Experimental procedures to simulate essential process steps in glass melting

Marco van Kersbergen, Mathi Rongen, Ruud Beerkens, Hans van Limpt

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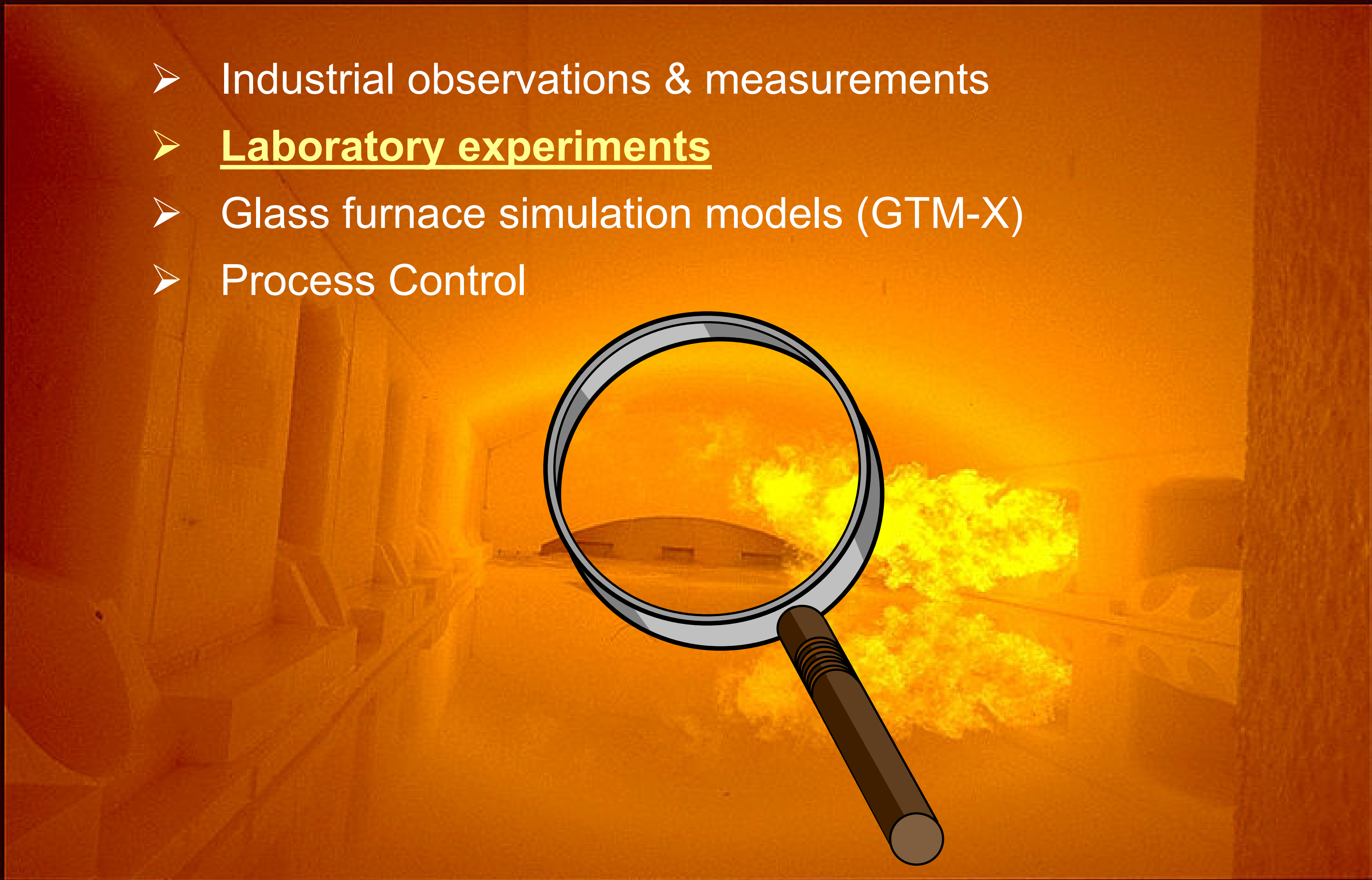
Activities TNO Glass Group

- Industrial observations & measurements
- **Laboratory experiments**
- Glass furnace simulation models (GTM-X)
- Process Control



Contents

Lab-experiments to investigate process steps for industrial glass melting:

Examples

1. **Bubble observation in glass melts**
2. **Foaming behavior of batches**
3. **Evolved gas analysis during melting-in and fining**
4. **Characterization of batch**
5. **Transpiration evaporation tests**

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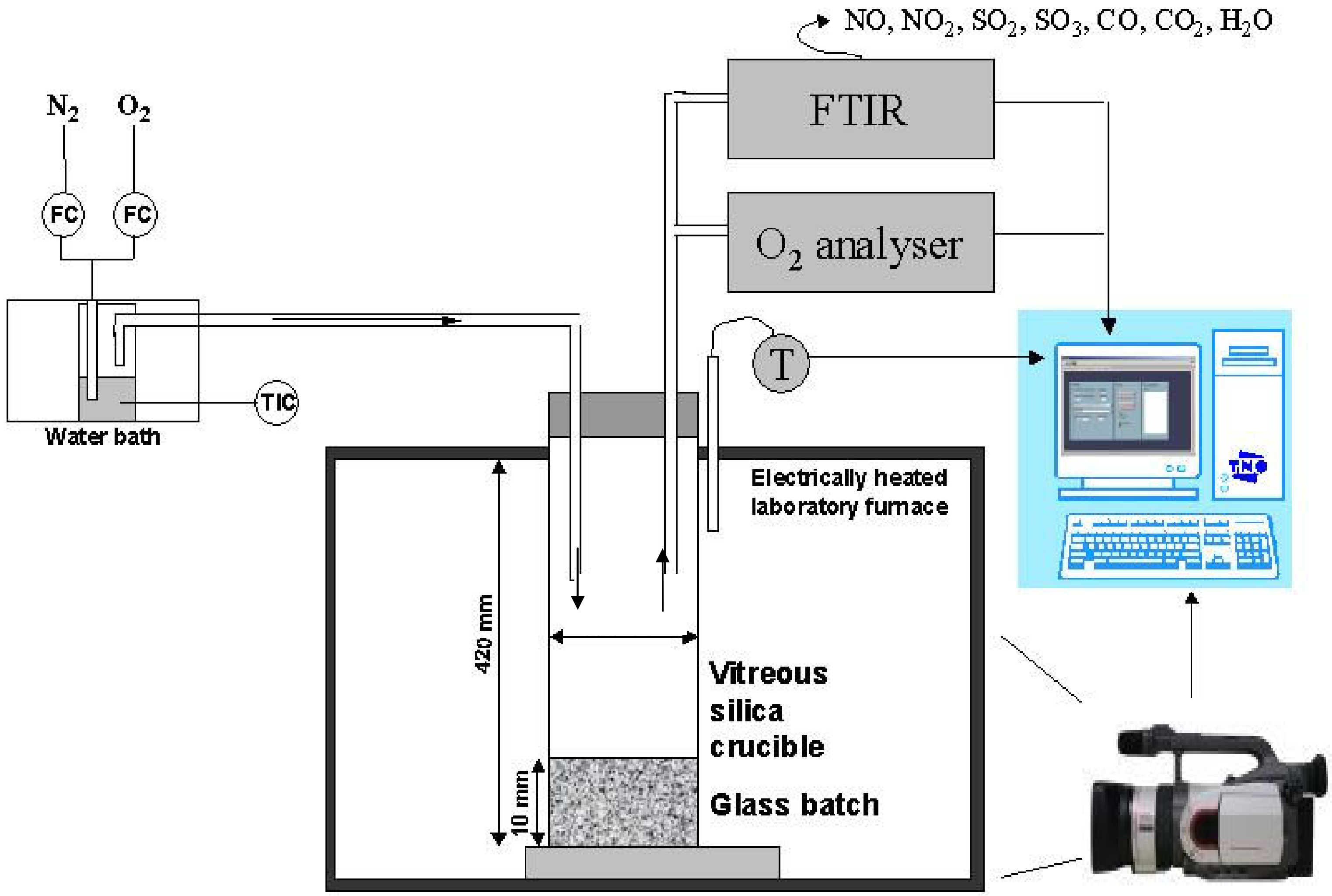
Bubble observation in glass melts

