



IMI-NFG Course on Processing in Glass

Spring 2015

(available online www.lehigh.edu/imi)

Lecture 2: Melting and Fining processes in industrial glass furnaces

Mathieu Hubert, PhD

CelSian Glass & Solar
Eindhoven, The Netherlands

mathieu.hubert@celsian.nl



Introduction

- In Lecture 1, the preparation of the batch has been described, from the selection of the raw materials to the charging of the batch in the furnace via the doghouse (or day-hopper)
- The batch is introduced in the furnace at high temperature, and the energy provided to the batch is used to convert the batch into a glass melt
- The **batch-to-melt conversion** implies a series of chemical reactions (decarbonation, dehydration, solid-state reactions, formation of low-melting eutectics, dissolutions)
- This lecture will highlight these different reactions and processes, from the introduced batch to an homogeneous and bubble-free glass melt (before the forming processes)

Outline of this lecture

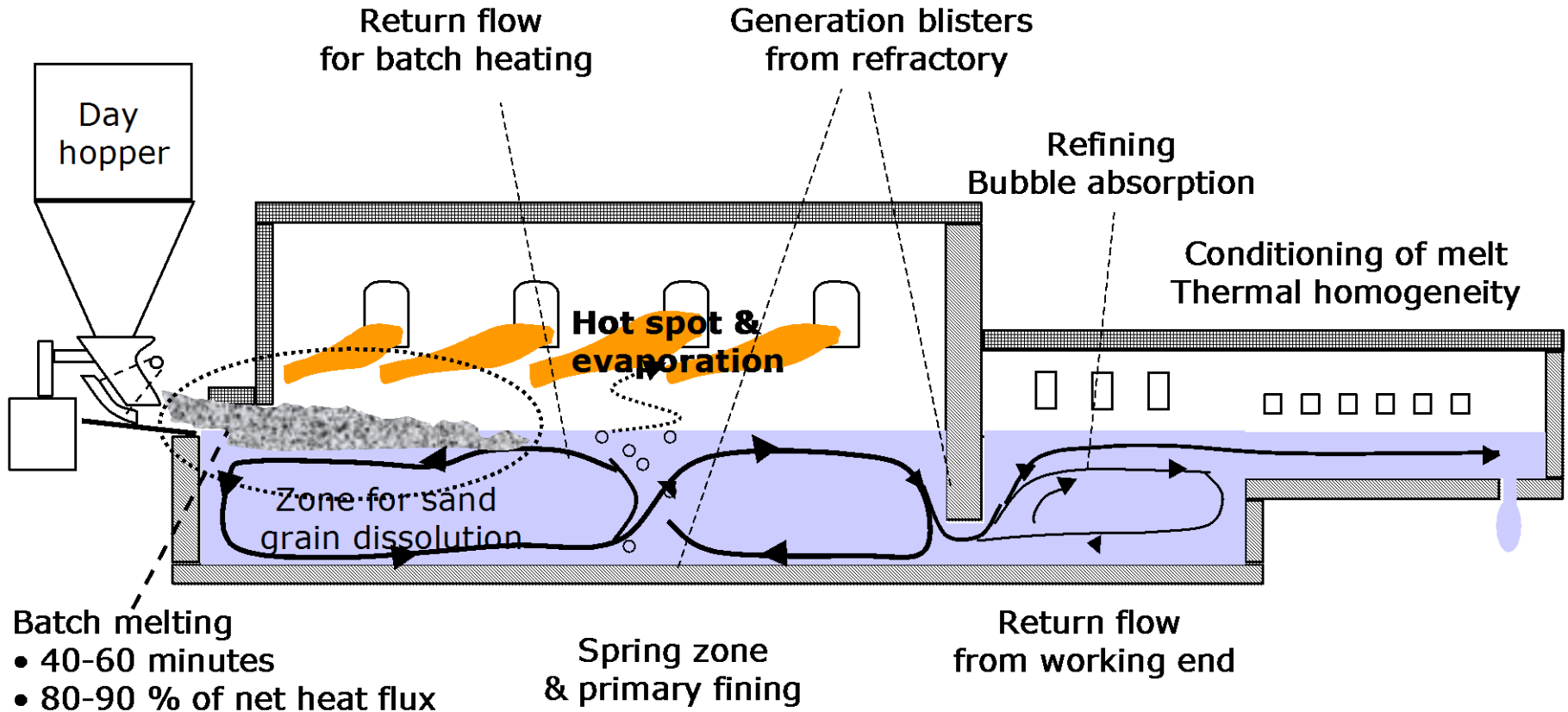
1. Melting of the batch

- From the batch to the melt
- Chemical reactions
- Sand dissolution

2. Fining of the melt

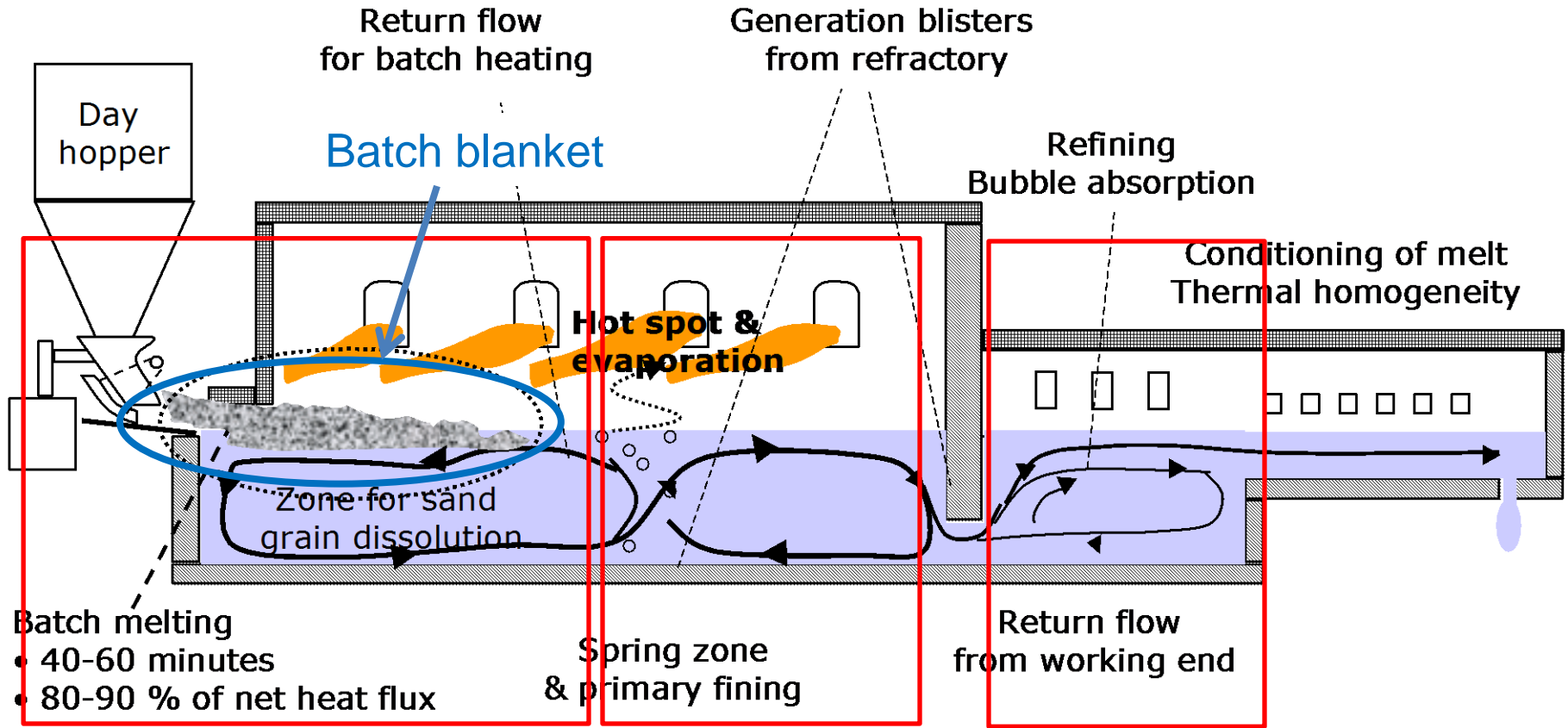
- Dissolved gases
- Fining mechanisms
- Removal of bubbles and seeds

Schematic of an industrial glass melting tank



** This is a schematic representation, but many different furnace designs exist (more on that in Lecture 3)*

Melting and fining in the furnace

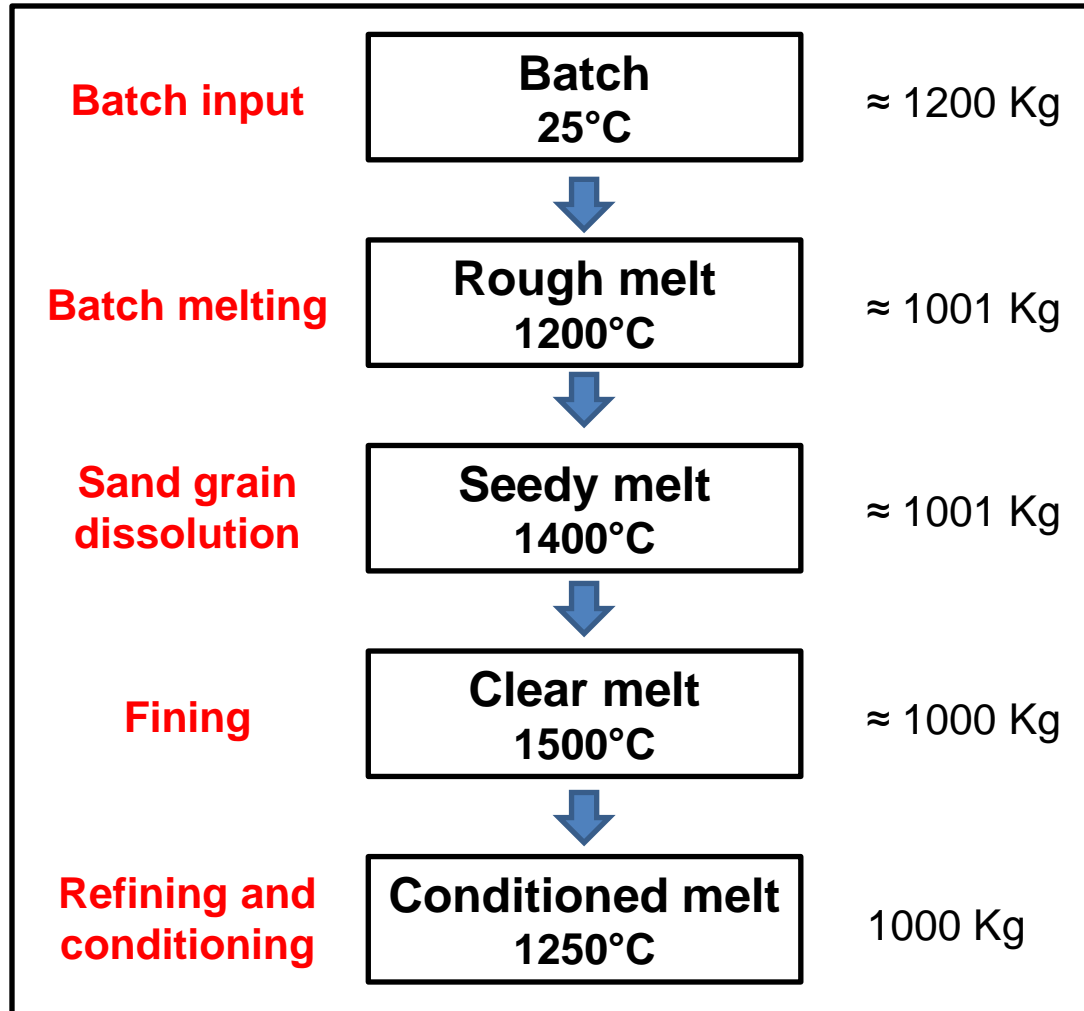


Melting and sand dissolution

Primary fining

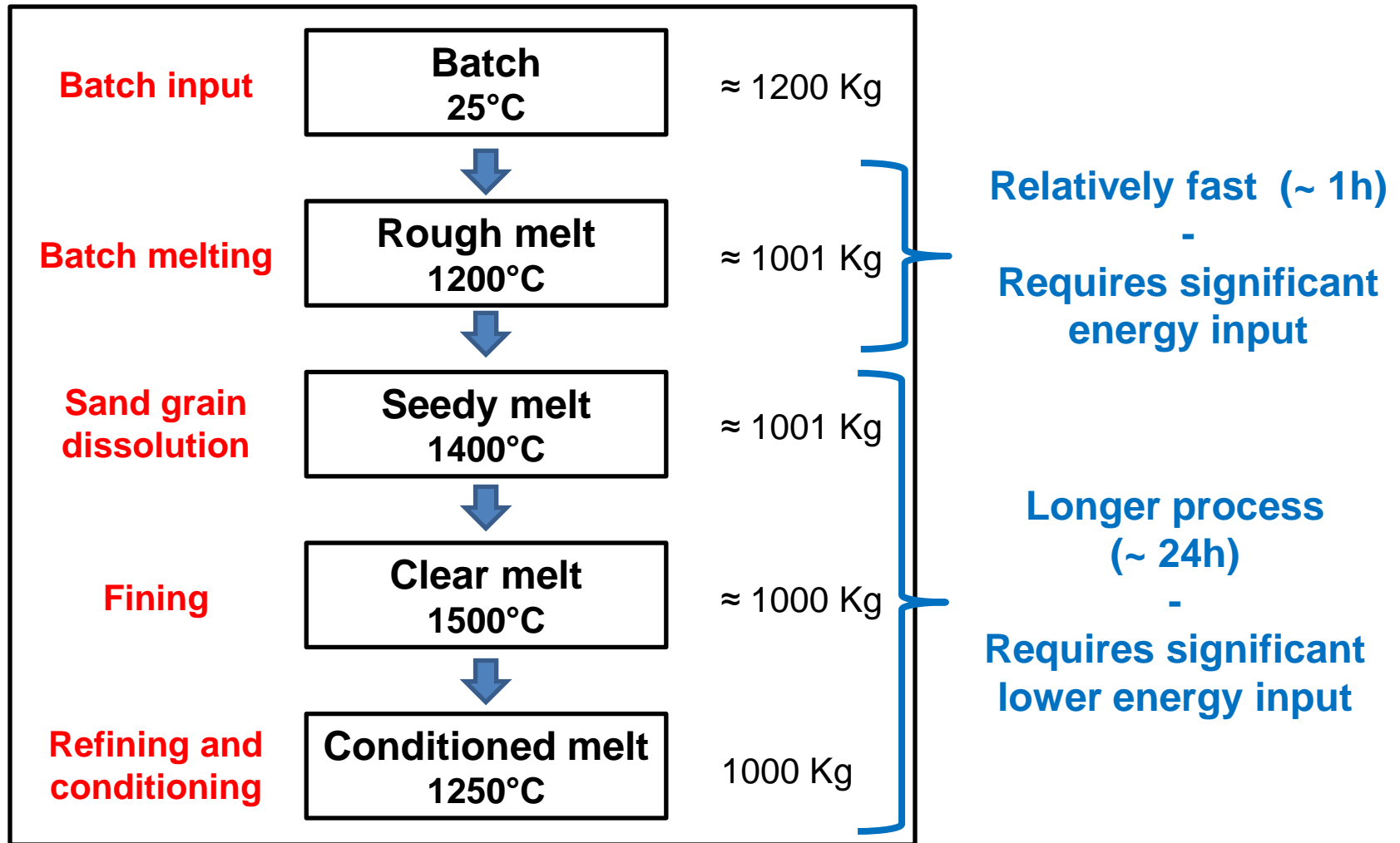
Secondary fining (refining)

