Sustainability in Glass Manufacturing:

Contribution from Silica and Silicates

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Dessel, Belgium

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Contents

1. Sibelco ?

Minerals

SIBELCO’S PRODUCT RANGE IS DERIVED FROM FIVE CORE MINERAL CATEGORIES

SILICA

Silica (SiO_2) is the term used to describe a group of minerals composed of oxygen and silicon. Whilst it is the world’s second most abundant mineral, products containing at least 98% SiO_2 are needed for industrial use.

CLAYS

Ball clays (also referred to as plastic clays) are fine-grained, highly plastic sedimentary clays, valued by customers across the ceramics industry for their plasticity, rheology, unfired strength and light-firing colour. Kaolin is an aluminosilicate mineral derived from the decomposition of feldspar from igneous rock.

FELDSPATHICS

Feldspathic minerals make up over half of the earth’s crust, valued across a range of industrial applications for their high alumina and alkali content.

OLIVINE

Sibelco olivine is a high-purity magnesium–iron silicate mineral with the chemical formula $(Mg, Fe)_2 SiO_4$. Its two main components are iron-rich fayalite and magnesium-rich forsterite, the levels of which determine an olivine’s properties and commercial value.

RECYCLED GLASS

Recycled glass (cullet) enables container glass manufacturers to reduce energy costs, CO_2 emissions and virgin material consumption, as well as diverting waste glass from landfill.

Sibelco Overview

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Non-financial key figures

EMPLOYEES
5,017

TECHNICAL CENTRES
6

CLUSTERS
43

COUNTRIES
32

Financial Key figures 2022

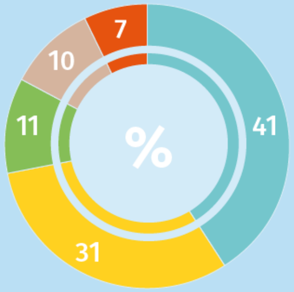
REVENUE
€2,009 million

FOCF
€161 million

EBITDA
€339 million

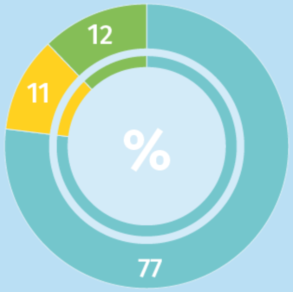
ROCE
7.4%

Revenue by sector



- Construction
- Glass & Electronics
- Industry & Consumer
- Metallurgy
- Recycling