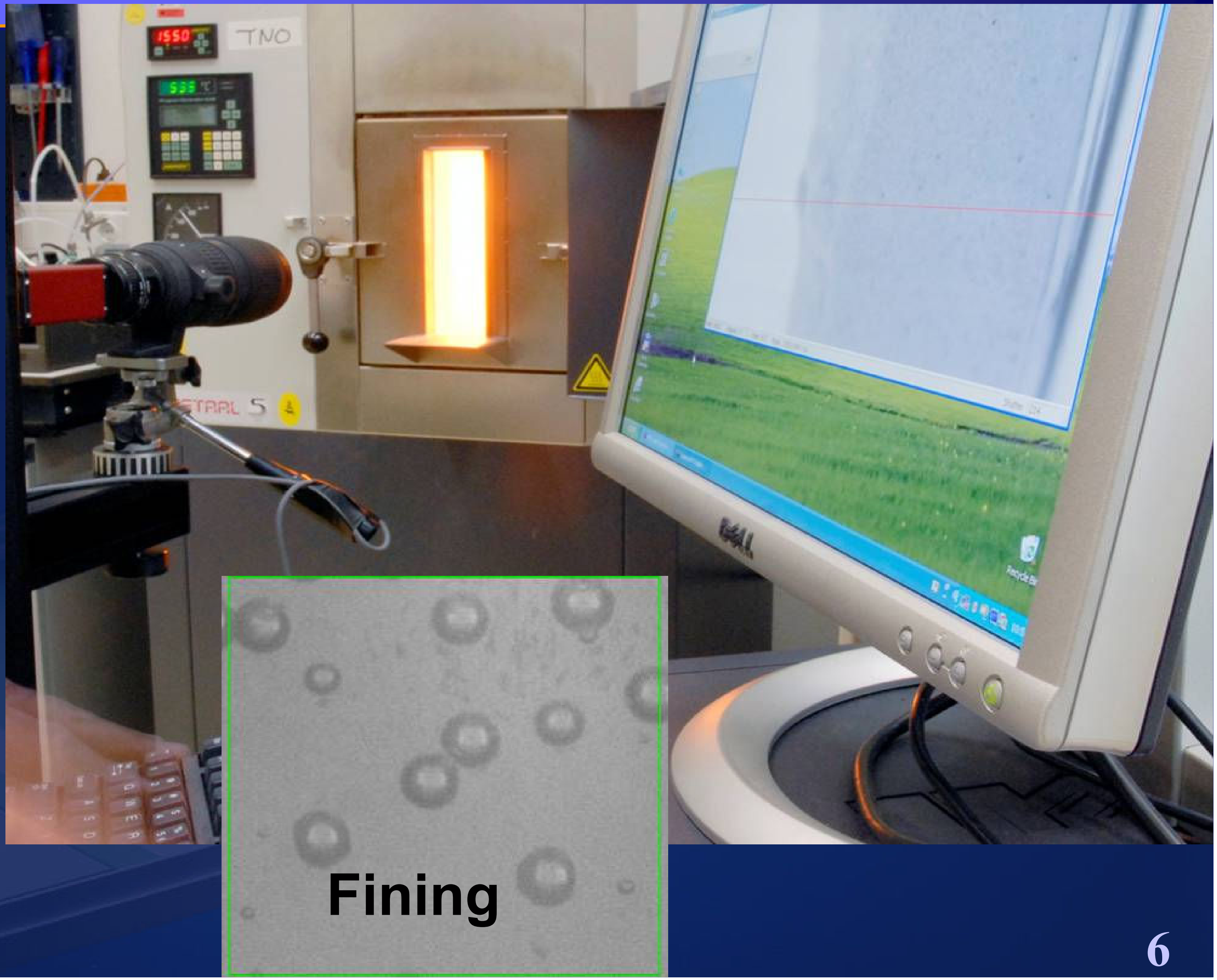
Features

- Detailed monitoring of bubbles: Bubbles > 60 µm visible
- Maximum furnace temperature: ± 1650ºC
- Dynamic bubble characteristics are measurable:
  Diameter, size distribution, bubble growth, rising velocity
- Control of furnace atmosphere: e.g N_2, O_2, H_2O
- Analyzing released gases during melting and fining
- Accessory to supply Helium to melt (Helium enhanced fining)
  - bubbling or atmosphere
- Possibility for vacuum (reduced pressure) experiments

Bubble observation in glass melts



Bubble observation in glass melts



Bubble observation in glass melts

- Experimental set-up available to look in detail and in-situ to fining process:
  - By measuring bubble growth and bubble ascension, the fining onset temperature can be determined accurately (+/- 10°C)
- Investigated aspects:
  - Batch composition
  - Oxidation state
  - Type and amount of fining agent
  - Effect of furnace atmosphere (e.g. air-fuel, oxy-fuel)
  - Pre-treatment of melt by Helium (bubbling/atmosphere)
  - Sub-atmospheric pressure

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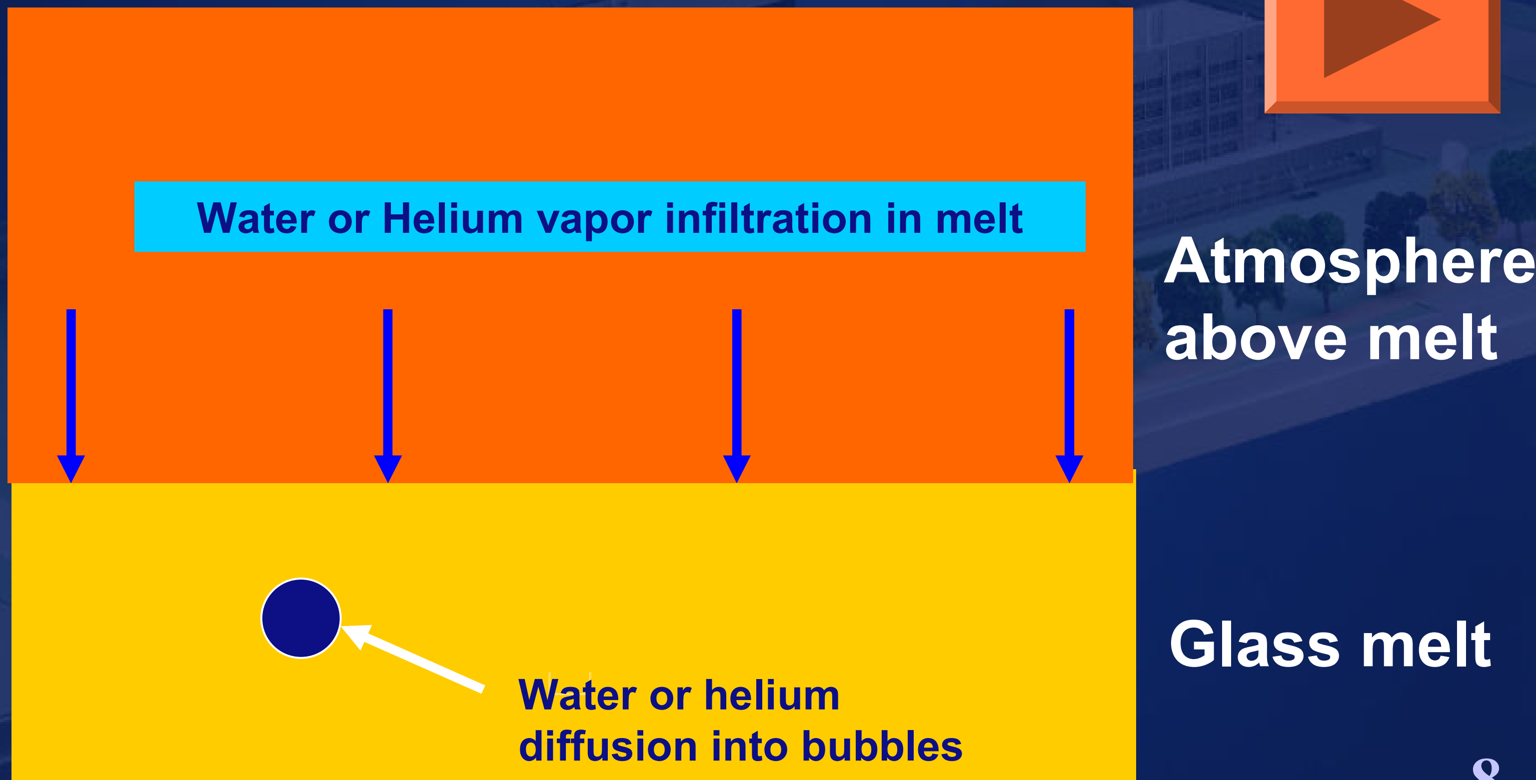
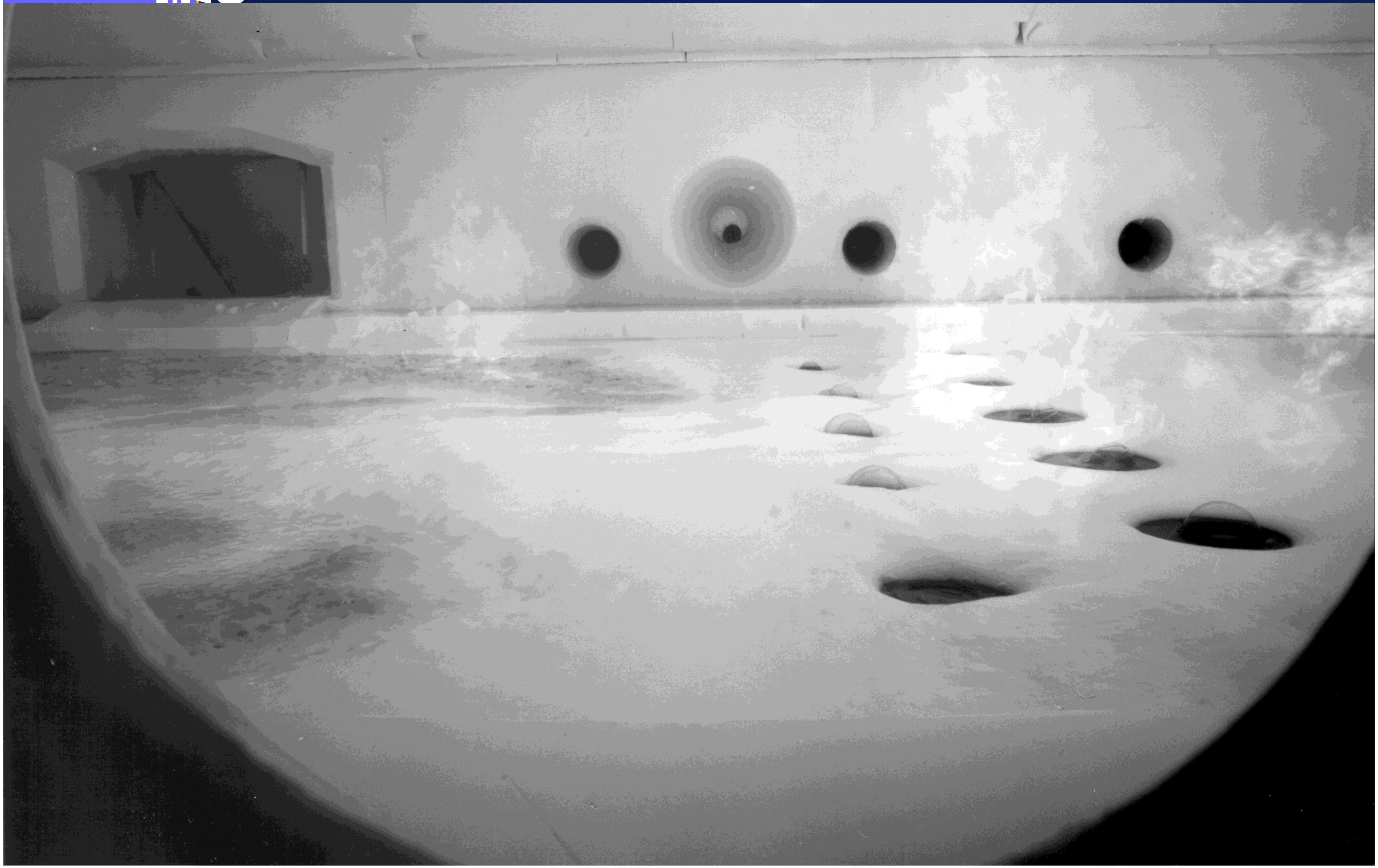
Bubble observation in glass melts

Helium enhanced fining

- Exposing glass melt to furnace atmosphere with Helium
- Bubbling the melt with e.g. helium



Foam behavior



Foam behavior

Experimental set-up to investigate foam behavior of batches during:

- Melting-in of batch (primary foam)
- Fining (secondary foam)