Melting and fining in the furnace



Inspired from R. Conratt, Thermodynamics and Energy Demand for Batch-to-Melt Conversion, presented at the 6th ICG summer school, Montpellier, France, July 2014

Melting and fining in the furnace

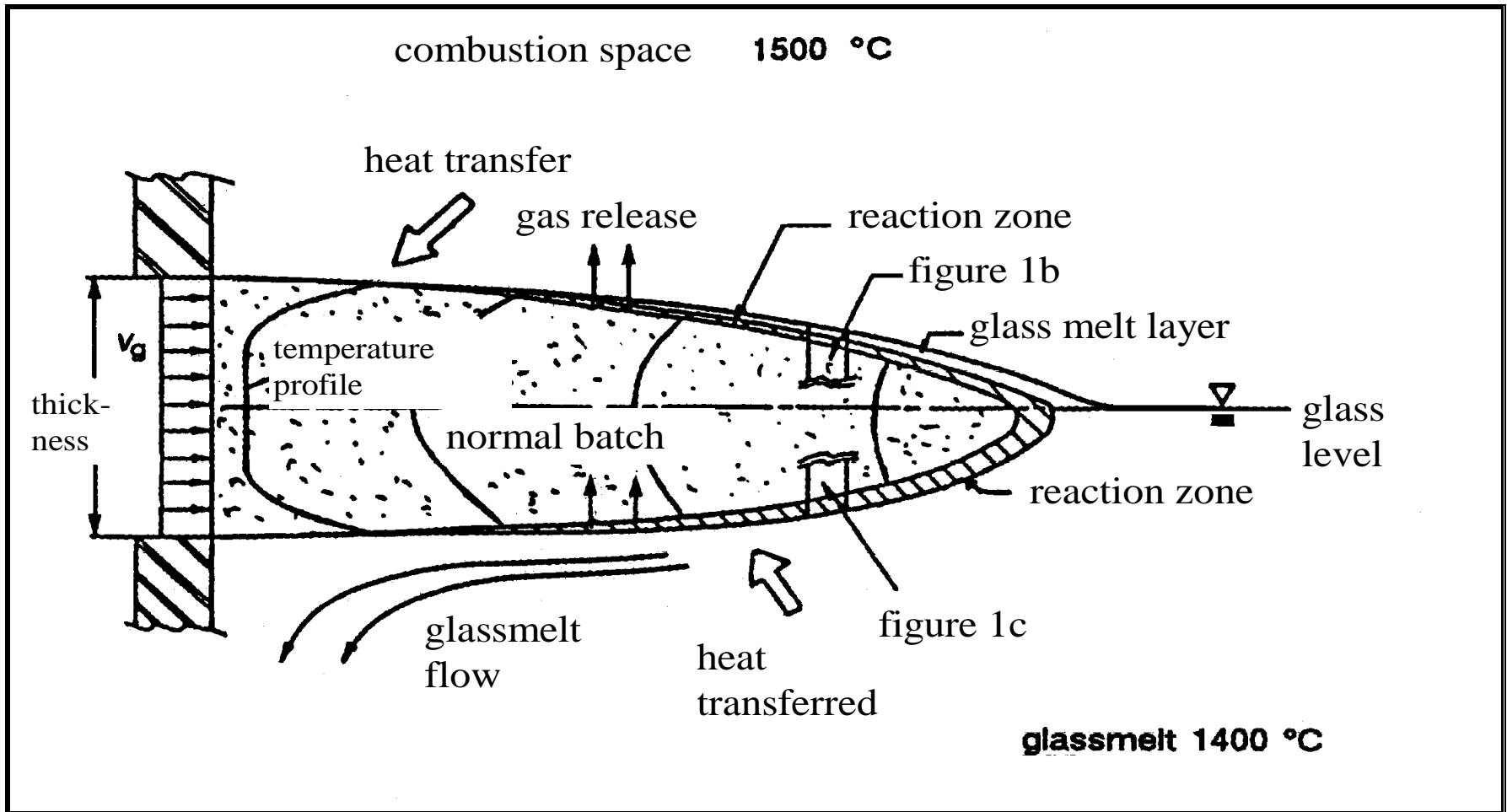


Inspired from R. Conratt, Thermodynamics and Energy Demand for Batch-to-Melt Conversion, presented at the 6th ICG summer school, Montpellier, France, July 2014

Batch melting-in

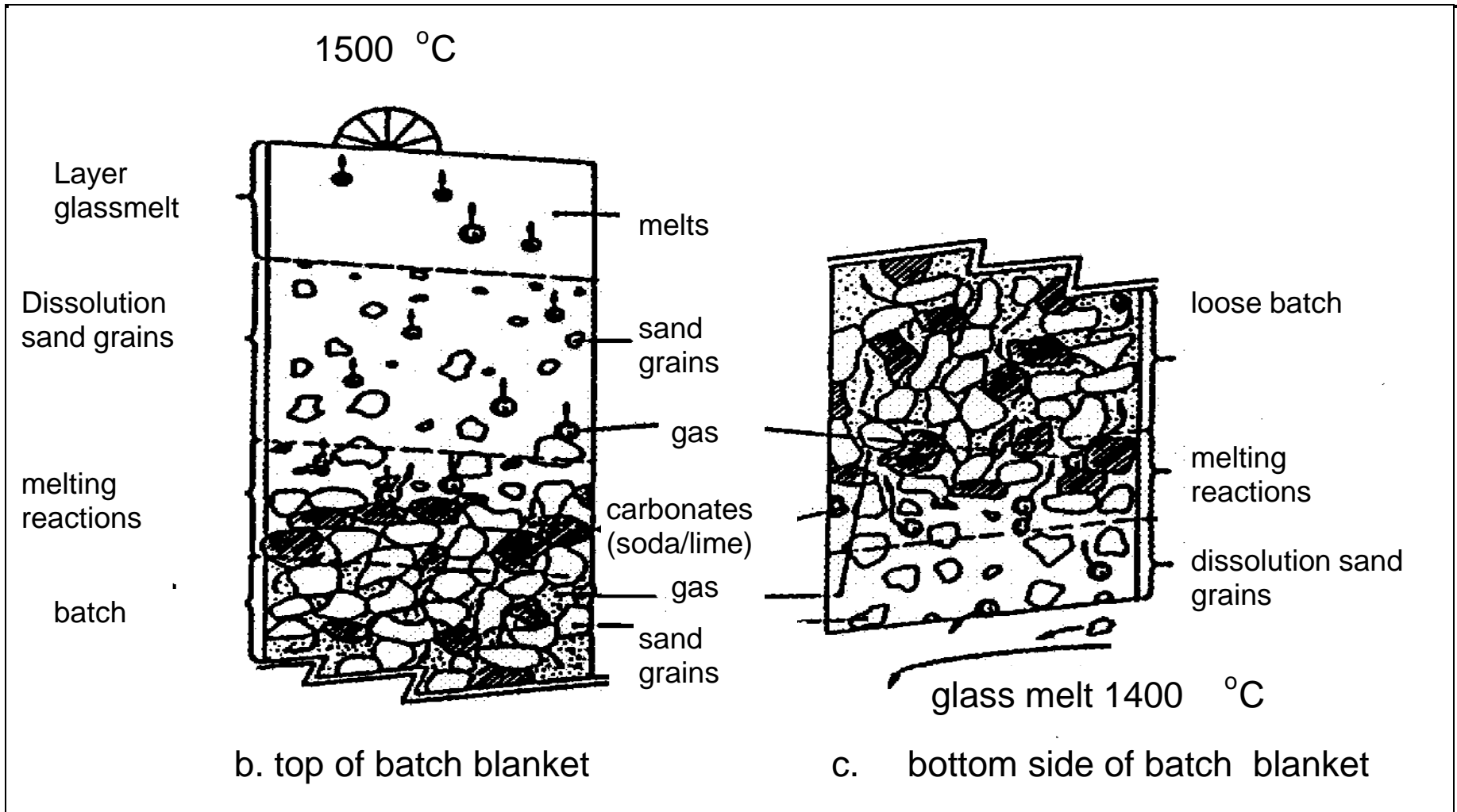
- The **melting-in** process occurs mainly **by reactions within the batch blanket** forming liquid phases.
- In the heated batch piles or blanket:
 - ✓ The **first aggressive melt phases** are formed, which will strongly attack and largely dissolve the components that are difficult to dissolve, like quartz sand or feldspar/china clay particles.
 - ✓ The melt phases thus formed flow from the batch blanket area into the glass melt. So the batch blanket becomes increasingly thinner
 - ✓ Still some of the **non-dissolved sand particles** will arrive in the glass melt itself, where these particles will have to dissolve further by diffusion of SiO_2 in the molten glass, away from the sand grain surface.

Melting process of the batch blanket



From Ungan and Viskanta, "Melting Behavior of Continuously Charged Loose Batch Blankets in Glass Melting Furnaces", *Glastechnische Berichte*, 59 (10), 1986, pp. 279-291

Detailed representation of batch melting process



From Ungan and Viskanta, "Melting Behavior of Continuously Charged Loose Batch Blankets in Glass Melting Furnaces", *Glastechnische Berichte*, 59 (10), 1986, pp. 279-291

Different steps of the melting process

- Melt reactions
- Melt energy (enthalpy of heating the batch and decomposition melting/fusion reactions)
- Melting kinetics / heat transfer
- Melting parameters:
 - ✓ effect of the temperature
 - ✓ grain size (especially for sand and alumina raw materials)
 - ✓ glass composition

Melt reactions

Melting reactions

- **De-hydration** of some raw materials and **water evaporation**
- **Solid state reactions** between individual raw materials
- **Formation of primary melt phases** and melting of alkali rich carbonates. (typically in the temperature range: 700-900°C)
- **Dissociation** or **decomposition** reactions of Ca- and Mg-containing carbonates (e.g. limestone and dolomite), resulting in development of CO₂-gas. (Temperature range 500-1000°C) (Na₂CO₃ will not decompose spontaneously, but reacts with sand or limestone).
- **Dissolving of the SiO₂** in the alkali rich carbonate melt phases, typically above 1000°C. Sand reacts between about 750-1000°C with sodium silicates or soda to form liquid sodium silicates (associated with the release of CO₂-gas when limestone or soda or dolomite is reacting with sand)

Dehydration

- Takes place at $\pm 100^{\circ}\text{C}$ for physically bonded water
- In case of clay in the batch, de-hydration may occur up to 650-700 $^{\circ}\text{C}$
- Dehydration (water evaporation) is **very energy intensive**, and it represents an important part of the total energy consumption

Sand dissolution

- **Pure silica melts at very high temperature (> 1700°C)**
- In standard glasses (except e.g. pure silica glass) sand is incorporated in the glass melt by dissolution, and not by melting
- **Sand dissolution is a critical step** in industrial melting process
- It is highly dependent on the **initial grain size distribution** of the sand grains in the batch, as well as the presence of aggressive molten phases (e.g. alkaline phases)
- Sand grains react with other batch components or dissolve in the obtained melt in most glass melting processes. The optimum grain size depends on the glass type.

Grain size distribution of quartz sand, recommended for different applications, values in mass%

Application	Indication	Grain size (mm)						
		Size class	<0.03	<0.06	<0.125	<0.25	< 0.35	<0.5
Container glass	Coarse sand	-	-	1	25	55	75	95
Container & Float	Medium sand	-	-	10	50	75	95	100
Float glass	Fine sand	-	1	5	70	85	100	100
Float glass	Very fine sand		3	15	85	100	100	100
E-glass & alkali-borosilicate	Coarse silica powder	40	70	95	100	100	100	100
E-glass	Medium silica powder	70	95	99	100	100	100	100
E-glass	Fine silica powder	98	100	100	100	100	100	100

Solid-state reactions in the batch

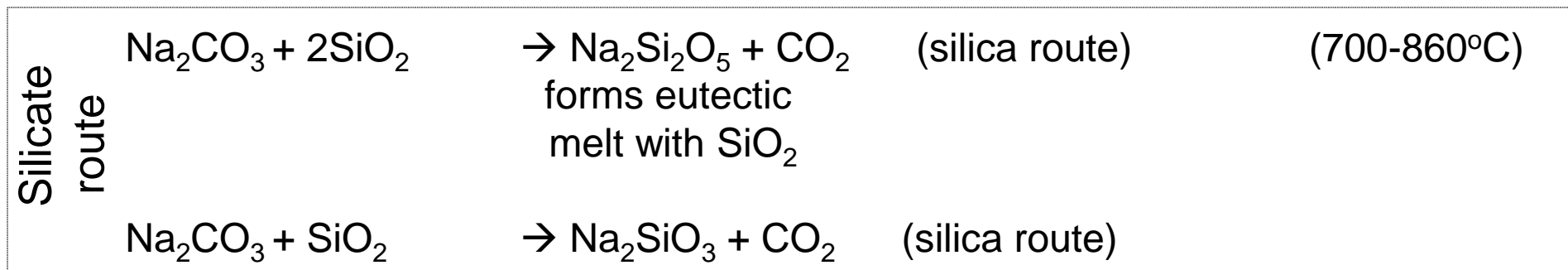
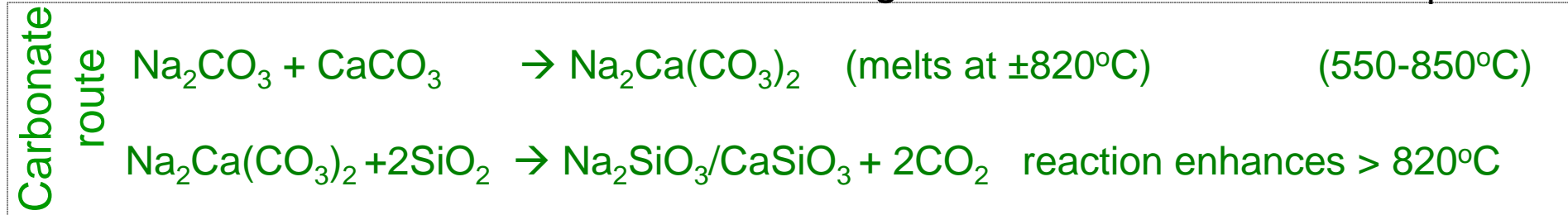
- Solid-state reactions can be divided into two routes: the carbonate route and the silicate route
- **The carbonate route** (path) is characterized by **reactive dissolution of silica sand** with a binary melt phase of soda ash and limestone below about 900°C. Soda ash and limestone, in contact with each other, may form a double carbonate by a solid state reaction forming the species $\text{Na}_2\text{Ca}(\text{CO}_3)_2$
- At about 820°C, this intermediate reaction product starts to melt and becomes suddenly more reactive (better contact) towards silica sand grains.
- Silica reaction with $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ forms a viscous $\text{Na}_2\text{O}\cdot\text{CaO}\cdot\text{SiO}_2$ melt plus CO_2 gas.

