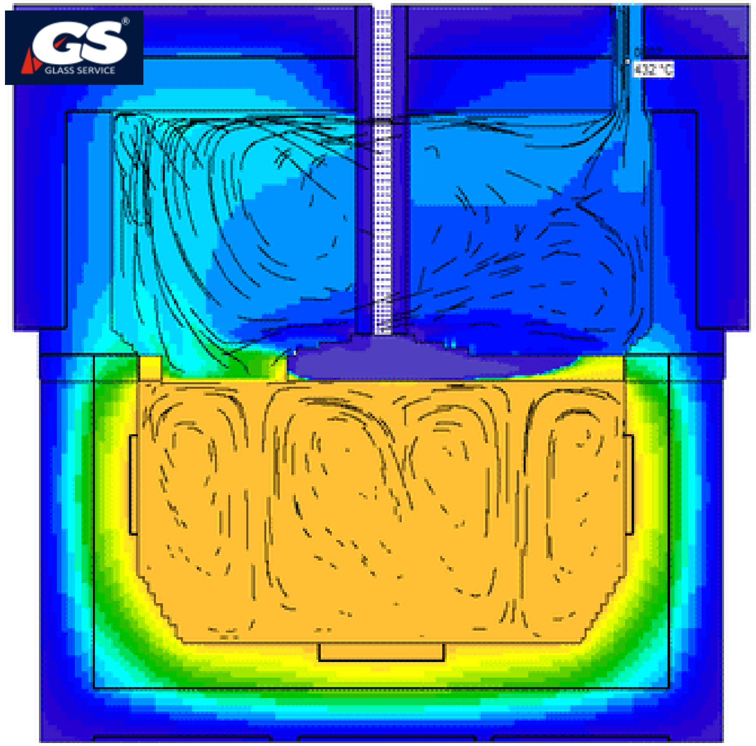
Hujova M, Pokorny R, Klouzek J, et al. Determination of heat conductivity of waste glass feed and its applicability for modeling the batch-to-glass conversion. J Am Ceram Soc. 2017;00:1–11. https://doi.org/10.1111/jace.15052

Conclusions

- ▶ The cold cap model considers both **enthalpy balance** and **batch-to-glass conversion kinetics,** represented by the **kinetics of primary foam evolution and collapse**
- ▶ **Melting rates** predicted by the model are within the range of values measured in pilot-scale melters, simulated and LSM temperature profiles are **in good agreement**
- ▶ We need to better understand the **foam behavior and heat transfer**







Thank you for your attention! – Questions?

Acknowledgement

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- The authors acknowledge the financial support by the Czech Science Foundation (project No. 19-14179S)

THANK YOU!

Supplementary material

Glass compositions

—— **deleted**

Glass		A19	HWI-Al-19	HWI-Al-28	HLW-E-Al-27	HLW-E-M-09	HLW-NG-Fe2
Waste Loading		45%	45%	50%	45%	44.2%	42%
No.	Composition	mass %	mass %	mass %	mass %	mass %	mass %
1	Al_2O_3	24.16	23.97	26.63	23.97	10.69	5.58
2	B_2O_3	19.12	19.19	20.21	15.19	14.57	13.81
3	BaO		~~0.05~~	~~0.06~~	~~0.05~~	~~0.01~~	~~0.08~~
4	Bi_2O_3	1.16	1.14	1.27	1.14	3.47	
5	CaO	5.74	5.58	9.20	6.08	1.18	0.52
6	CdO		~~0.02~~	~~0.03~~	~~0.02~~		
7	Ce_2O_3						0.11
8	Cr_2O_3	0.52	0.52	0.58	0.52	3.00	0.26
9	F	0.67	0.67	0.74	0.67	0.95	
10	Fe_2O_3	5.92	5.90	6.55	5.90	6.26	16.01
11	K_2O		0.14	0.16	0.14	5.52	
12	La_2O_3						0.09
13	Li_2O	3.59	3.57	5.01	3.57	3.09	1.55
14	MgO		0.12	0.13	0.12	0.08	0.16
15	MnO						3.23
16	Na_2O	9.64	9.58	4.98	9.58	9.57	14.17
17	NiO	0.40	0.40	0.44	0.40	0.00	0.47
18	P_2O_5	1.06	1.05	1.17	1.05	1.59	0.64
19	PbO	0.41	0.41	0.45	0.41	0.23	0.62
20	SO_3	0.20	0.20	0.22	0.20		0.22
21	SiO_2	27.01	27.00	21.62	30.50	38.22	41.05
22	SnO_2						~~0.07~~
23	SrO						0.19
24	TiO_2		~~0.01~~	~~0.01~~	~~0.01~~		
25	ZnO		0.08	0.09	0.08	1.50	0.03
26	ZrO_2	0.40	0.39	0.44	0.39	0.05	1.13
	SUM	100.00	100.00	100.00	100.00	100.00	100.00
	η @ 1150°C	3.5 Pa s	3.3 Pa s	1.6 Pa s	4.6 Pa s	3.8 Pa s	3.0 Pa s