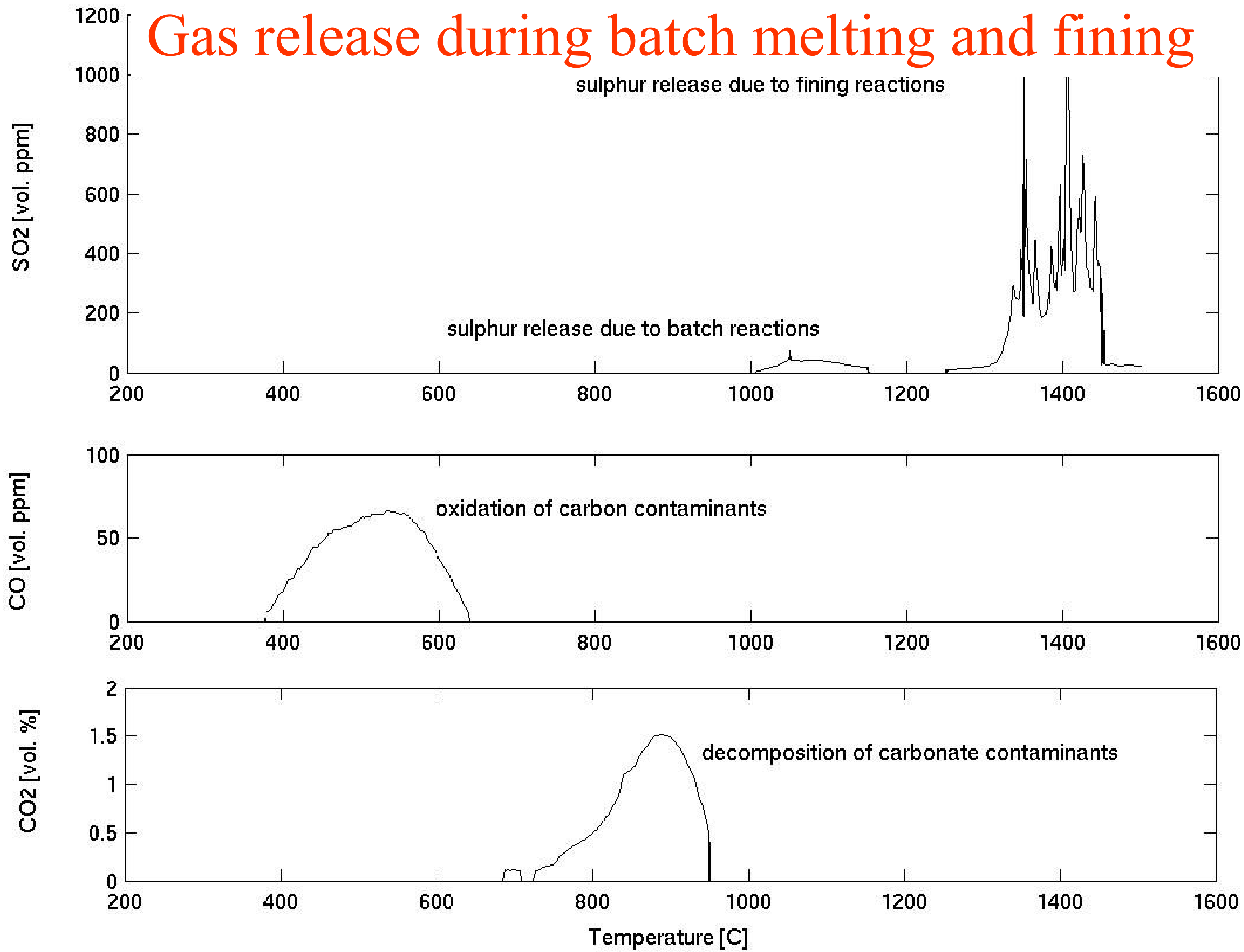
1. Analysis of released gases provides information on reactions and reaction kinetics during:
   - decomposition of the batch
   - decomposition of fining agents
2. Foam height

Investigated parameters:

- Batch recipe, atmosphere, redox state, fining agents

Foam behavior

Gas release during batch melting and fining



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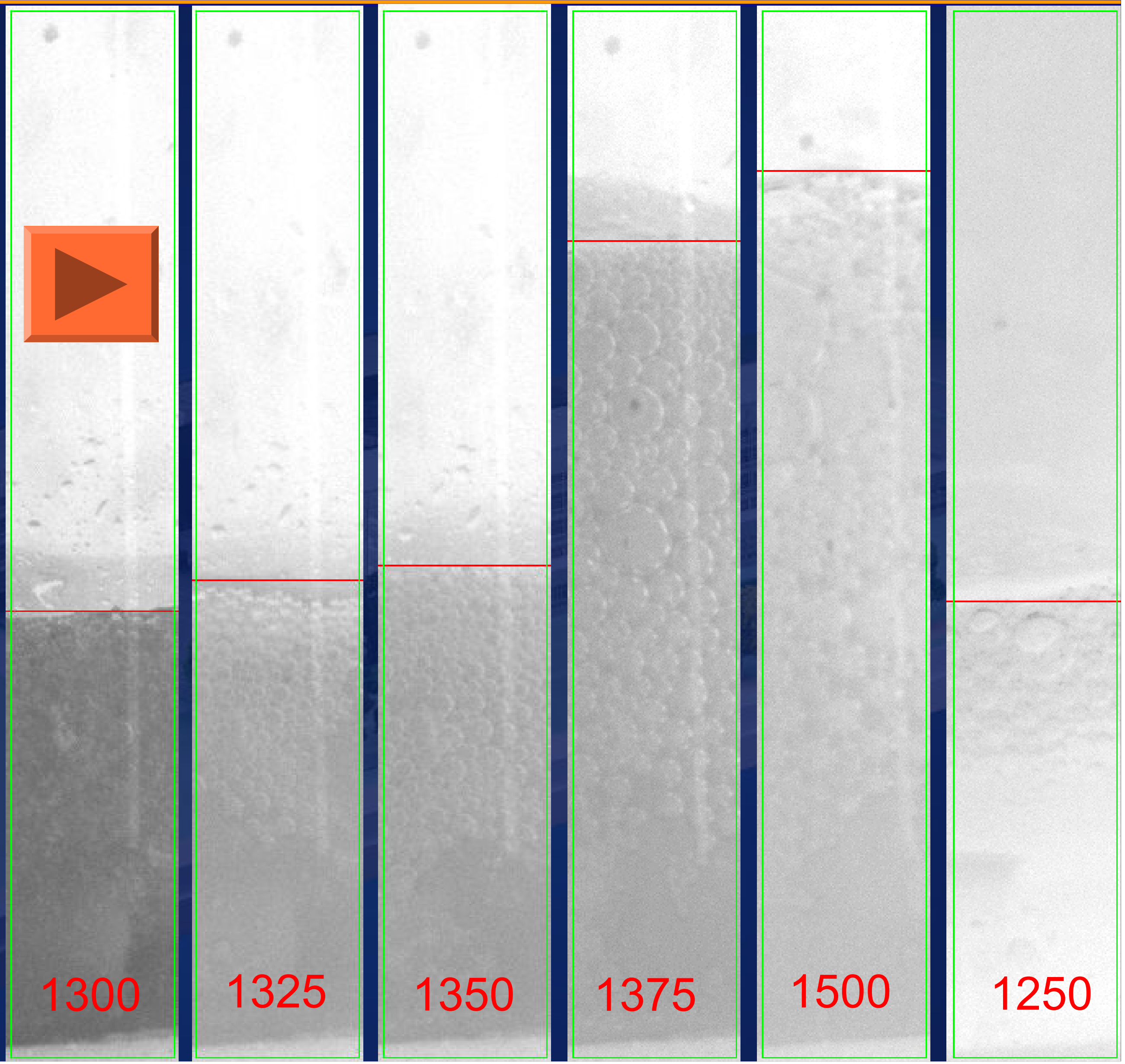
Foam behavior

Glass level



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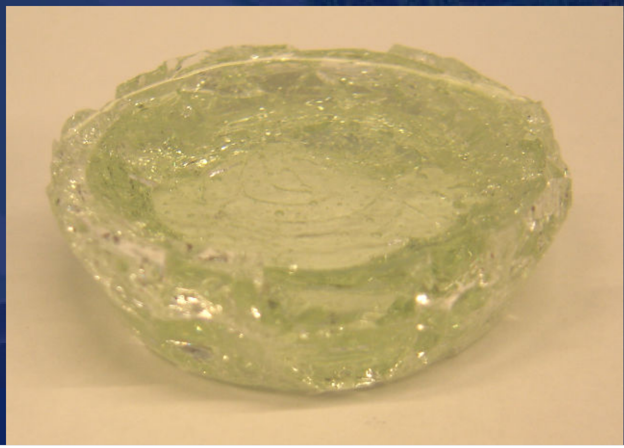
Characterization of batch

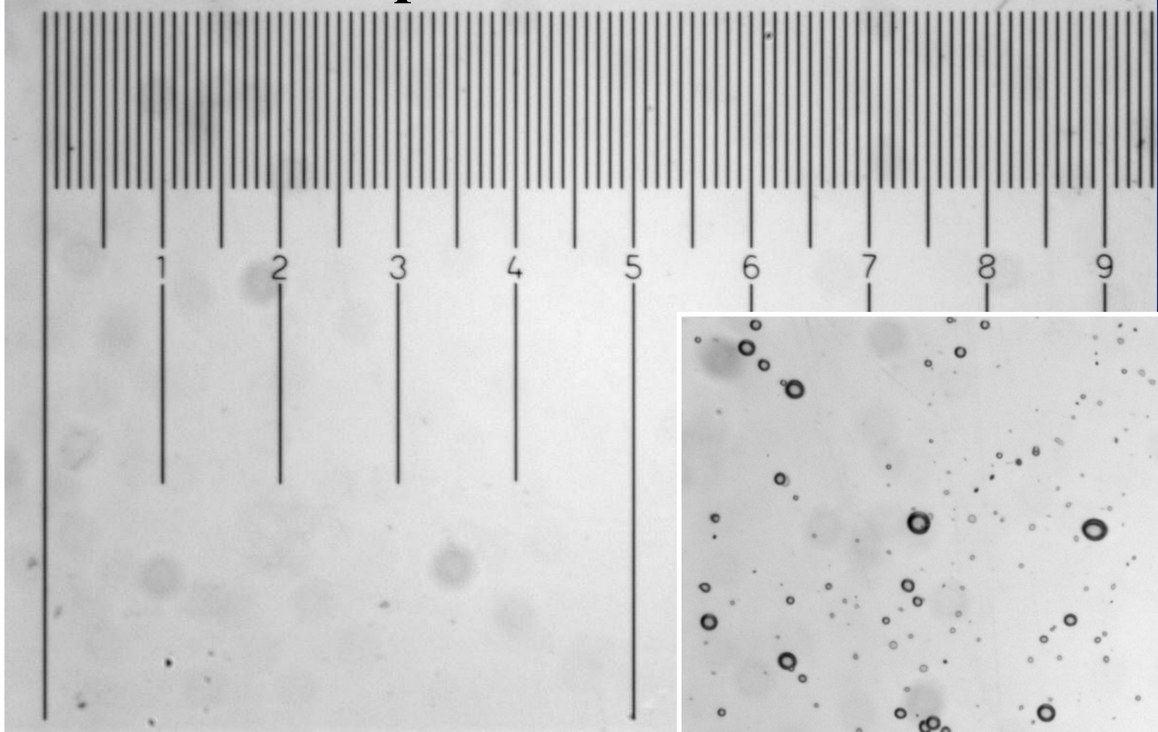
Aim: Investigation of batch materials/batch recipe on initial bubble size/melting behavior

- Raw material (batch) in Pt-crucibles
- Introduce crucibles in furnace at specific temperature (e.g. 1400 ^{o}C)
- Quenching glass sample
- Preparation of cross section
- Inspection of sample on bubbles / un-melted batch.