Solid-state reactions in the batch

- The **silica/silicate route** is based on **eutectic melting** of a mixture of components, including the sodium disilicate phase, formed by solid state reactions between sand and soda.
- The **eutectic melting** of SiO_2 and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ takes place at 799°C and silicate rich melts are formed.
- The degree to which these reactions occur depends on the mutual contact between the components.
 - ✓ Within a **compacted batch** (pellets, granules) the reactions will be more intensive than in a loose powder batch.
 - ✓ **Finer powders** may give a better contact between the interacting raw material grains compared to coarse powders. Thus finer powdered batch is often more reactive and may give a better glass homogeneity

Melting reactions – Silicate route for SLS batch

- **Solid state** reactions, formation of silicates, e.g.:
Carbonate route < 900°C at fast heating rate High amount of heat required



The rate of the reactive calcination of soda ash with silica increases sharply when heating above 825°C up to about 855°C.

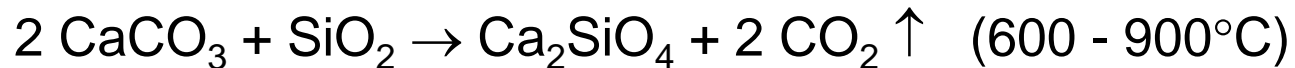
- Formation of **primary melt** phases (alkali rich carbonates), e.g.:

$$T_m \text{ Na}_2\text{CO}_3 = 850^\circ\text{C}$$

$$T_m \text{ Na}_2\text{Ca}(\text{CO}_3)_2 = 820^\circ\text{C}$$

Limestone –sand solid-state reactions

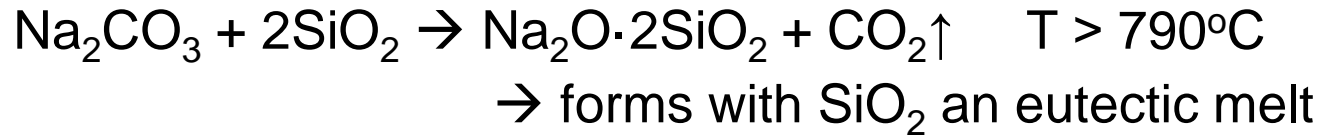
- The main part of the limestone or dolomite will **decompose** above the thermodynamic calcination temperature of limestone, this depends on the CO₂ partial pressure in the batch. Some limestone may react directly with silica:



- These reactions occur only on the contacting interfaces and they are much slower than solid state/liquid reactions.

Melting reactions – Silicate route for SLS batch

- **Reactive calcination:**



- Or at further heating

→ fast $\text{Na}_2\text{O} \cdot \text{SiO}_2$ formation (850°C) plus limestone decomposes and:



- **Silicate route:**

Silicate melt + $\text{SiO}_2 \rightarrow$ silica enriched melt $T > 1000\text{-}1100^\circ\text{C}$

Eutectic melt phases are formed above $\pm 800\text{-}840^\circ\text{C}$

Silicate melting points / eutectics

The melting points of the meta-silicate Na_2SiO_3 and of the di-silicate $\text{Na}_2\text{Si}_2\text{O}_5$ are:

- $T_s (\text{Na}_2\text{SiO}_3) = 1089^\circ\text{C},$
- $T_s (\text{Na}_2\text{Si}_2\text{O}_5) = 874^\circ\text{C}.$

Eutectics:

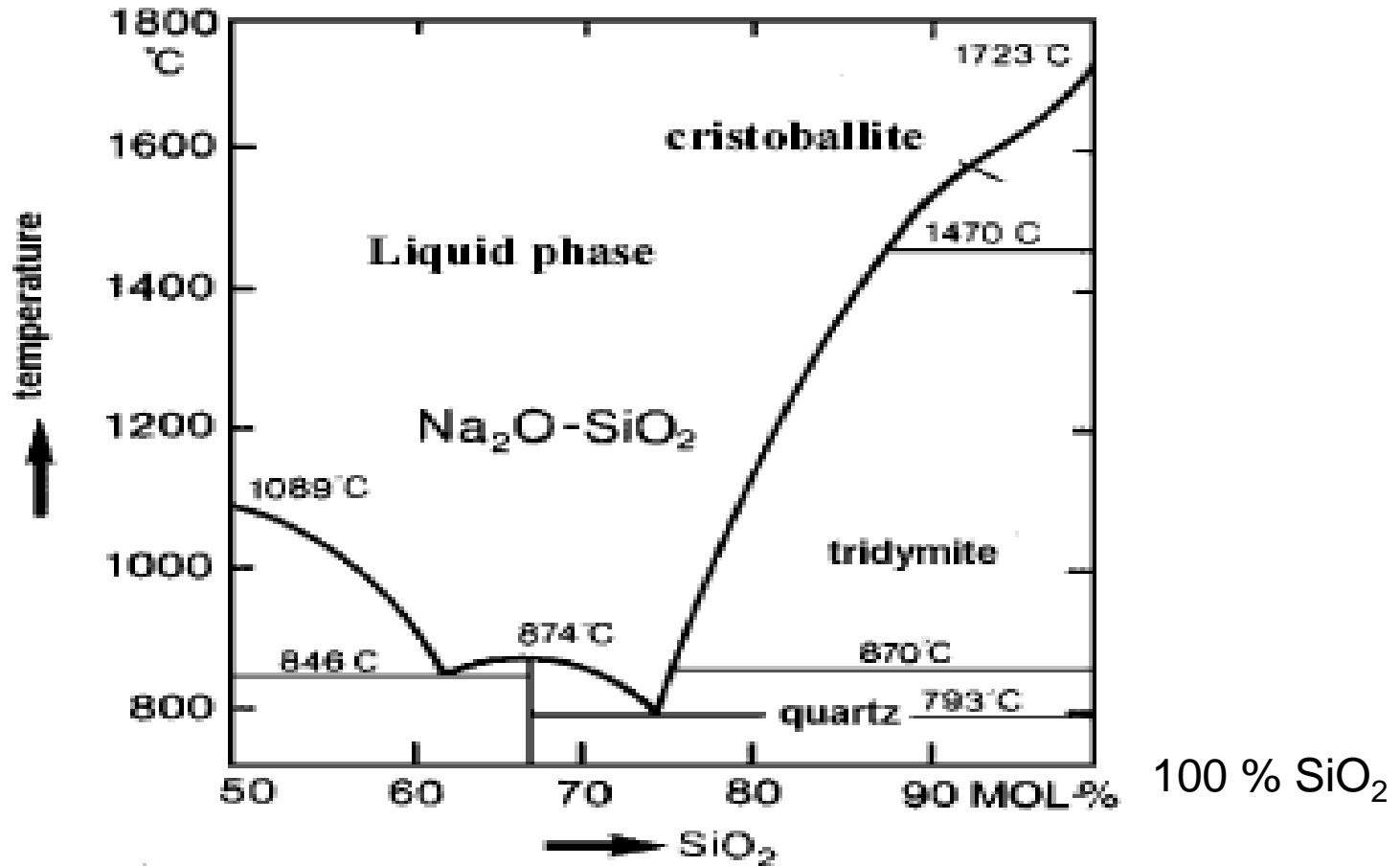
- $T_{\text{eut}} (\text{Na}_2\text{O} \cdot 2\text{SiO}_2 + \text{SiO}_2) = 793^\circ\text{C}.$
- $T_{\text{eut}} (\text{Na}_2\text{O} \cdot 2\text{SiO}_2 + \text{Na}_2\text{O} \cdot \text{SiO}_2) = 846^\circ\text{C}.$
- $T_{\text{eut}} (2\text{Na}_2\text{O} \cdot \text{SiO}_2 + \text{Na}_2\text{O} \cdot \text{SiO}_2) = 1020^\circ\text{C}.$

In combination with calcium oxide, an even lower (ternary) eutectic temperature may occur:

- $T_{\text{eut}} (\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2 + \text{SiO}_2 + \text{Na}_2\text{O} \cdot 2\text{SiO}_2) = 725^\circ\text{C}.$

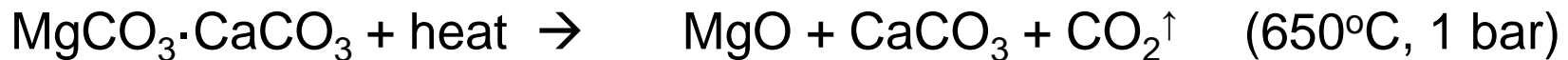
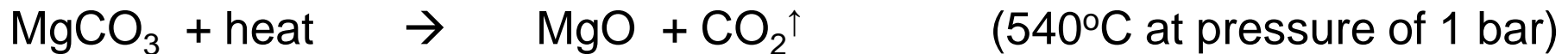
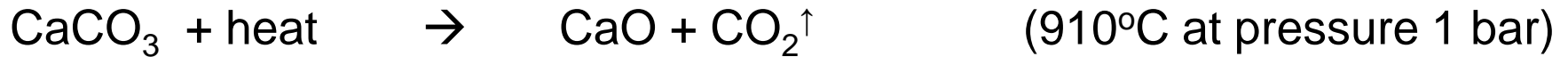
Silicate melting points / eutectics

Phase diagram for the system $\text{Na}_2\text{O} - \text{SiO}_2$ showing eutectic sodium silicate melt phases



Dissociation – decomposition reactions

- **Decomposition** reactions of (Ca- and Mg-) carbonates:



MgO still present up to 1150°C.

Gas release during melting-in

- During these initial (melting) reactions in most batches, much CO₂-gas is released.
- **About 14 - 20 % of the mass of normal soda-lime-silica batches is transferred into volatile CO₂**
- This means that from **1 kg of normal batch about 100 liters of gas** at normal pressure and room temperature (or about 500 liters gas, at the furnace temperature level), will be released in the furnace.
- Besides CO₂-gas, the melting loss consists of water vapor (several mass percents, depending on: batch humidity, water content in cullet and presence of hydrated raw materials) and any possible evaporation products

(SO₂, HBO₂, HCl, NaCl, HCl, KOH, PbO, Pb, NaOH, Se-components).

Summary of the different reactions

1089 °C: T_s Na_2SiO_3

910 °C : $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ (gas)

850 °C : T_s Na_2CO_3

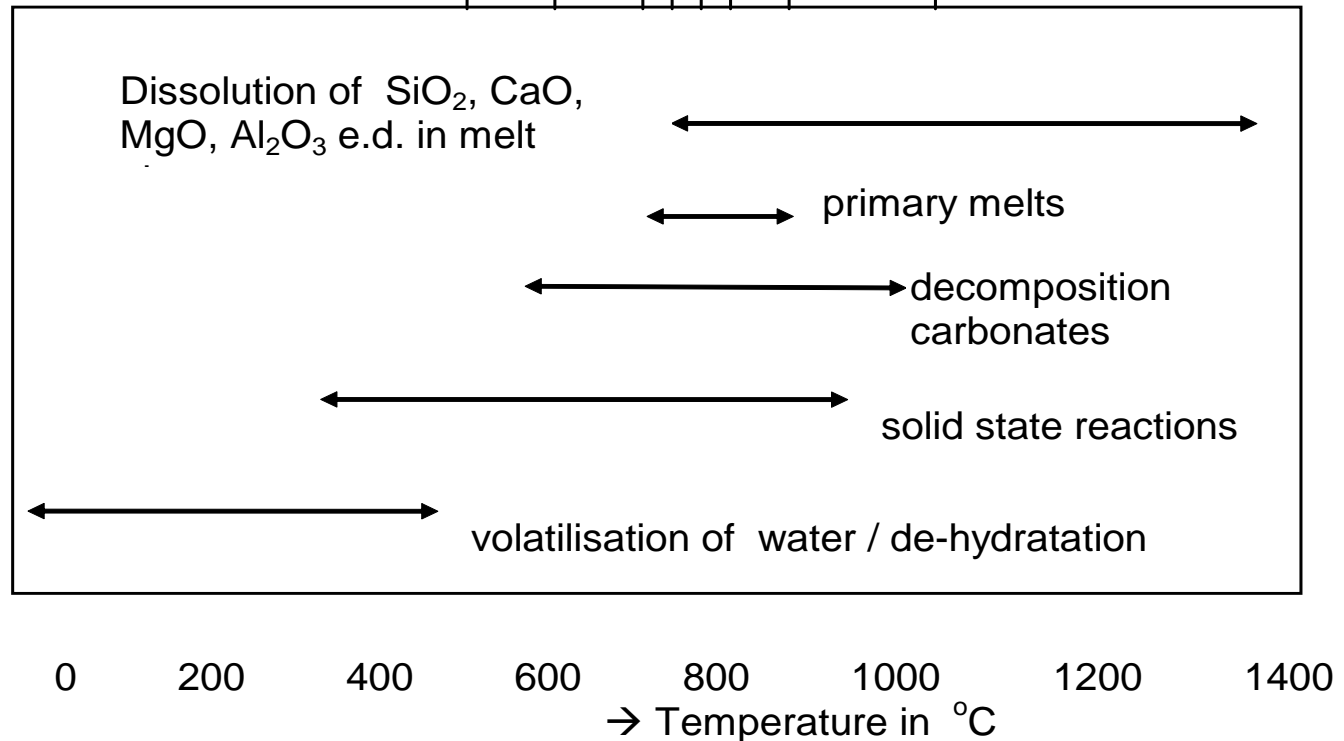
820 °C : T_s $\text{Na}_2\text{Ca}(\text{CO}_3)_2$

793 °C : T_{eut} $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 + \text{SiO}_2$

740 °C : T_{eut} $\text{Na}_2\text{Ca}(\text{CO}_3)_2 + \text{Na}_2\text{CO}_3$

650 °C : $\text{MgCO}_3 \cdot \text{CaCO}_3 \rightarrow \text{MgO} + \text{CaCO}_3 + \text{CO}_2$ (gas)

540 °C : $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$ (gas)



Energy demand (enthalpy)

The quantity of required energy (excluding energy losses) is determined by:

- the heat needed to bring the raw materials up to the reaction temperatures
- the net heat required for the fusion reactions (determined by both endothermic reactions, requiring energy and exothermic reactions that generate thermal energy)
- the heat required for the further heating of the melt phases and the volatile reaction products up to the temperature at the furnace exit (throat, canal, exhaust ports).