Feed (to make 100g of glass)		A19	HWI-Al-19	HWI-Al-28	HLW-E-Al-27	HLW-E-M-09	HLW-NG-Fe2
No.	component	Mass (g)	Mass (g)	Mass (g)	Mass (g)	Mass (g)	Mass (g)
1	$Al(OH)_3$	37.18	36.90	41.00	36.90	16.42	8.61
2	H_3BO_3	34.16	34.16	35.97	3.05	25.95	0.56
3	$Na_2B_4O_7{\cdot}10H_2O$				37.11		37.16
4	~~$BaCO_3$~~						
5	Bi_2O_3	1.17	1.16	1.29	1.16	3.51	
6	CaO	1.09	1.10	1.22	1.10	1.18	
7	$CaCO_3$						0.94
8	~~CdO~~						
9	CeO2						0.12
10	$Cr_2O_3{\cdot}1.5H_2O$	0.62	0.62	0.68	0.62	3.53	0.30
11	NaF	1.50	1.49	1.65	1.49	2.13	
12	$Fe(OH)_3$	7.44	7.38	8.20	7.38	8.37	15.62
13	→ slurry = 14.83%	65.99	65.41	72.67	65.41	74.19	138.41
14	NaI			0.12			
15	K_2CO_3					8.19	
16	KNO_3		0.30	0.34	0.30		
17	$La(OH)_3{\cdot}3H_2O$						0.11
18	Li_2CO_3	8.92	8.92	12.51	8.92	7.73	3.87
19	MgO		0.12	0.13	0.12	0.08	
20	$Mg(OH)_2$						0.24
21	MnO_2						3.98
22	NaOH	1.99	1.96	2.18	1.96		0.81
23	Na_2CO_3	10.66	10.66	2.11	0.35	10.67	4.04
24	$Ni(OH)_2$	0.50	0.50	0.55	0.50		0.59
25	$Fe(H_2PO_2)_3$	1.25	1.25	1.39	1.25		
26	FePO4·2H2O						1.71
27	Na_2HPO_4					3.21	
28	PbO	0.42	0.41	0.46	0.41	0.23	0.63
29	Na_2SiO_3						8.04
30	Na_2SO_4	0.36	0.36	0.40	0.36		0.39
31	SiO_2	22.14	22.11	12.79	25.07	38.43	37.33
32	~~SnO_2~~						
33	$SrCO_3$						0.28
34	~~TiO_2~~						
35	ZnO		0.08	0.09	0.08	1.50	0.03
36	$Zr(OH)_4{\cdot}xH_2O$ (x=0.654)	0.55	0.55	0.61	0.55	0.07	1.57
37	$NaNO_2$	0.35	0.35	0.39	0.35	0.28	0.01
38	$NaNO_3$	1.24	1.24	1.38	1.24	1.15	0.45
39	$Na_2C_2O_4$	0.13	0.13	0.14	0.13	0.12	0.06
40	$CaSiO_3$ (wollastonite)	9.71	9.71	17.26	10.79		
	Sum	141.38	141.46	142.86	141.19	132.75	127.45