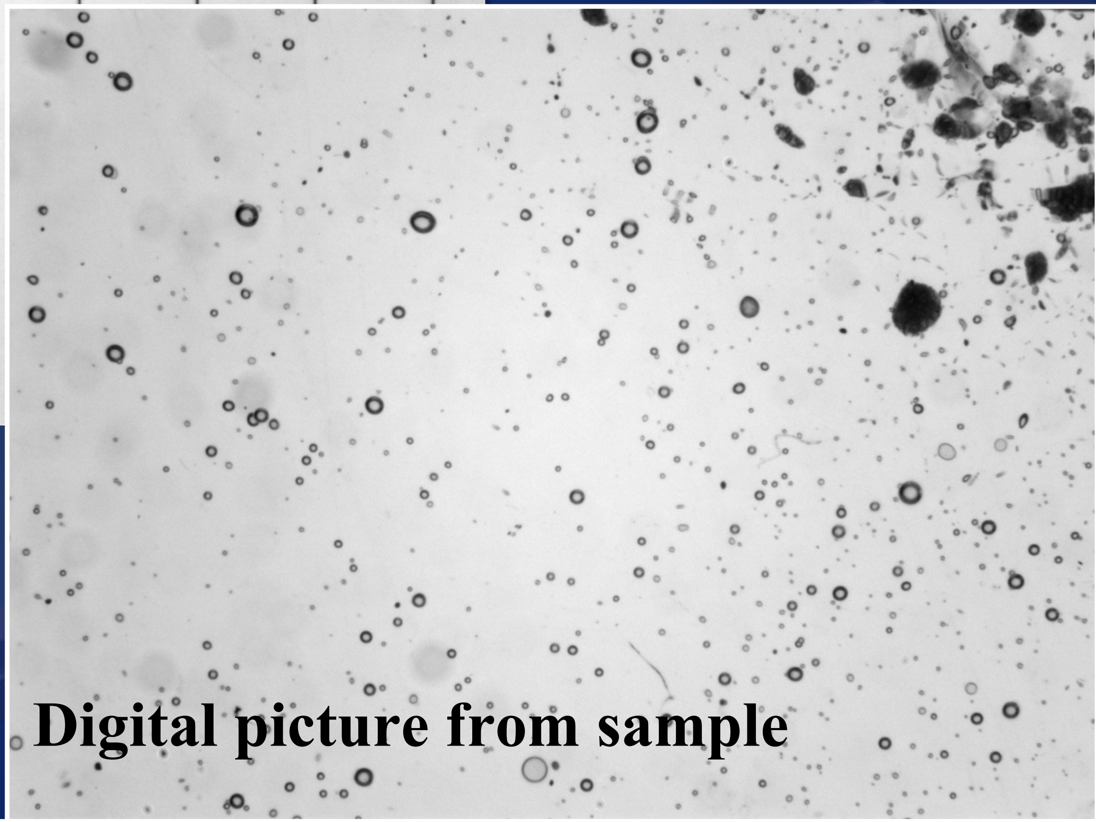


Characterization of batch

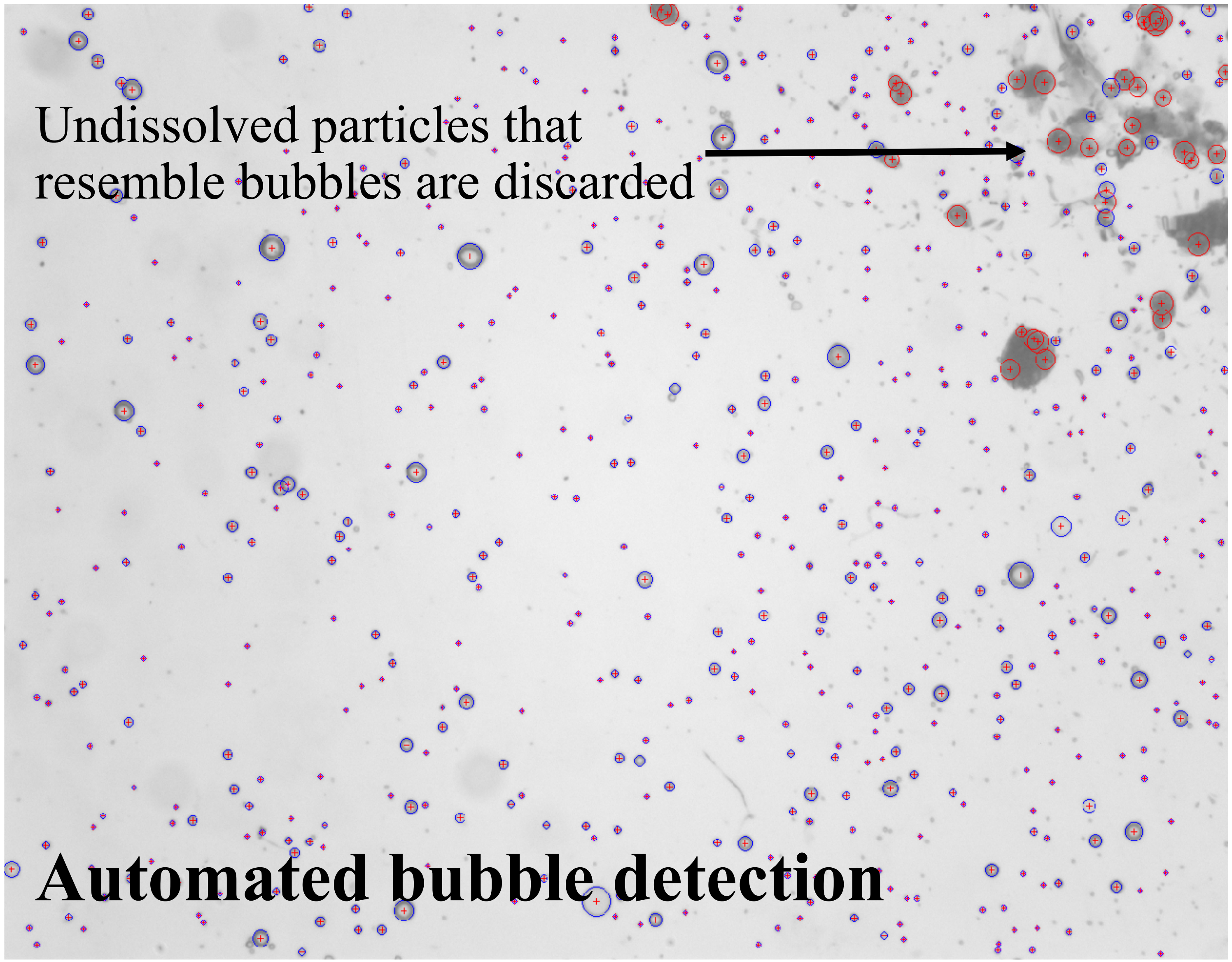
Calibration pixel size to real dimension