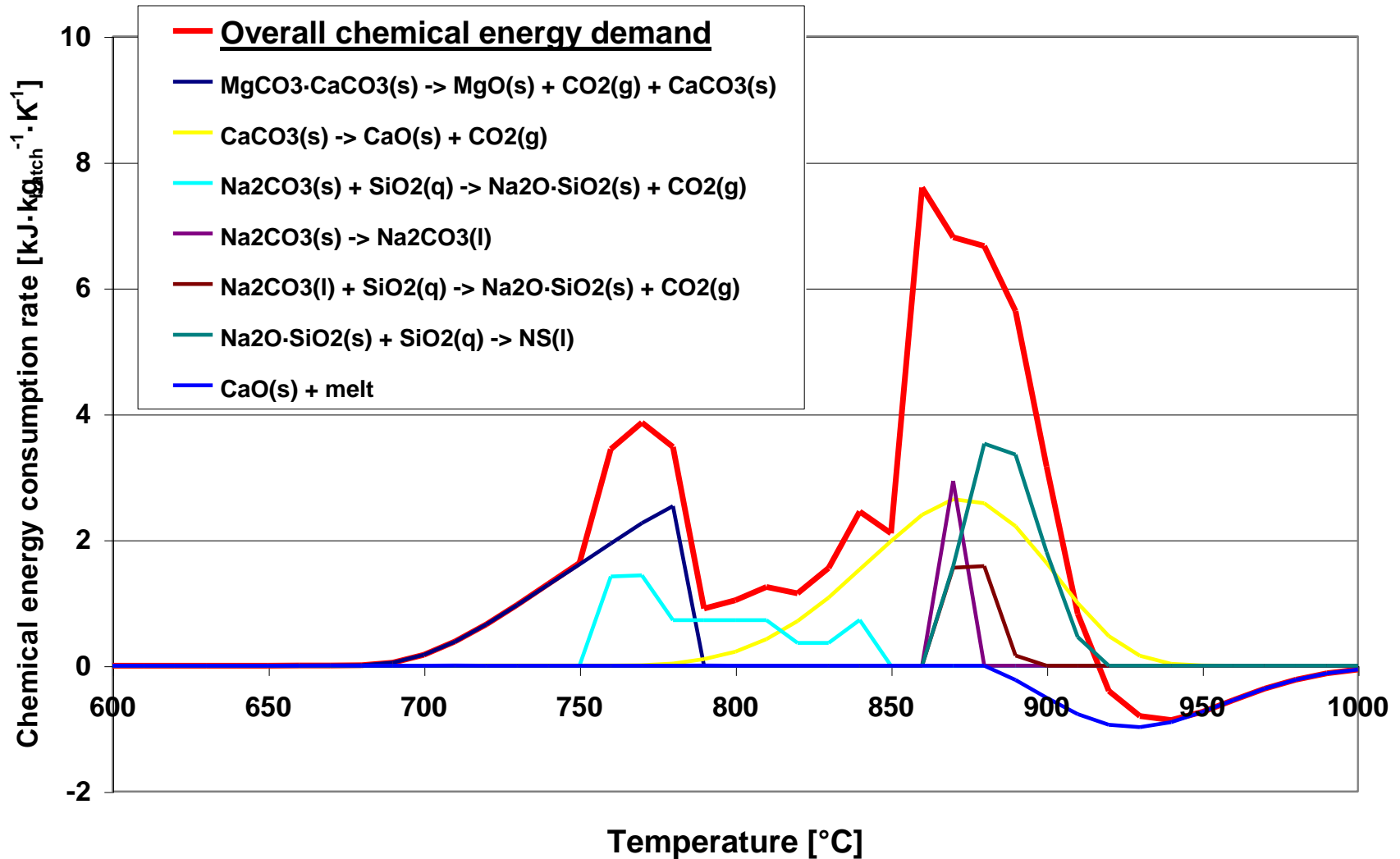
Paths of energy consumption (theoretical)

- Heating of from ambient T of batch till first reactions: H1
- Further heating of batch H2 plus adding net energy during batch reactions H3 for endothermic reactions
- Extra energy supply to heat the released gases to the combustion chamber exit temperature: H4
- Further heating of the melt till maximum temperature: H5
- Decrease of temperature for melt from maximum temperature to outlet temperature (throat, canal), heat delivered: H6

Thus, total energy input for melting in the furnace:

$$H1 + H2 + H3 + H4 + H5 - H6.$$

Chemical energy demand



Typical values for theoretical heat demand of several batch types (without cullet)

	Soda lime glass [kJ/kg]	Lead glass (19 % PbO) [kJ/kg]	Sodium borosilicate glass (8 % B ₂ O ₃) [kJ/kg]	E-glass [kJ/kg]
Tangible heat of melt (0 - 1400 °C)	1775	1603	1609	1588
Reaction heat	487	403	412	roughly 400
Tangible heat volatile reaction products (0 - 1500 °C)	293	166	140	577
TOTAL	2555	2172	2161	2565

Effect of cullet on required energy:

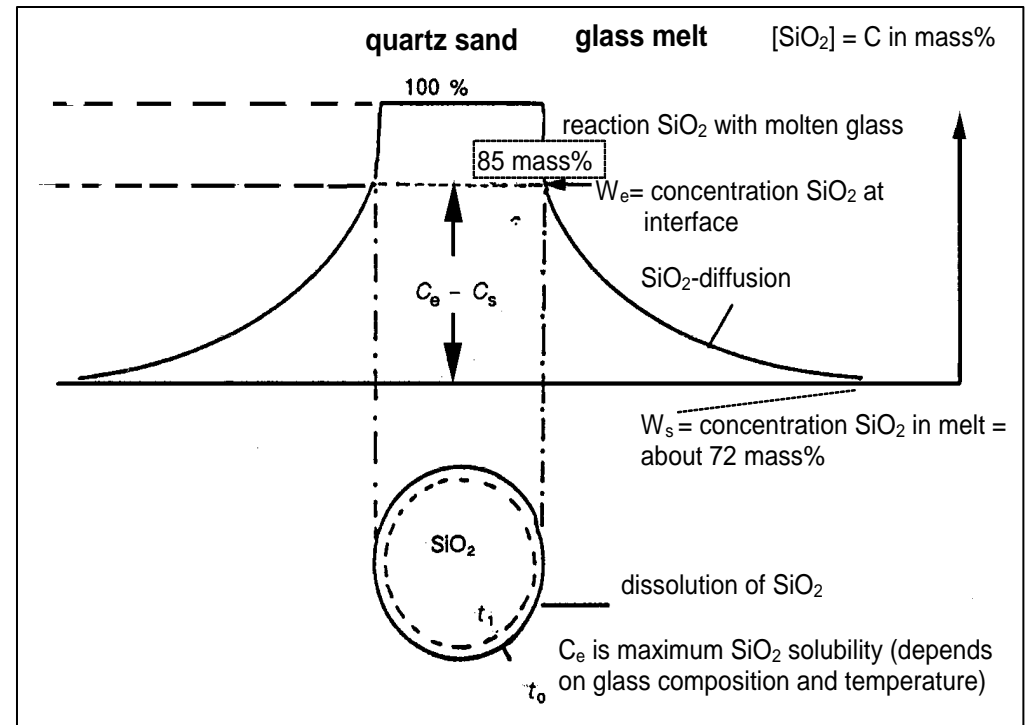
- Less reaction energy and less gaseous reaction products
- Faster batch heating due to better heat transfer

Kinetics of batch melting

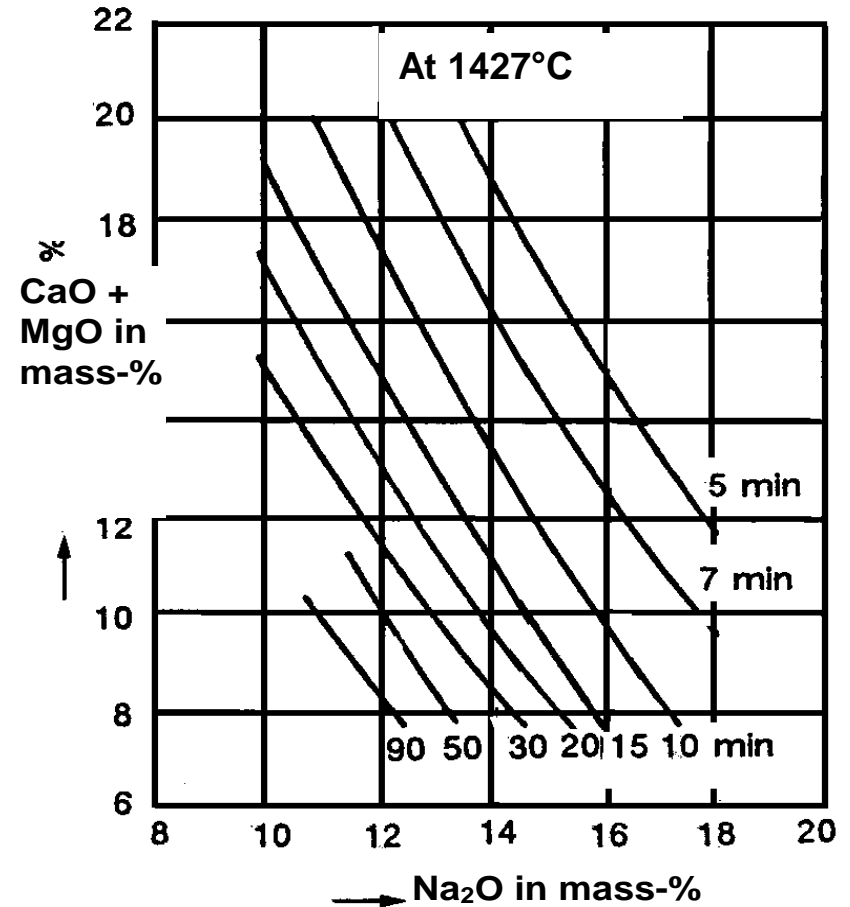
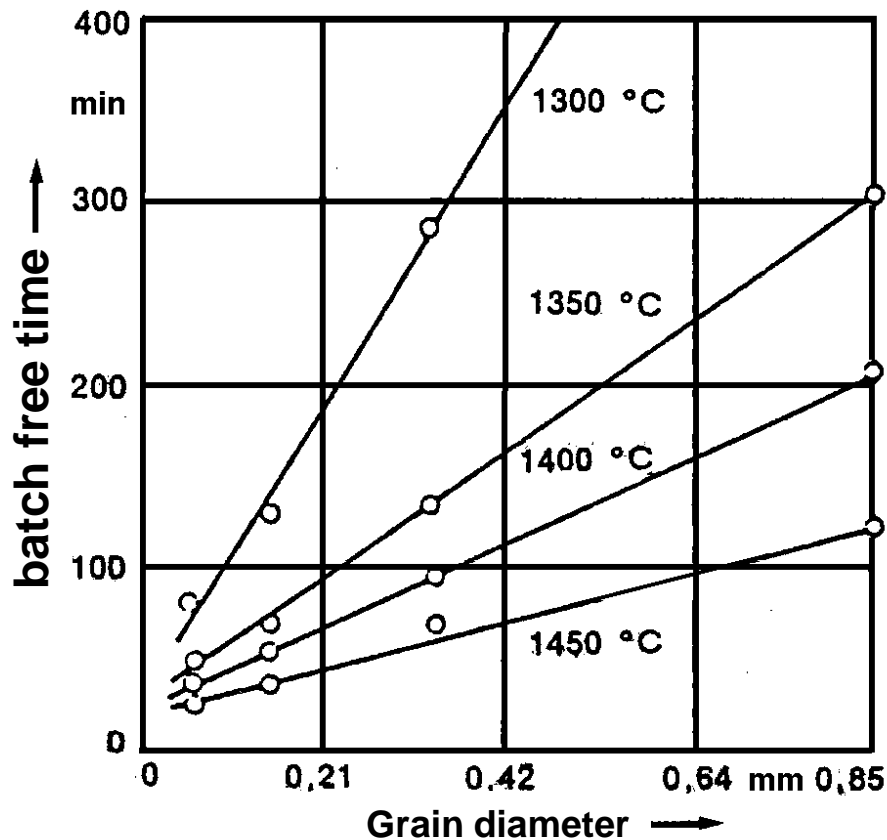
- The rates of batch conversion processes (formation of silicates, decomposition of carbonates) depend on the **reaction kinetics and the diffusion rates** of for instance the dissolving components in the melt
- Both of them are strongly determined by the **temperature**
- So the **heat transfer** into and within the batch blanket (heat conduction and radiation) is very important for the rate of the initial melting, and is the limiting factor for the fusion/melting kinetics
- This means, that as soon as a certain temperature level has been reached, the reactions will become fast, but below this temperature level reaction rates are very low
- The **compactness of the batch and grain sizes** may have an important effect on heating rate and contact area between reacting grains and thus on the overall reaction rates, especially in the regime of solid state reactions

Dissolution rate of sand grains in silicate melt

- The dissolution rates of single silica grains in silicate melts are **diffusion-controlled**
- The SiO_2 at the grain surface dissolved in the surrounding melt has to be transferred into the melt by diffusion.
- The driving force for the diffusion process is the difference of the **equilibrium concentration of SiO_2** in the molten glass (maximum SiO_2 solubility in the glass melt at that temperature) that exists at the interface of the silica



Examples: effect of batch composition and grain size on batch free time for SLS glasses



How to increase the melting kinetics

- **Increase of batch heating rate**
 - ✓ Higher packing density of batch materials
 - ✓ Higher cullet%
 - ✓ Promotion of occurrence of low melting glassy phases
- **Increase of reaction rate and dissolution kinetics of batch**
 - ✓ Dissolution of sand particles
 - ✓ Temperature should not be too high: loss of fining agent
 - ✓ Sand grain size distribution should no be wide
 - ✓ Depends on grain size, temperature, **convection** and glass composition
 - ✓ Dissolution of other slowly dissolving components (alumina, zircon, ..)
 - ✓ Depends on grain size, temperature, convection and glass composition

Fluxing agents

- Formation of **early melt phases** in the batch,

Examples: blast furnace slag, lithium-containing ingredients (spodumene), nitrates and salt cake (Na_2SO_4) in combination with sulfide

- **Decrease of the surface tension** of the melt phases.
- **Increase of the heat conductivity** of the batch.

Example: Cullet, compacted batch/pellets/granules of compacted fine batch materials.

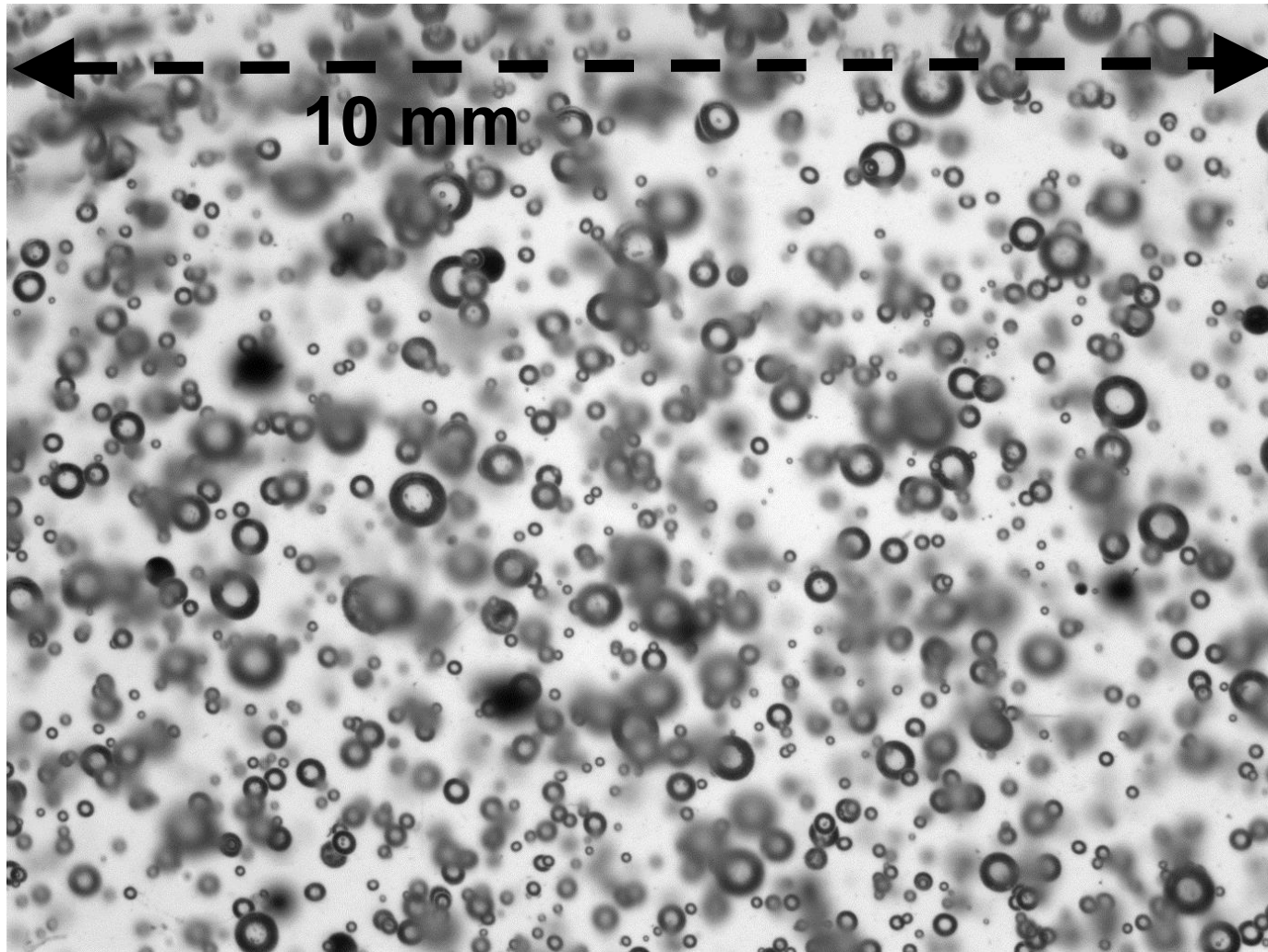
- **Reduction of the reaction (endothermic) enthalpy**

Examples: Addition of quick-lime (CaO) instead of limestone, Cullet

Fining of the glass melts

Gases in glass (dissolved) or in bubbles

- Many chemical conversions are taking place during the heating & the melting-in of the mixture of raw materials.
- **Removal of gas bubbles** is essential in order to obtain a (molten) glass without fine bubbles (seeds) or blisters.
- After melting of the raw materials, the glass melt may contain a large number density of bubbles: Typically in the order of **10^5 per kg**.
- Melts that are almost saturated with dissolved gases are sensitive for formation of new bubbles or growth of very small bubbles when:
 - ✓ changing the chemistry of the melt
 - ✓ changing temperature
 - ✓ agitating the melt mechanically
- The gases (SO_2 and CO_2) released from the melting batch do have a mixing effect within the batch blanket, increasing the dissolution rate of the sand grains



Glass just after batch melting
- sample thickness ± 5 mm

Gases in glass (dissolved) or in bubbles

- Besides formation of the desired silicate melt phases, a large amount of gases is produced:
 - ✓ From carbonates: **CO₂** gas is formed
 - ✓ From carbonates and cokes: **CO** gas
 - ✓ Hydrated ingredients give water vapor
 - ✓ From nitrates: **O₂** gas, **N₂/NO_x** gases;
 - ✓ Sulfates and sulfides can give sulfur gases, such as **SO₂**, **S₂**, **H₂S** or even **COS**.
- **Degassing** the glass melt and **removing all bubbles** including also all very small bubbles (seeds) from the molten glass.
- The very small bubbles (D=0.1-0.4 mm) are called **seeds**, the larger bubbles are called **blisters**. Bubbles with diameters smaller than 0.1 are often called **micro-seeds**.

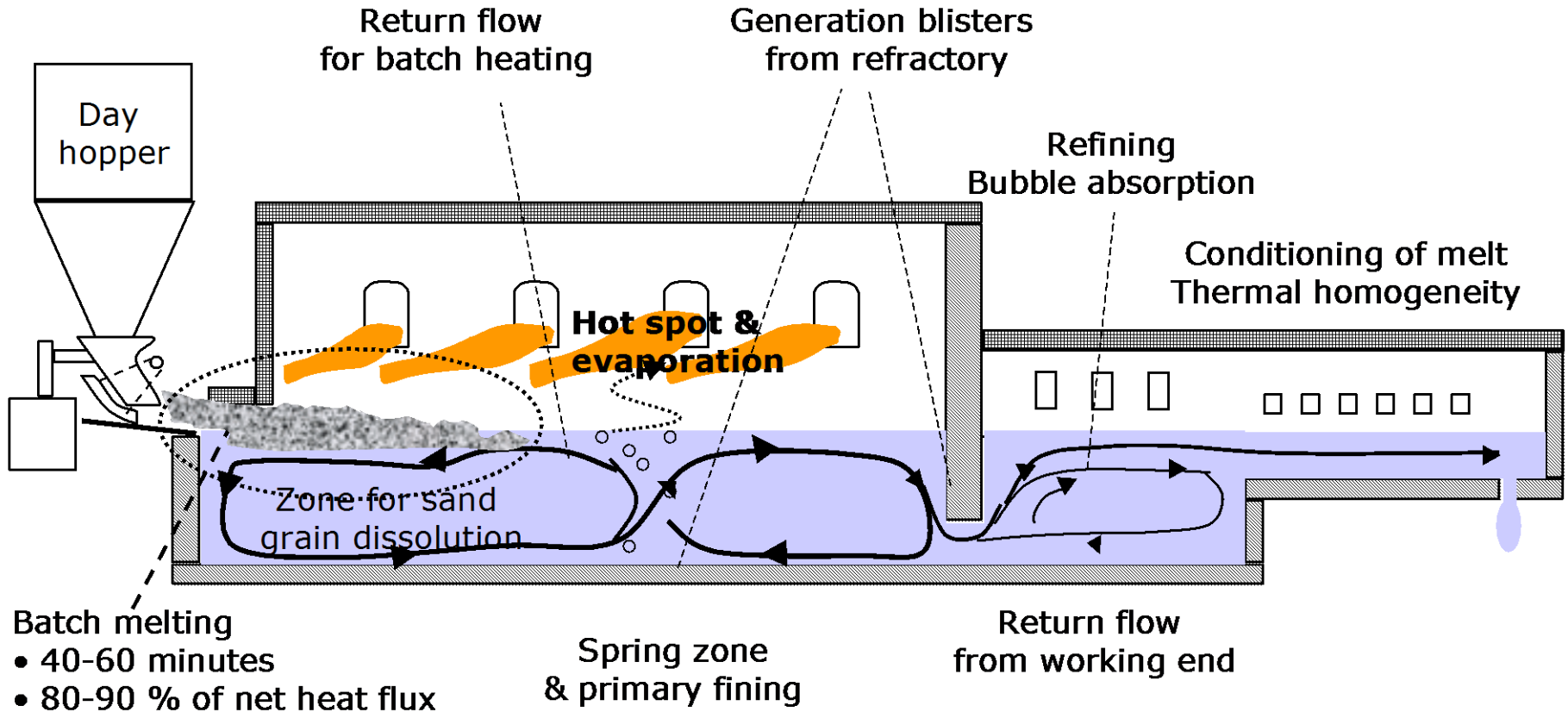
Other gases

- **Air** (volume concentration Ar:N₂ = 0.9 : 80)
 - ✓ Inclusions of air (pores) in batch blanket
 - ✓ From open cracks in refractory walls
 - ✓ Oxygen from, air is generally dissolved in glass melt
- **Furnace atmosphere gases** (N₂, Ar, H₂O, CO₂)
 - ✓ Oxygen from furnace atmosphere generally dissolves completely in glass
- **Volatile glass & batch components or decomposition gases:**
 - ✓ NO_x, CO₂, H₂O, SeO₂, ...
- **Refractory gases** (CO, N₂, CO₂, oxygen bubbles)
 - ✓ Refractory-glass melt interaction
 - ✓ Blistering of refractory
- **Contamination** of melt by corrosion products of electrodes, carbon (soot) deposits etc.

Fining agents

- To promote the removal of bubbles from the glass melt, **fining agents** are added
- The function of a fining agent is the production of **fining gases** at the temperatures, being achieved by all glass melt trajectories in the tank at lowest level of its viscosity.
- The process of high temperature decomposition of a fining agent in a low viscous melt will result in **simultaneous bubble growth, gas stripping plus high ascension rates**.
- NB: Excessive fining may lead to formation of foam (may lead to defects in the glass, may be detrimental for heat transfers in the glass furnace => Lecture 4)

Schematic of an industrial glass melting tank



** This is a schematic representation, but many different furnace designs exist (more on that in Lecture 3)*

Occurrence of gases in glass melts

- **Physically dissolved:**

- ✓ Interstitial in open space of silicate network
- ✓ No chemical bonding with silicate component
- ✓ N_2 , Ar, He are mainly physically dissolved in oxidized glass melt

- **Chemically dissolved:**

- ✓ Absorbed by melt by chemical reaction
- ✓ Orders of magnitude higher than physical solubility
- ✓ CO_3^{2-} (CO_2), OH^- (H_2O), Sb_2O_5 (O_2), N^{3-} (N_2), SO_2 & O_2 (SO_4^{2-})

- **In gas bubbles:**

- ✓ When concentration of gases > maximum solubility in melt
- ✓ Sizes of bubbles: 10 μ m – few mm

Two fining steps

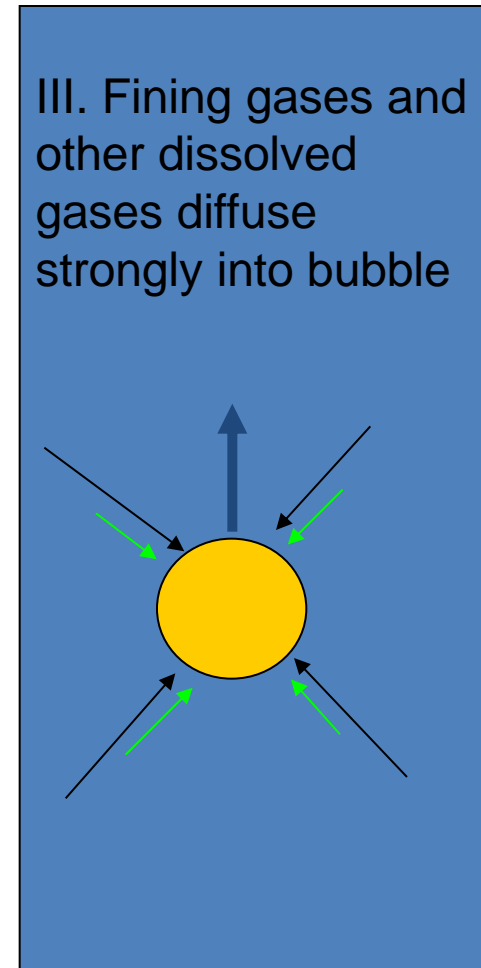
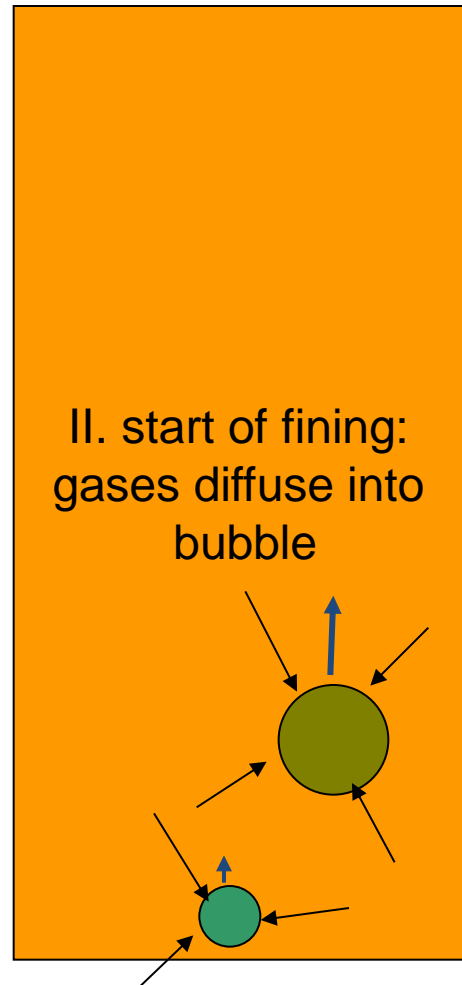
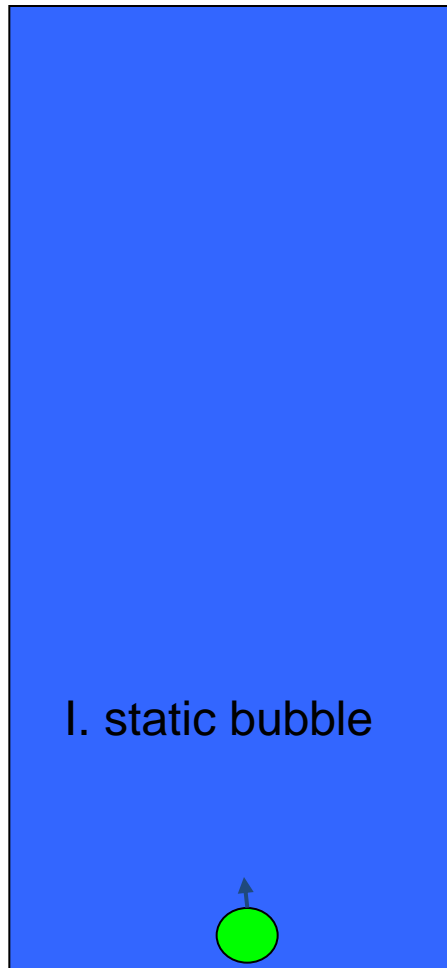
- **First step: primary fining**

- ✓ High temperatures
- ✓ Bubble agglomeration and bubble size growth
- ✓ Dissolved gases diffuse from melt in to bubbles (like bubbles in soda drinks)
- ✓ Ascension of growing bubbles to glass melt surface