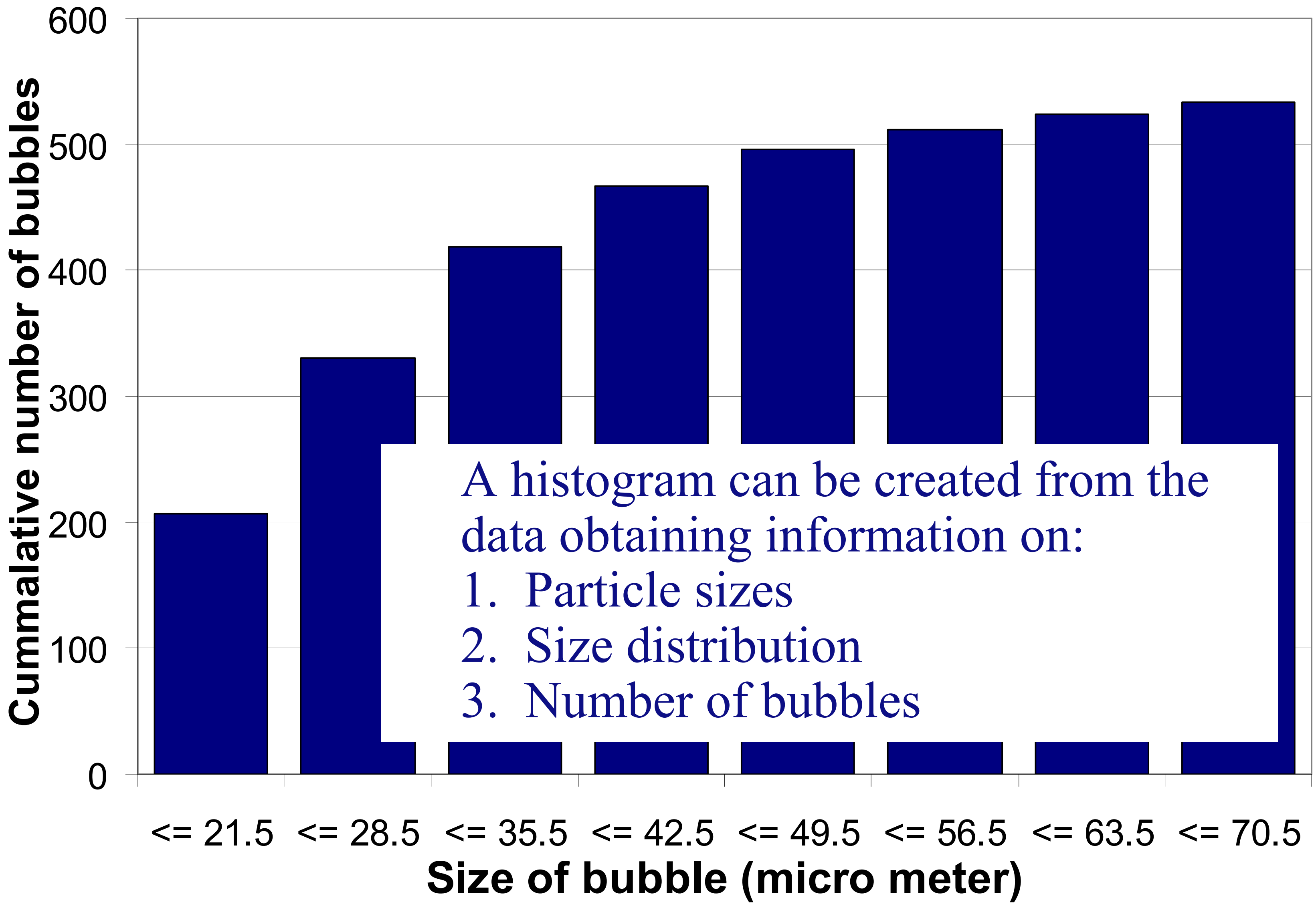
Digital picture from sample



Characterization of batch



Characterization of batch

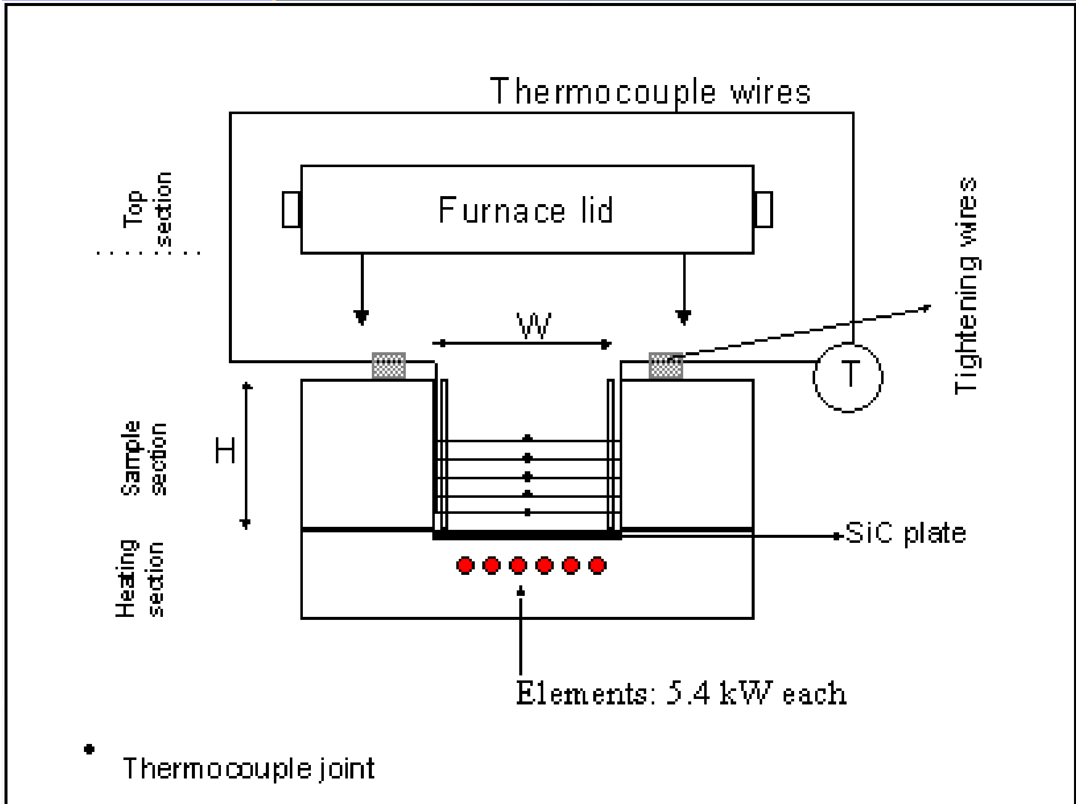


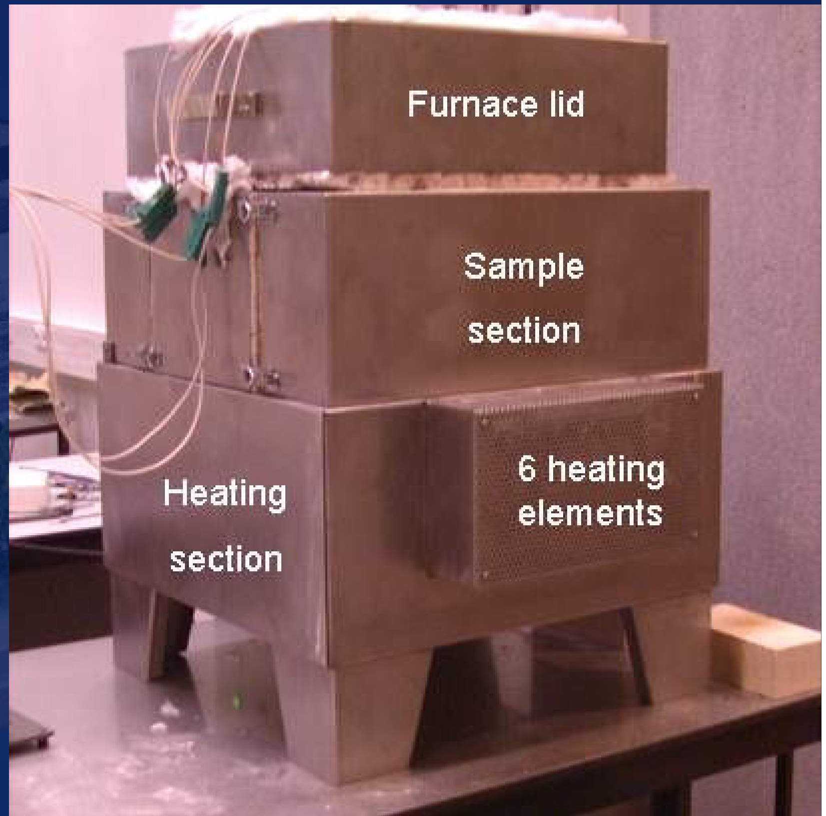
A histogram can be created from the data obtaining information on:

1. Particle sizes
2. Size distribution
3. Number of bubbles

Characterization of batch

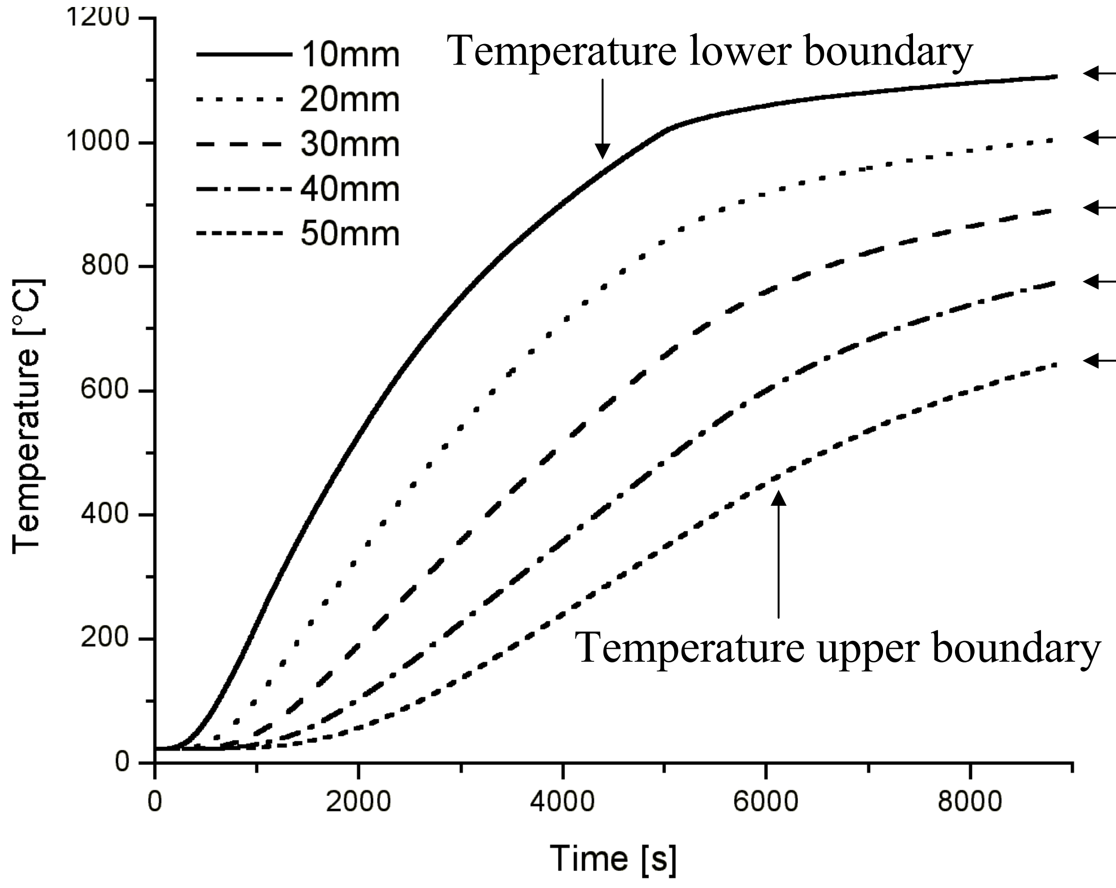
Experimental set-up for determination of thermal heat conductivity of batch