- **Second step: Secondary fining/Refining**

- ✓ Dissolution of (small) remaining bubbles
- ✓ Only effective if bubble contains gases (CO_2 , O_2 , SO_2+O_2) that dissolve in cooling melts
- ✓ Glass melt should be lean in dissolved gases

Primary fining



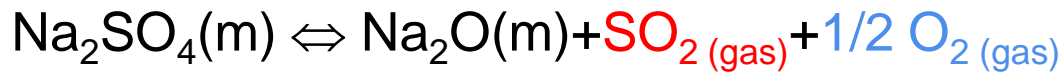
Reaction in melt: release of fining gases

$$P_{\text{gases melt}} > p_t \text{ (} p_t \text{ is pressure in bubble)}$$

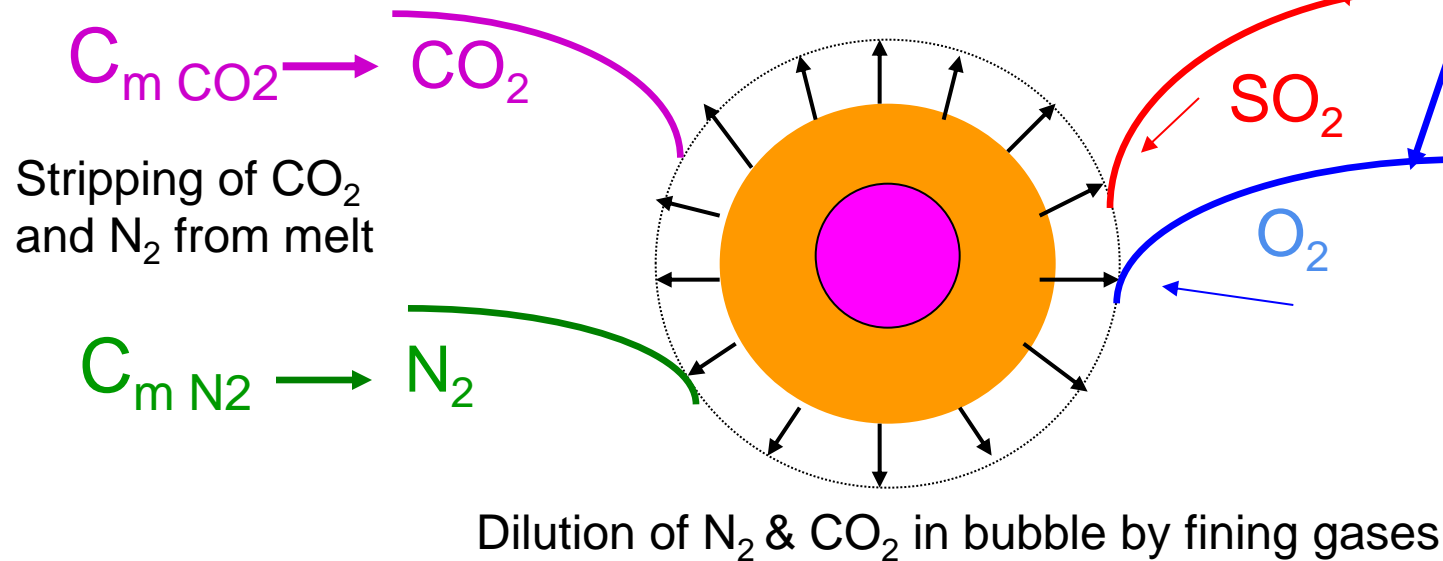
Primary fining – Example sulfate fining

Often used fining agent: Sodium sulfate Na_2SO_4 (salt cake)

Fining reaction: $T > T_{\text{Fining onset}}$



$$K' = \frac{p\text{SO}_2 \cdot \sqrt{p\text{O}_2}}{[\text{SO}_3]}$$



Acceleration of bubble ascension

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

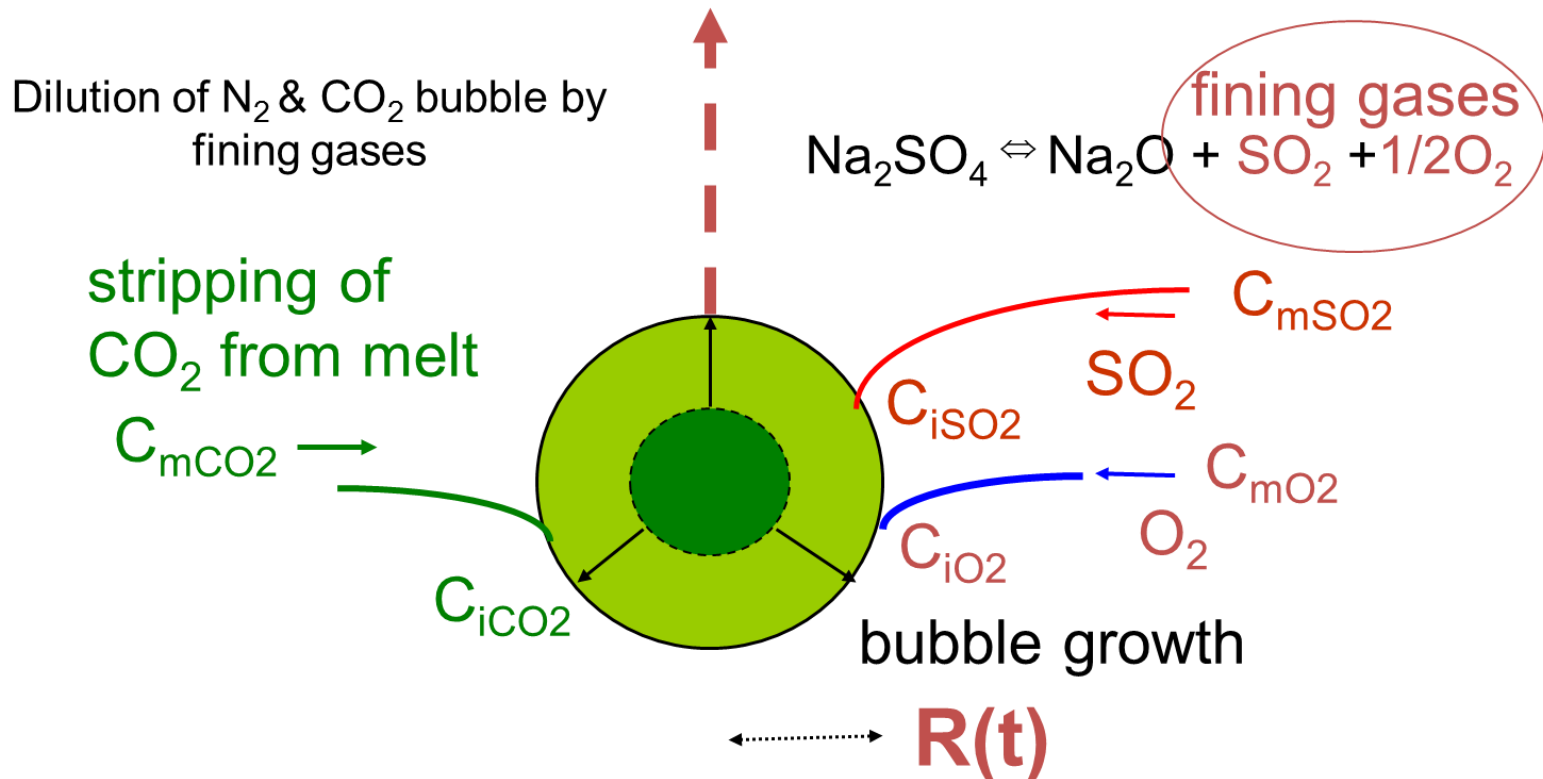
ρ : density of the glass melt [Kg/m³]

η : viscosity of the glass melt [Pa.s]

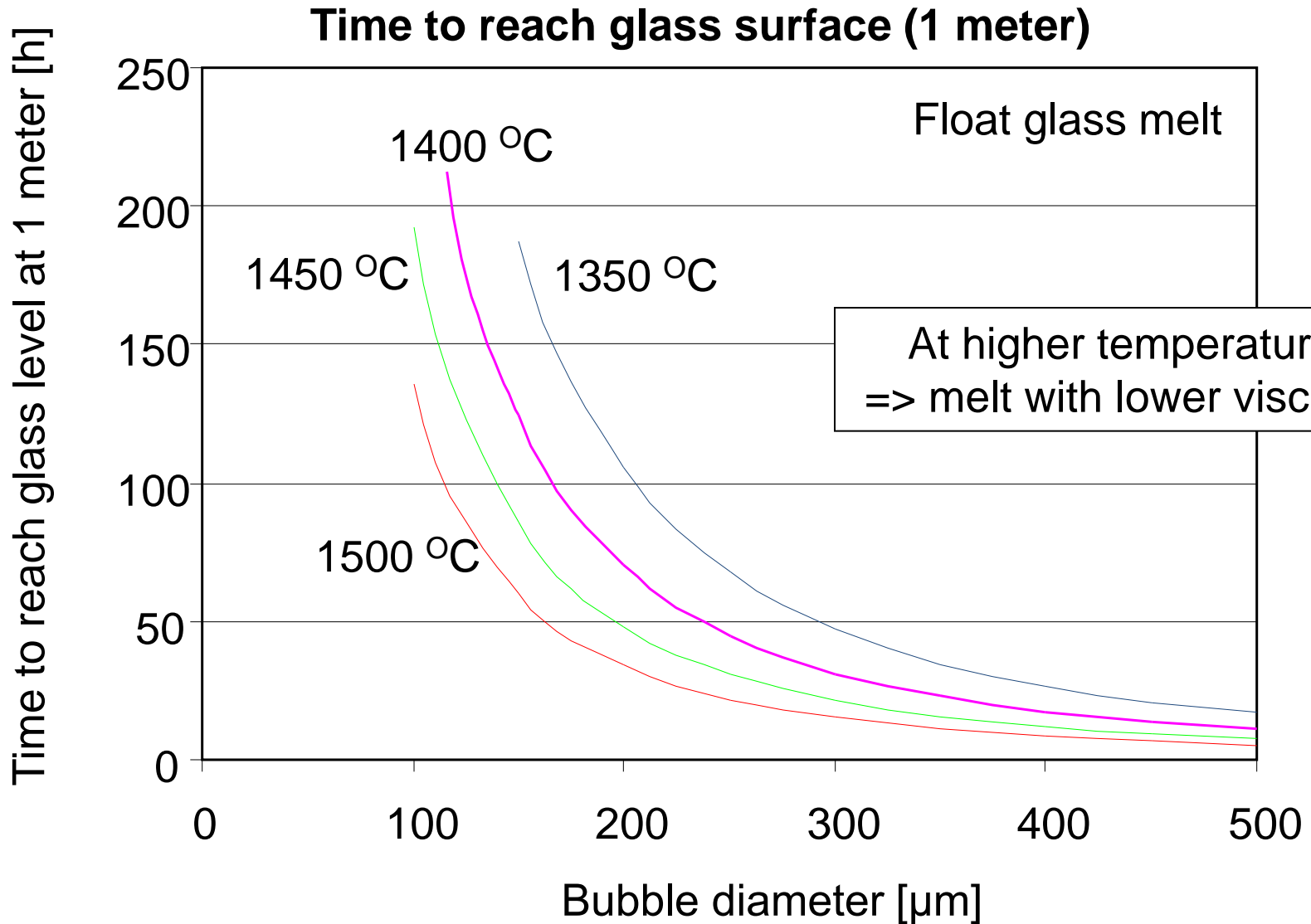
R : bubble radius [m]

g : gravity [9.81 m/s²]

c : factor (e.g. Stokes $c = 2/9$)



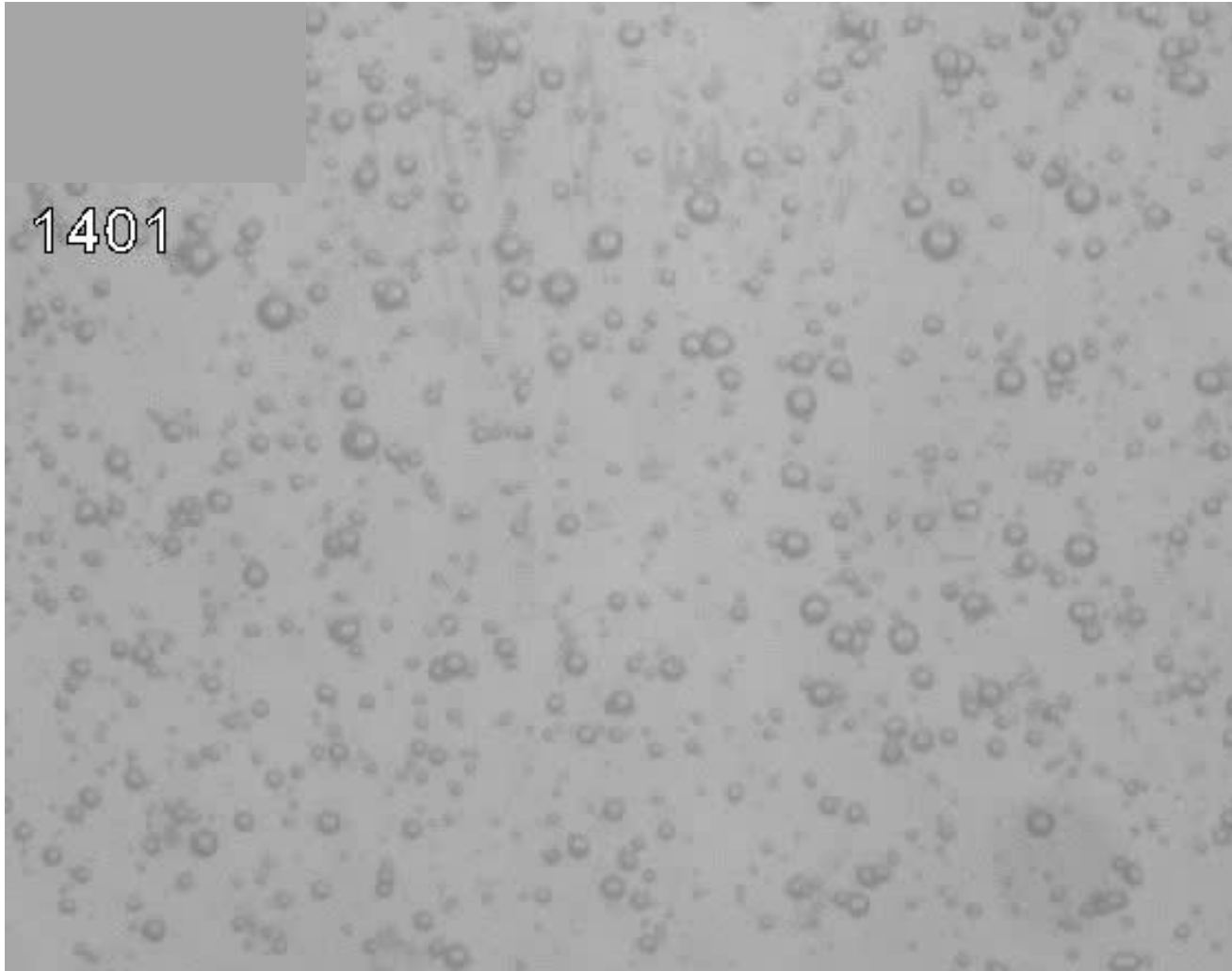
Primary fining



Primary fining – video example

Temperature:
(°C)

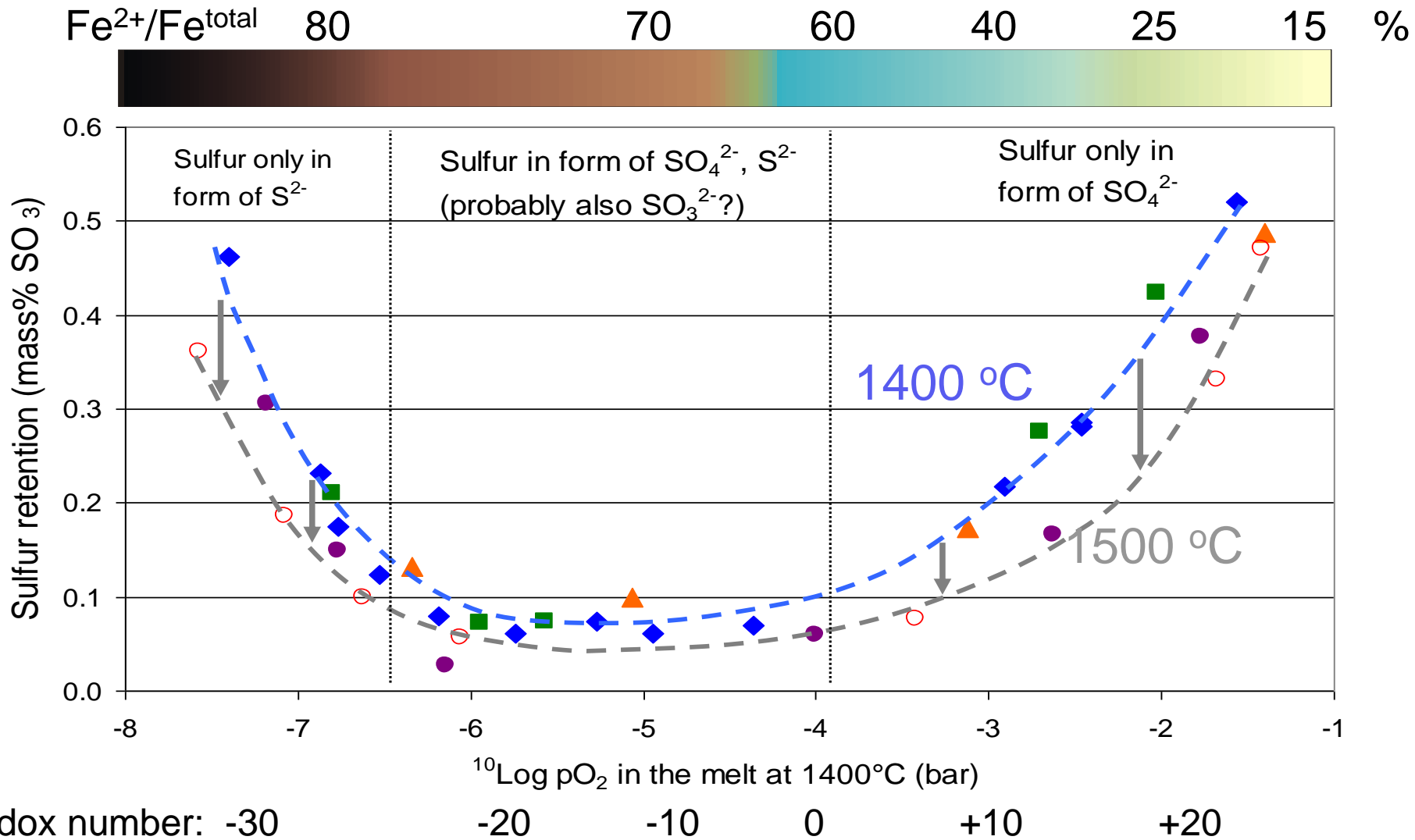
1401



Secondary fining – during controlled cooling

- The **secondary fining (or refining)** corresponds to the dissolution of the remaining bubbles in the melt
- It takes place in a rather narrow temperature window
- The **solubility of the gases** in the melt **increases with decreasing temperature**
- Because a temperature decrease will reverse the fining reactions (meaning that the fining gases will be chemically absorbed again), the fining gases (e.g. O_2 , SO_2) can re-dissolve into the melt during **controlled cooling down** of the melt (refining) if the melt is sufficiently lean of dissolved gases after the primary fining process.
- The gases of the bubbles will dissolve into the glass melt. The bubble shrinks and disappears (it “dissolves”). This mechanism is especially important for the remaining smaller bubbles ($< 100 \mu\text{m}$), which are hardly able to rise.

Sulfur solubility in SLS glass melt



Redox number: -30

-20

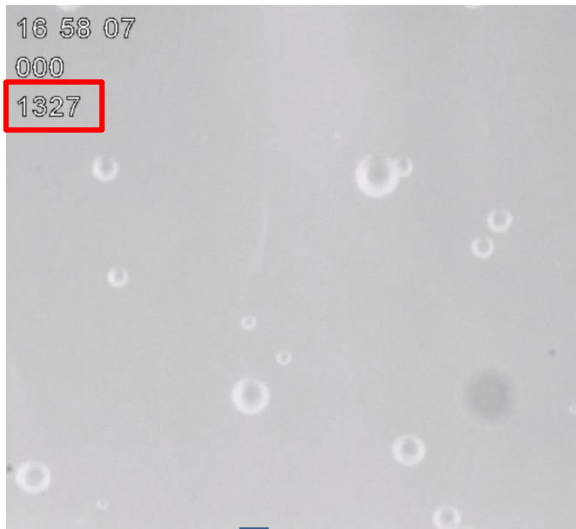
-10

0

+10

+20

Secondary fining – video example



- Controlled cooling of the melt
- Bubbles are re-dissolved into the melt
- The bubble shrinks and disappears

Ex: for float glass: secondary fining occurs at about 1350-1275°C



Fining agents

- Depending on the type of glass produced, the temperatures involved and/or potential limitations on the composition of the glass, different fining agents may be employed
- The most commonly used fining agents include:
 - ✓ Sodium sulfate (with/without cokes)
 - ✓ Arsenic oxide
 - ✓ Antimony oxide
 - ✓ Tin oxide
 - ✓ Sodium chloride

Sodium sulfate – Na_2SO_4

- **90 mass-% of world's glass production** uses sulfate raw materials in the batch
- **Sodium sulfate** is used especially for fining of:
 - ✓ container glass
 - ✓ float glass
 - ✓ E-glass for continuous filament fibres (textile, reinforcement)
 - ✓ some technical glasses
 - ✓ soda-lime-silica tableware glasses
 - ✓ soda-lime-silica glass tubes
 - ✓ C-glass for insulation glass wool (here fining is not essential)
- The fining onset temperature for sodium sulfate will depend on the **redox state** of the glass melt
- NB: Na_2SO_4 also helps improving **melting kinetics** (in the primary melting phases it will reduce the surface tension of these phases)

Sodium sulfate in oxidized melts

- In oxidized melts, **thermal sulfate decomposition** is often the main sulfate fining mechanism:



This reaction takes place at temperatures of 1430-1480°C
(fining onset temperature)

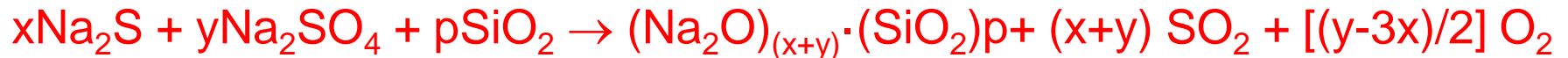
- Sodium sulfate can also **react with the sand particles**:



This reaction is generally not observed below 1100°C

Sodium sulfate in reduced melts

- Some sulfate reacts with reducing agents in batch (cokes or organic contamination, i.e. carbon). Examples of reactions:
 - ✓ $2 \text{ C} + \text{Na}_2\text{SO}_4 \rightarrow 2 \text{ CO} + \underline{\text{Na}_2\text{S}}$
 - ✓ $4 \text{ CO} + \text{Na}_2\text{SO}_4 \rightarrow 4 \text{ CO}_2 + \underline{\text{Na}_2\text{S}}$
 - ✓ $4 \text{ C} + \text{Na}_2\text{SO}_4 \rightarrow 4 \text{ CO} + \underline{\text{Na}_2\text{S}}$
- formation of sulfides S^{2-}
around 700-800°C
- Then, **sulfate-sulfide reactions** occur in the temperature interval 1140-1350°C (one example below, but other reactions are also possible)



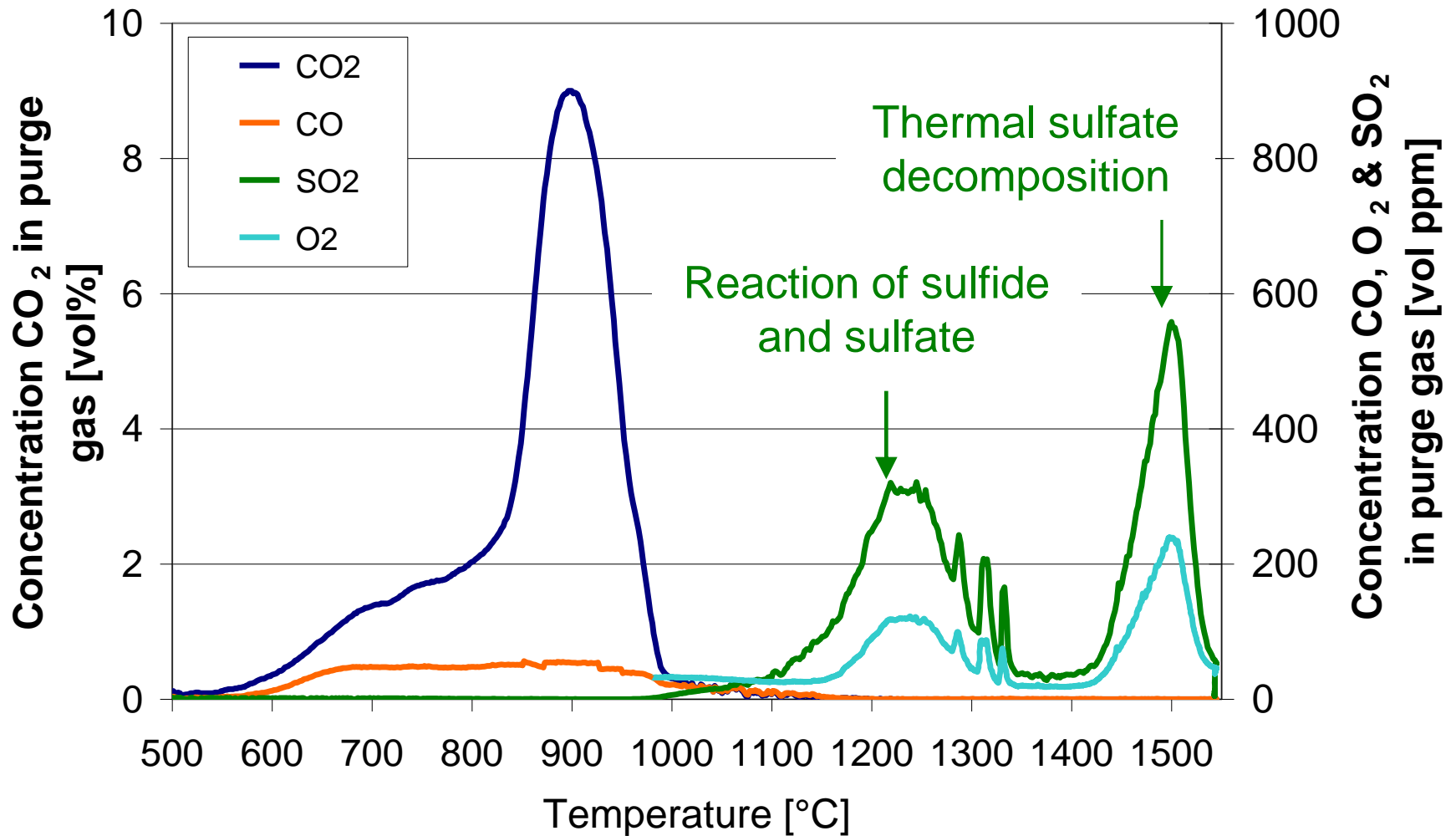
Sodium sulfate in reduced melts

- Sulfates can also react directly with the reducing agent
 - ✓ $C + 2Na_2SO_4 + mSiO_2 \rightarrow CO_2 + \underline{2 SO_2} + (Na_2O)_2 \cdot (SiO_2)_m$
 - ✓ $CO + Na_2SO_4 + nSiO_2 \rightarrow CO_2 + \underline{SO_2} + (Na_2O) \cdot (SiO_2)_n$