Characterization of batch

Measured temperature profiles in silica sand



10 mm from bottom

20 mm from bottom

30 mm from bottom

40 mm from bottom

50 mm from bottom

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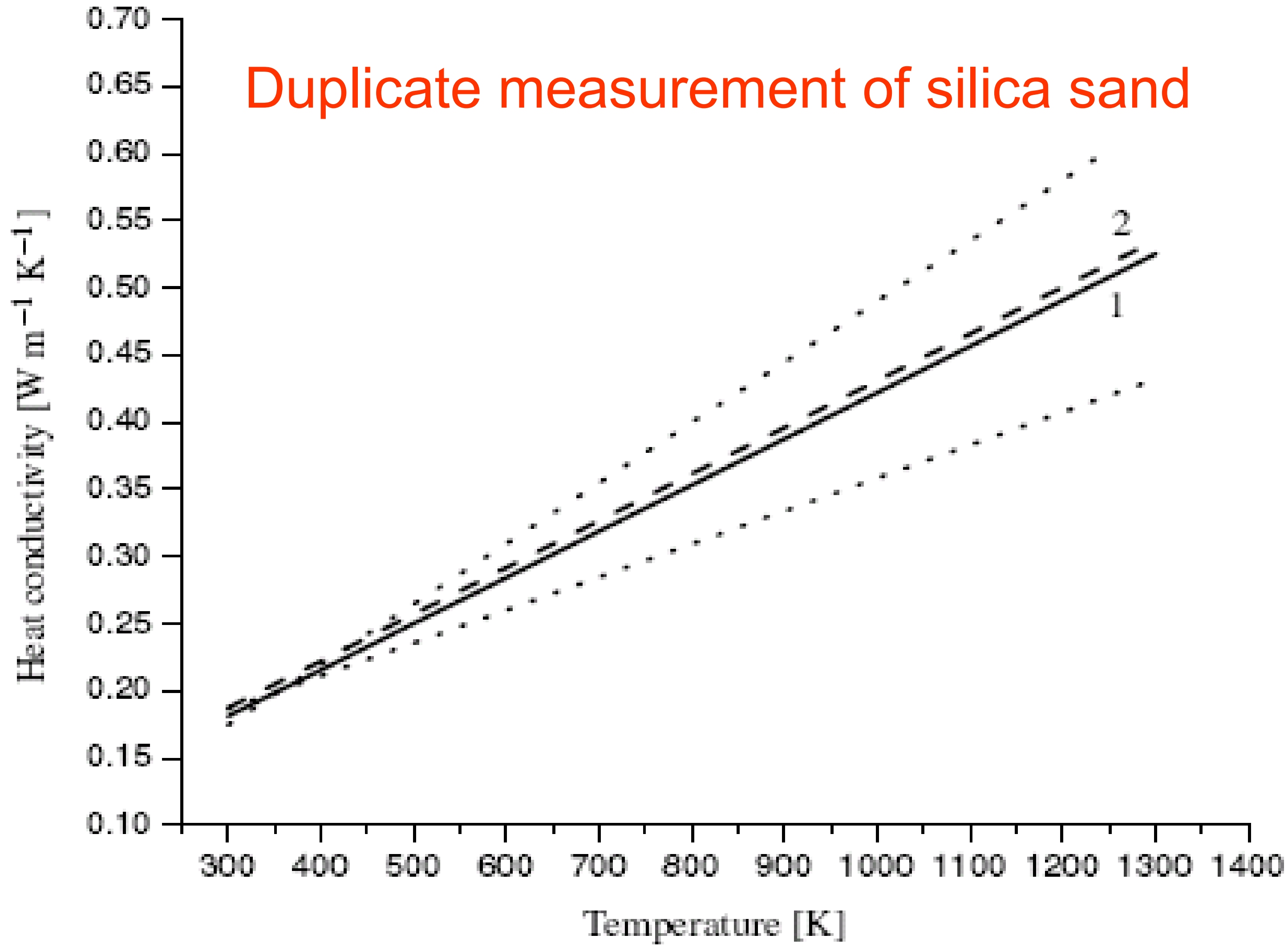
Characterization of batch



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Transpiration evaporation tests

Importance of evaporation:

- Emissions of dust (sulfates, borates, heavy metal) or gases (SO_2, HF, HCl, SeO_2)
- Depletion of volatile glass components at glass surface: formation of surface cord
- Attack of refractory material in superstructure:
  e.g. silica by glass melt vapors (Na, K, Pb)
- Loss of expensive raw materials (lead, boron, selenium)

Transpiration evaporation tests

Evaporation test facility:

- Kinetics of evaporation of volatile components can be determined experimentally (evaporation rate, kind of evaporating species)
- Parameters to be studied
  - Furnace atmosphere
  - Glass composition (alkali, F, Cl, Boron)
  - Temperatures

- Chemical activities of volatile components can be derived from evaporation measurements
- A thermodynamic (validated) model for evaporation is available

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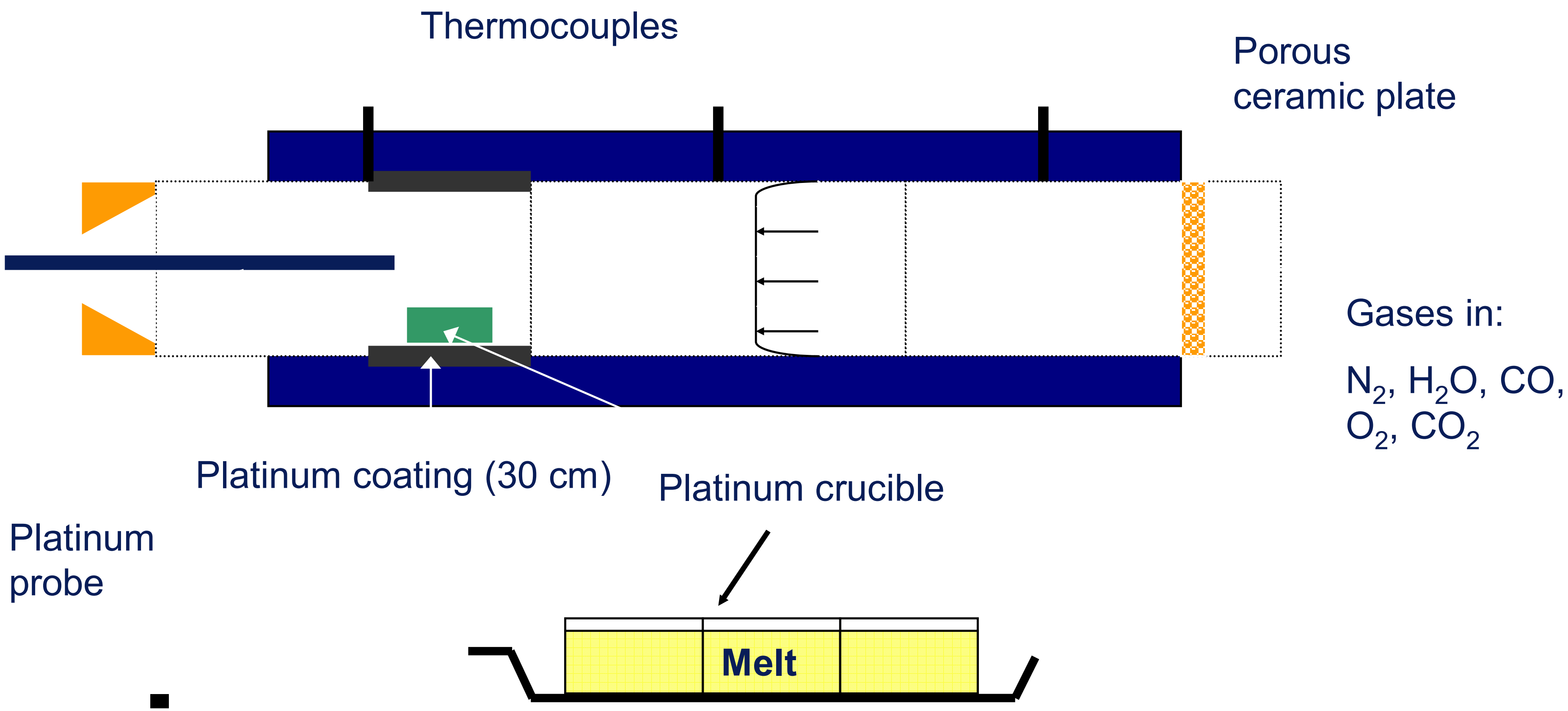
Transpiration evaporation test methods



Corrosion tests for refractory material

- Test facility for corrosion of refractory materials (e.g. regenerator checkers or furnace crowns)
- Refractory material exposed to typical combustion gases or flue gases
- Stable controlled reducing or oxidizing atmosphere (O_2, N_2, H_2O, CO_2, CO, NaOH, and SO_2)
- Temperature range: $900 < T < 1500$ °C
- Realistic sodium concentration for regenerator atmosphere and combustion space/crown:
  - Evaporation of Na_2CO_3 or Na_2SO_4. Concentration can be varied by temperature in the ‘evaporation space’.

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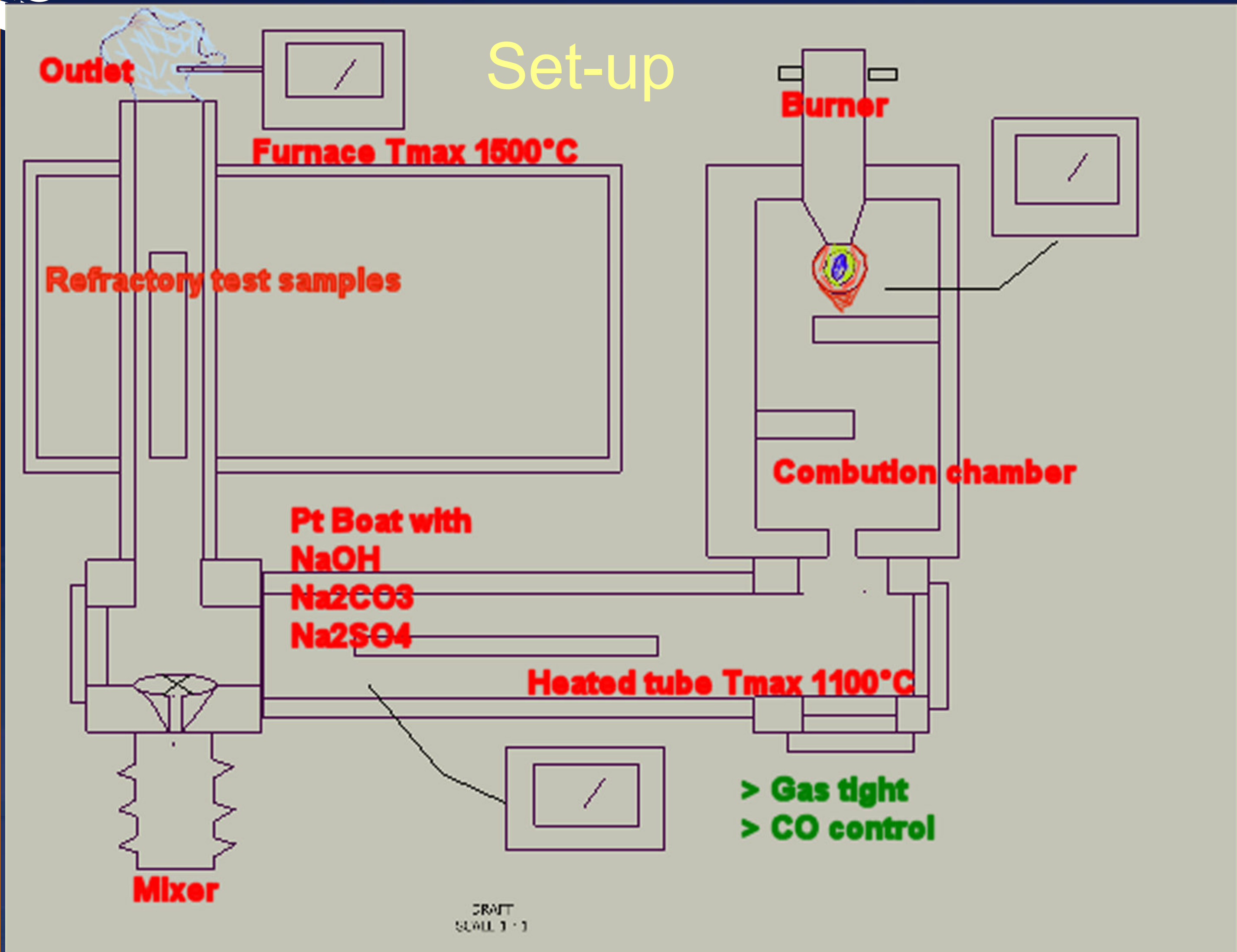
Corrosion tests for refractory material