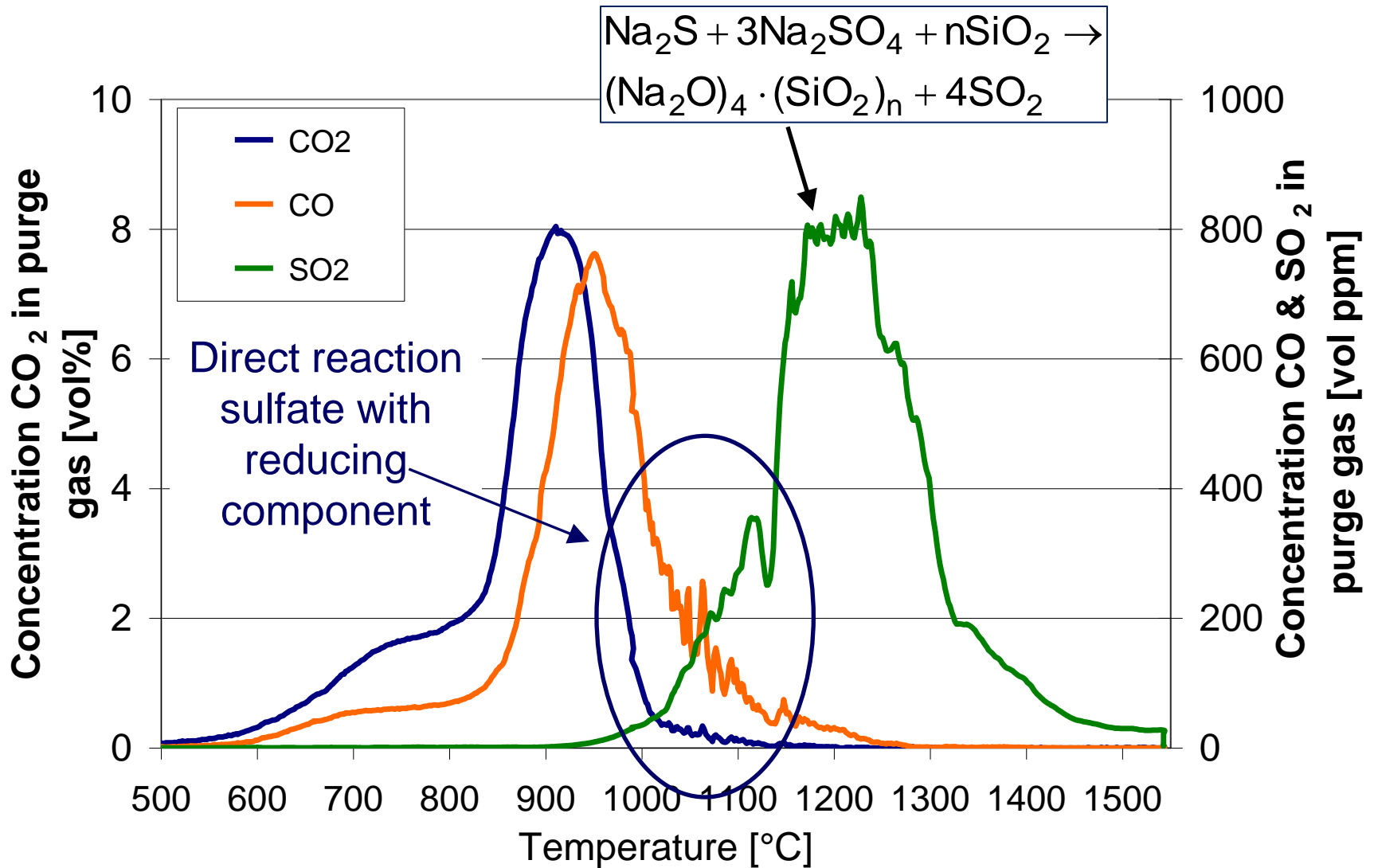
These reactions occur in the temperature interval 900-1100°C

- For sulfate fining, the **control of the redox** is of utmost important.
- The **optimal fining range depends on the glass produced** and can be optimized (to a certain extent) by controlling the redox (addition of oxidizing or reducing agents)
- Organic contaminations may lead to fluctuations on the fining range, and thus to defects (bubbles, seeds) in the final product

Gas evolution for an oxidized batch with sulfates

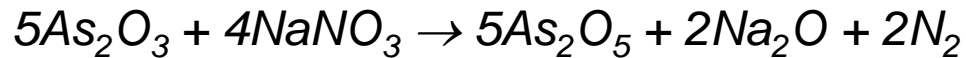


Gas evolution for an reduced batch with sulfates



Arsenic oxide – As_2O_3

- Arsenic oxide is an important fining agent up to a temperature of 1400 - 1500°C for glasses being melted under **strongly oxidizing conditions**
- **Arsenic trioxide (As_2O_3)** is added in **combination with oxidants**, e.g. nitrates ($NaNO_3$) to convert trivalent arsenic into pentavalent arsenic which will be dissolved into the melt as As_2O_5



- Arsenates (arsenic in 5+ valence state) can also be used
- During fining, in the molten glass, at temperatures exceeding 1250°C, oxygen gas starts to be formed, creating arsenic (III) oxide:



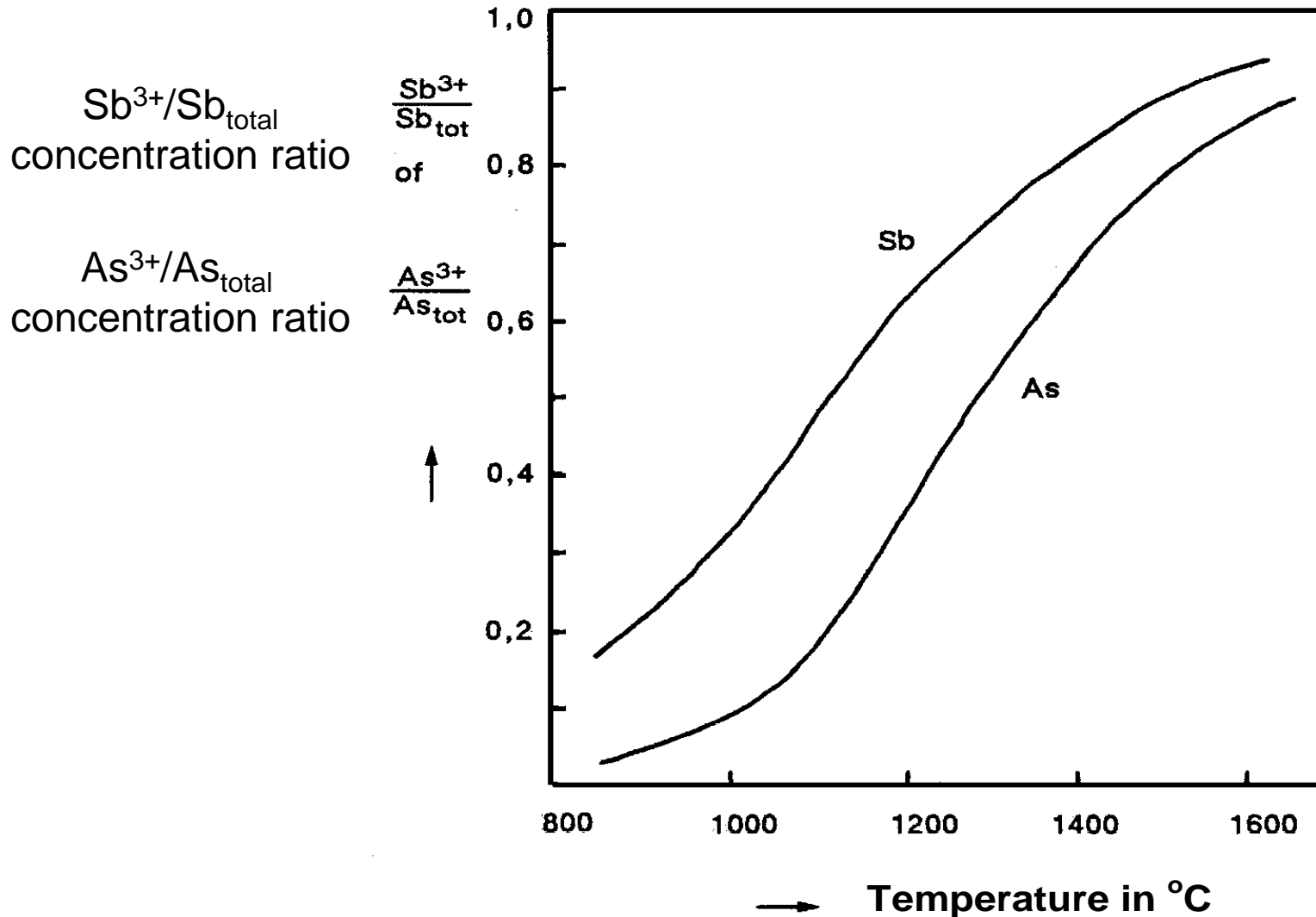
Antimony oxide – Sb_2O_3

- Similar to arsenic oxide, this component is also applied **together with an oxidant**.
- The fining mechanism is similar to the action of arsenic oxide:



Thus, also here, similar as for arsenic fining, oxygen is the fining gas.

Reduction of antimony and arsenic oxide as a function of the temperature in a glass melt in equilibrium with air



Tin oxide – SnO₂

- For **alkali free glasses**, such as LCD display glass products, with **high melting temperatures**, other fining agents are required than arsenic oxides or antimony oxides.

- The fining gas formation reaction (oxygen gas) is:



- Nitrates are generally applied to keep the tin valence in the 4+ state during melting

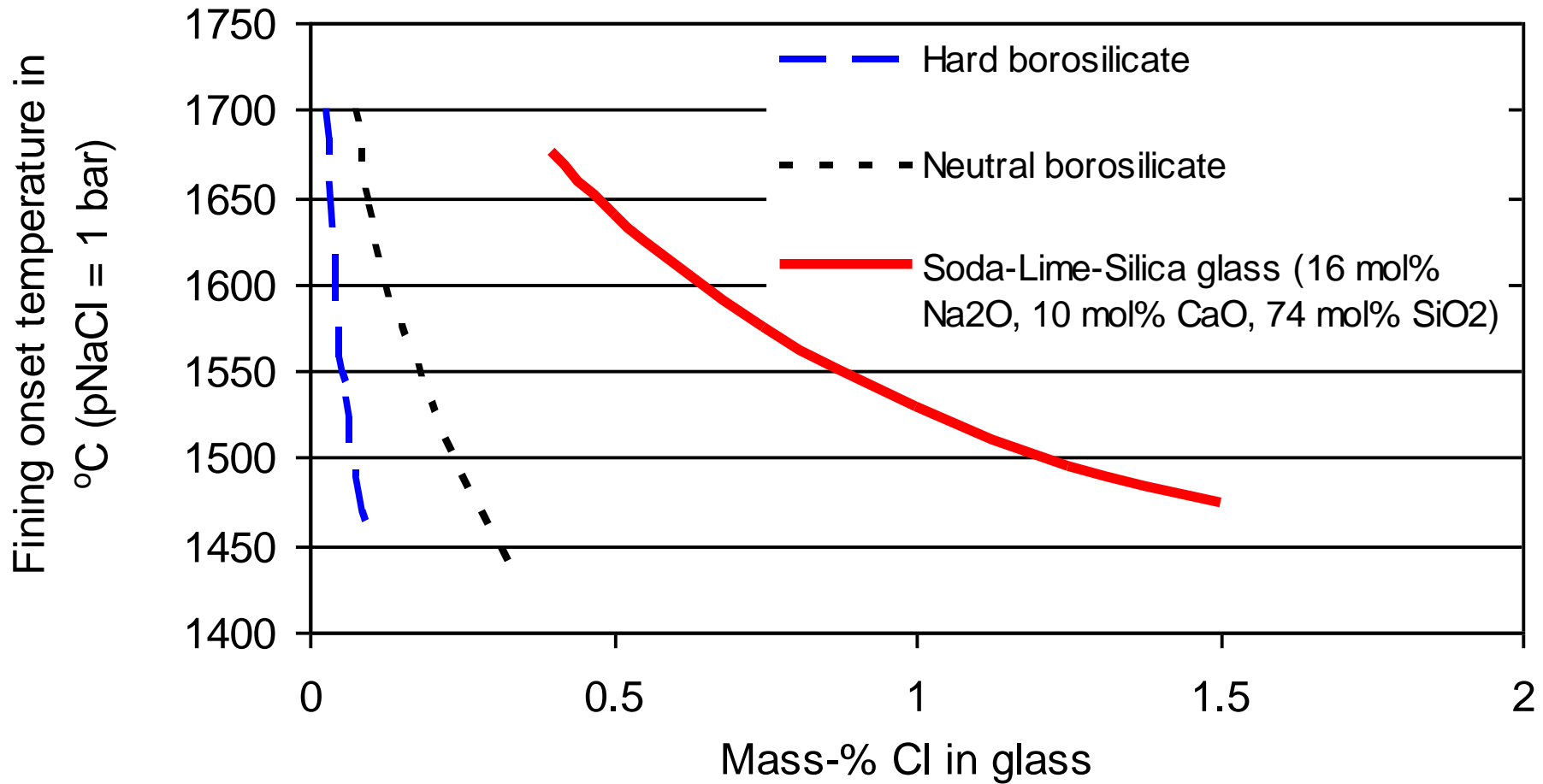
Oxygen release is observed between 1500-1630°C

Halogenides (*Sodium Chloride NaCl*)

- For glass types, which can only be **melted at relatively high temperatures** (like some borosilicate glasses), the application of sodium sulfate is less effective, because fining gases are released at temperatures where the viscosity of the glass melt still is too high
- In such situations often **NaCl** is used as a fining agent. Addition of halogenide salts (NaCl, NaBr, NaI, KCl, KBr, KI) to a raw material batch will lead to limited solubility of these salts in the molten glass obtained
- The fining temperature will depend on the type of glass and the amount of fining agent added
- **Important:** in NaCl-fined glasses, the emissions of environmentally hazardous chlorides from the melter in the form of HCl-gas may cause problems (increased particulates emissions, corrosion of refractories and/or mold materials)

Sodium Chloride - NaCl

Fining temperature (calculated, Koepsel, 2000) as function of chloride concentration in the glass (fining onset: $p_{\text{NaCl}} = 1$ bar)



Bubbles in glass and origin of the bubbles

- In case of high levels of reject caused by large bubbles or unacceptable large numbers of bubbles/seeds in the glass, it is important to find to origin/cause of these bubbles.
- Important information is:
 - ✓ size of bubbles,
 - ✓ distribution / location of bubbles in the product,
 - ✓ internal bubble pressure and **gas composition**.
 - ✓ base level and type of bubbles during normal production
 - ✓ sometimes bubbles contain deposits (often very small droplets of condensation products) that can be observed by using light microscopy.
- Based on these information (collected on a sufficiently high number of bubbles analyzed), the origin of the problem can be identified (requires experienced analysts) and corrected

Conclusions - 1/2

- During industrial glass melting, a multitude of reactions occur to go from the introduced **batch to the molten glass** (dehydration, solid-state reactions, formation of primary molten phases, decompositions, dissolution of sand grains...)
- Glass melting is an **energy intensive process**, and effort is put to reduce the amount of energy required
- The **kinetics of glass melting** are often determined by the **sand dissolution**, which requires a long time
- Optimization of grain size, primary molten phase formation, increased heat transfer, good convection of the glass melt can help increase the sand dissolution rate

Conclusions - 2/2

- The reactions involved in glass melting lead to the formation of a **very high amount of bubbles in the melt**, which have to be removed by the fining process
- The fining process can be divided into **primary fining** (growth and ascension of bubbles) and **secondary fining (refining)** (dissolution of the remaining seeds).
- The fining efficiency will notably depend on the type of **fining agent** used and the viscosity of the glass melt at fining temperature
- The **choice of fining agent** will depend on the desired fining range (and thus on the type of glass produced)
- **Redox** plays a major role in the efficiency of the fining process, and should be carefully controlled

References and further reading

- Book “Introduction to Glass Science and Technology”, J. Shelby (RSC publishing, 2nd edition 2005)
- Book “Fundamentals of Inorganic Glasses”, A. Varshneya (Elsevier, 1993)
- Glass Technology journals (e.g. European Journal of Glass Science and Technology)
- NCNG’s Glass Technology course and handbook 2013
- Proceedings of GlassTrend meetings and seminars (www.glasstrend.nl)
- Proceedings of “Glass Problem Conferences” (Wiley, every year)
- Youtube video: [Production of Glass Bottles - How it's made](#)

Home assignment

- A multiple choice questionnaire (MCQ) including questions on industrial glass melting and fining processes is provided with this lecture
- The MCQ will be available online on IMI's website

Thank you for your attention



Questions ?

Visit us in Eindhoven

Contact me via email:

mathieu.hubert@celsian.nl