Set-up



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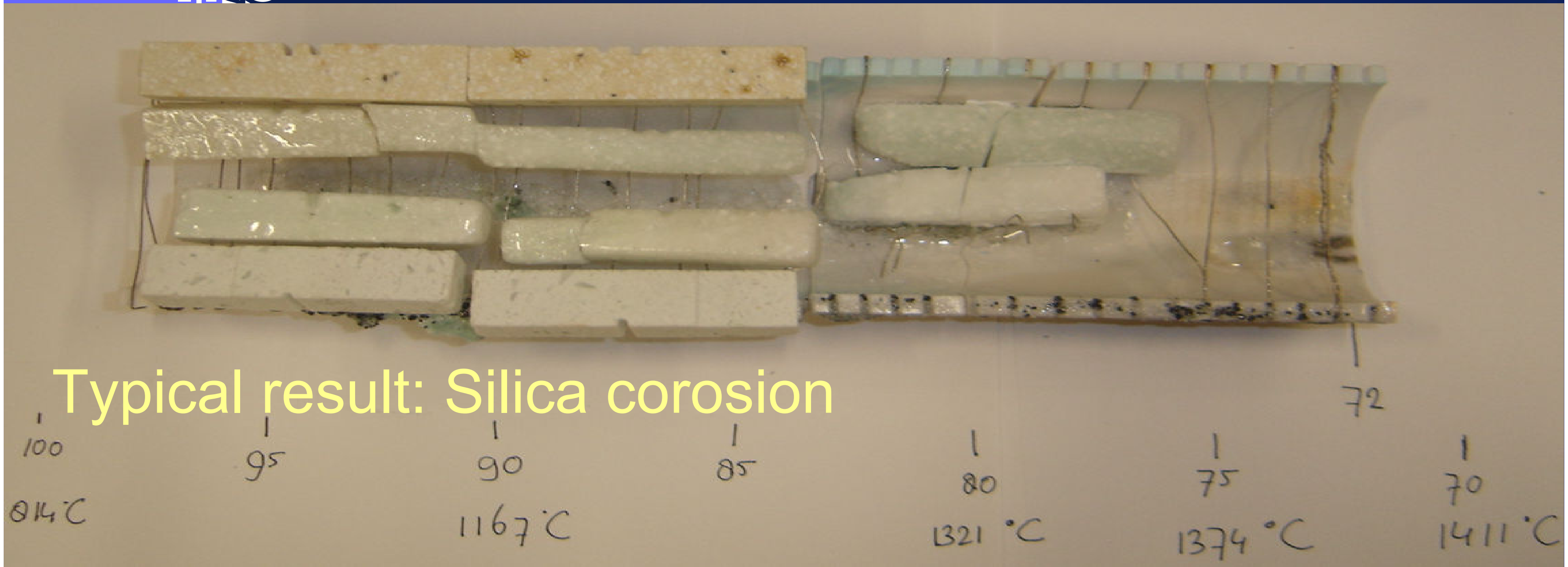
Corrosion tests for refractory material

Corrosion tests for refractory material



Typical result: Silica corosion

- After test:
  - Weight
  - Chemical attack
  - Change in structure (SEM analysis).

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Conclusions

- Overview given from experimental methods to investigate essential process steps for glass melting
- Results can be used to
  - Optimize industrial glass melting processes
  - Supply important data for models simulating glass melting process
    - ➢Fining, Foaming, Evaporation, Batch heating, Corrosion

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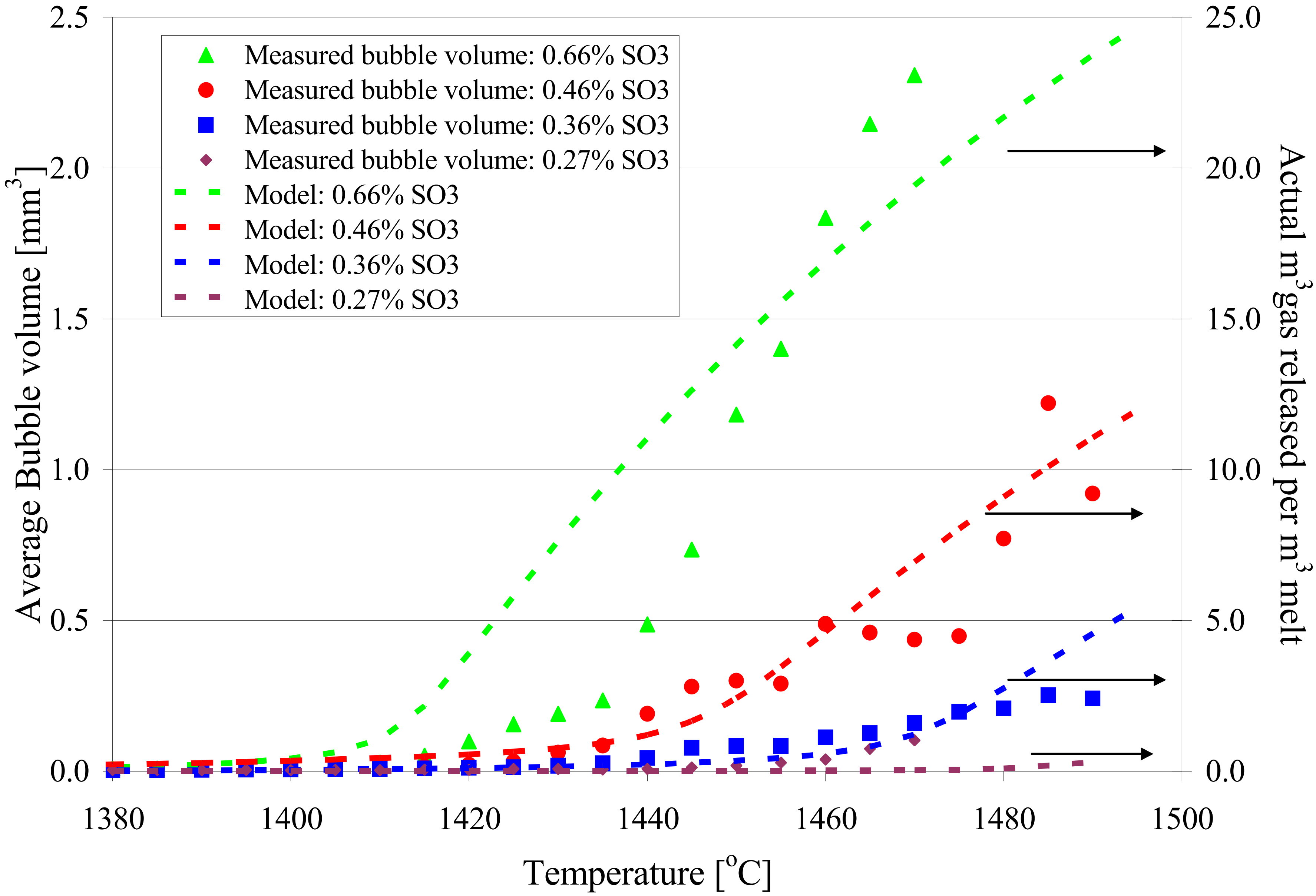
Bubble observation in glass melts



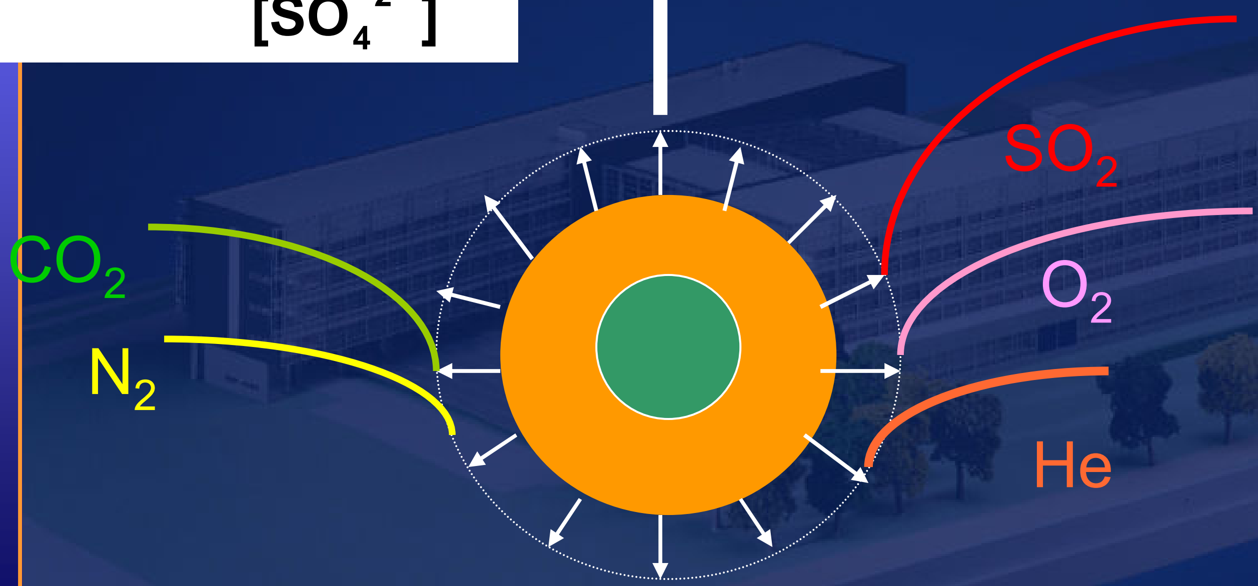
Bubble observation in glass melts

$v_{ascension} = c \cdot \rho \cdot g \cdot R^2 / \eta$

$$K^r_{sulfate}(T) = \frac{pSO_2 \cdot \sqrt{pO_2}}{[SO_4^{2-}]}$$

Fining reaction

$SO_4^{2-} \Rightarrow SO_2 + 1/2\ O_2 + O^{2-}$



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Bubble observation in glass melts

Helium enhanced fining

- Helium is a gas with a high solubility & high diffusion coefficient for (float) glass melts
- Experiments in float glass (containing 0.5 wt% Na_2SO_4) performed in which atmosphere above melt was flushed with helium
- Conditions:
  - During batch melting: nitrogen atmosphere
  - Isothermal period for 2½ hour (T_{melt} = 1325°C)
    - First ¾ hours: Nitrogen atmosphere
    - Last 1¾ hours: Helium atmosphere
- High temperature observation of bubbles + gas analysis (FTIR) at further heating

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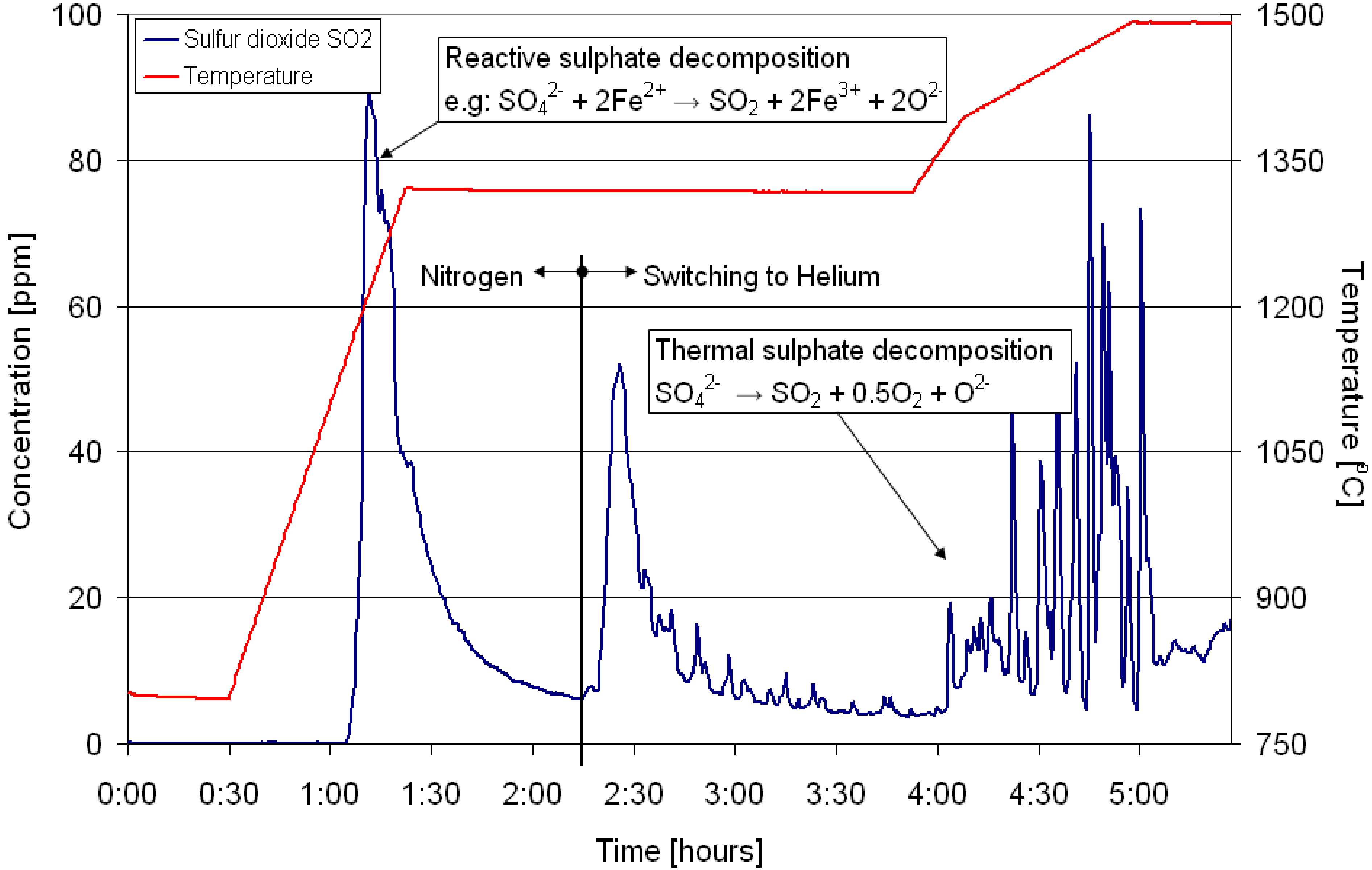
Bubble observation in glass melts



Bubble observation in glass melts

- Observation:

  Within 10 minutes after switching from Nitrogen to Helium: increase in SO_2 release.

- Explanation:
  - Tiny bubbles in top layer of glass melt are expanding in size due to fast diffusion of helium into bubbles
  - Rising speed increases and in same time interval more bubbles reach glass surface and release SO_2 gas

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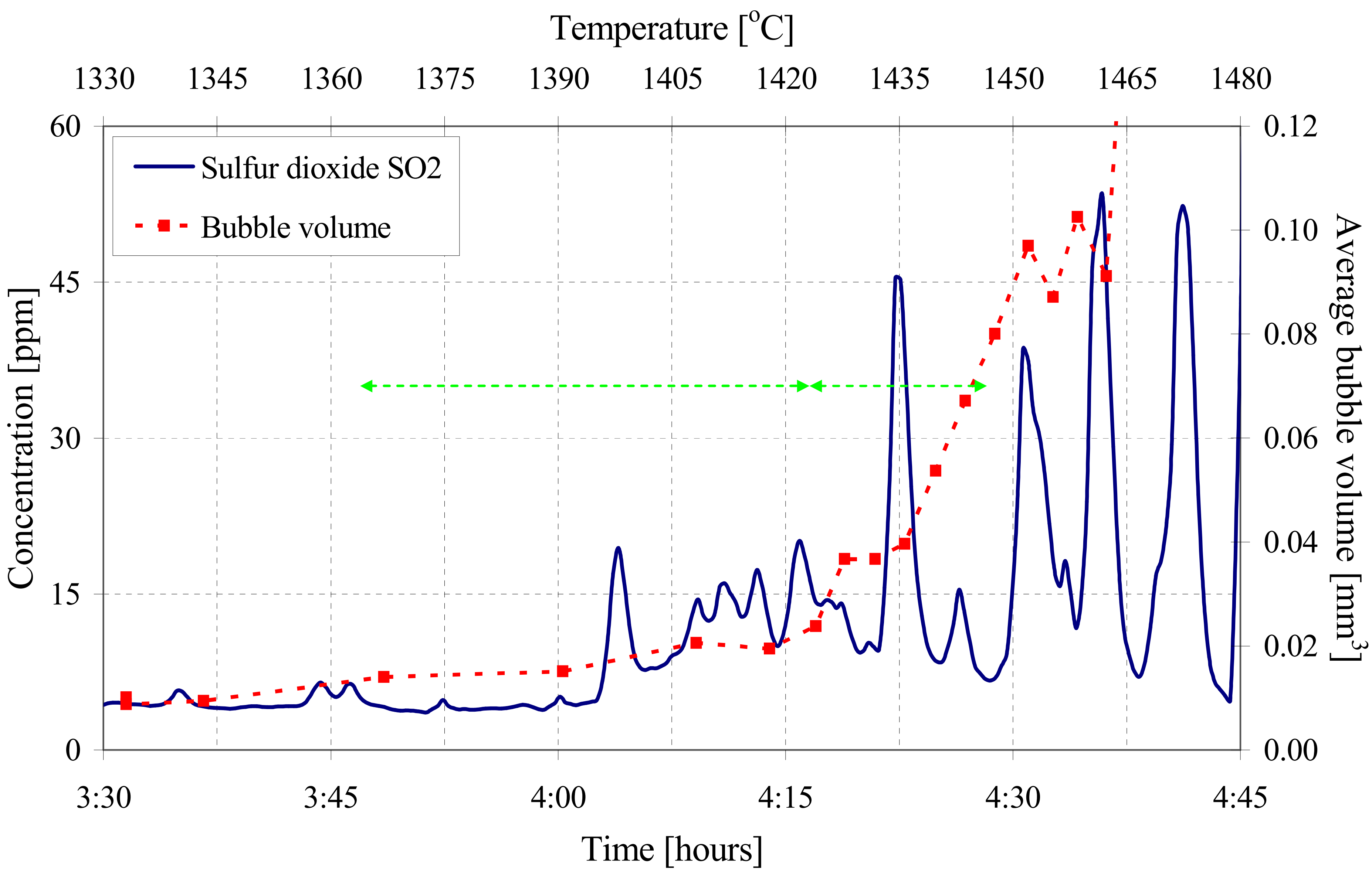
Bubble observation in glass melts



Bubble observation in glass melts

Helium enhanced fining

- Observations:
  - Around ± 1365°C an increment in the SO_2 release & slight bubble growth was measured.
  - Around 1420-1435°C even more SO_2 was released & bubble volume increased even more.
  - SO_2 release corresponds quite well with growth in bubble volume.
- Conclusion
  - Enhanced helium fining showed a lower fining onset temperature.
  - Helium diffuses into glass melt and into the existing bubbles: Bubbles grow

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Gas release model

Determination of volume of gas per unit volume of melt by:

- Equilibrium (temperature dependent) between dissolved gases in melt and gases in bubbles using Henry's law.
  Chemical equilibrium between fining agent & fining gases in melt & bubble
  Gases in melt: SO_2, O_2, H_2O, CO_2, N_2, Ar,…

$$G = \sum_{\text{i melt}} n_{\text{i melt}} \left[\mu^0_{\text{i melt}} + R_g T \ln\left(\gamma_{\text{i melt}} \frac{n_{\text{i melt}}}{n_{\text{melt}}} \right) \right] + \sum_{\text{i gas}} n_{\text{i gas}} \left[\mu^0_{\text{i gas}} + R_g T \ln\left(\gamma_{\text{i gas}} \frac{n_{\text{i gas}}}{n_{\text{gas}}} \right) + R_g T \ln\left(\frac{p}{p_0} \right) \right]$$

- Conservation of mass per chemical element j

$$b_j = \sum_{\text{i melt}} \upsilon_{\text{j,i melt}} n_{\text{i melt}} + \sum_{\text{i gas}} \upsilon_{\text{j,i gas}} n_{\text{i gas}}$$

- Total pressure in bubble is 1-1.3 bar

$$P_t = P_o + \rho \cdot g \cdot h + 2\sigma/R$$

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