Revenue by origin

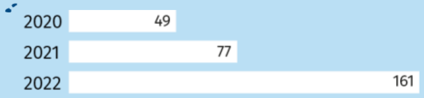


- Europe
- Americas
- Asia Pacific

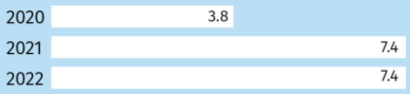
Revenue in € million

EBITDA in € million

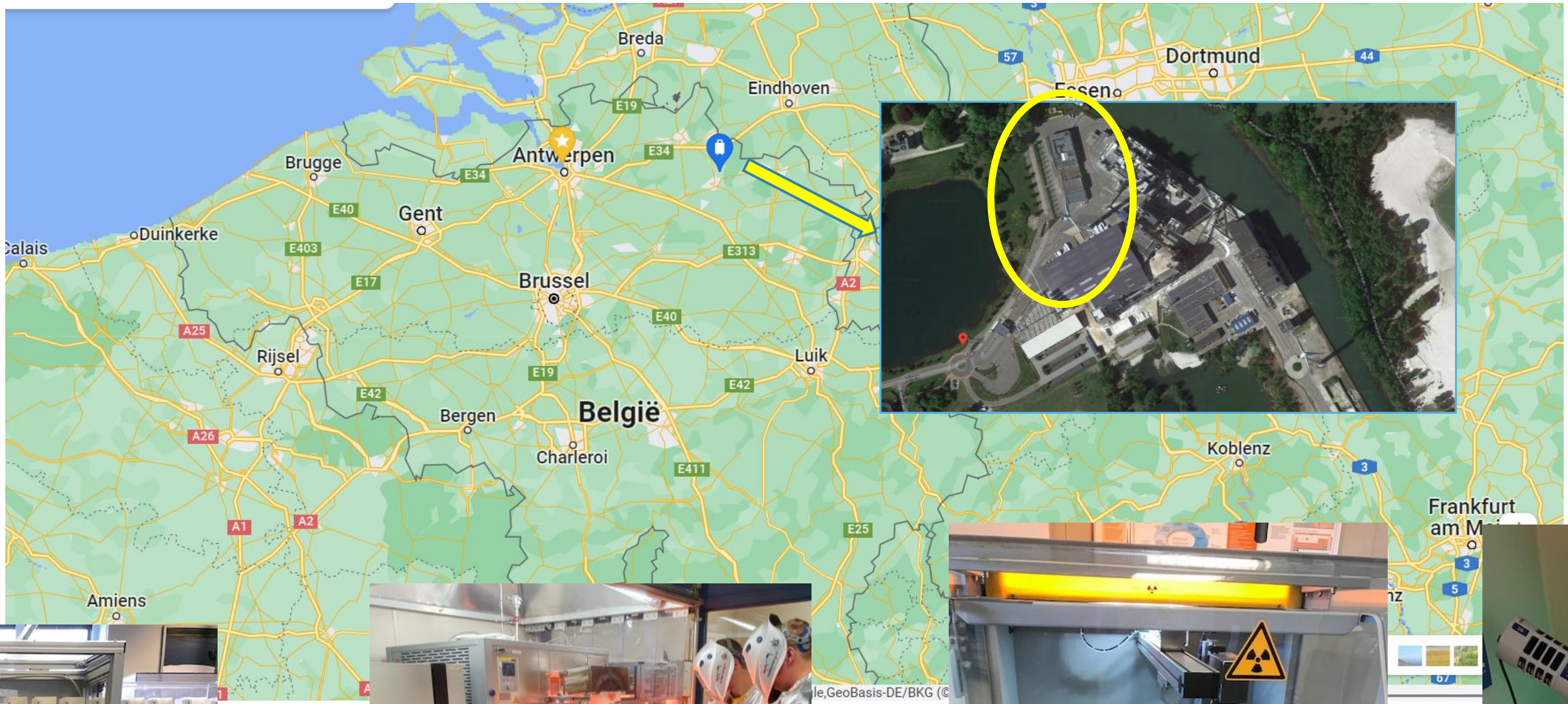
FOCF in € million

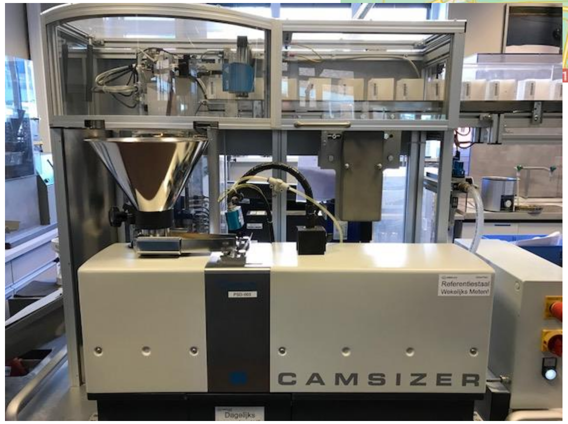


ROCE in %



Glass Research – Dessel (Belgium)





Protecting the Planet

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Focus area	Target by 2030		Progress 2022
Circularity	Increase the percentage of company revenue in circular business	at least 20%	**7.8%** of our revenue came from circular business in **2022**, compared to **7.2%** in **2021** (baseline year)
Climate change & carbon emissions	Reduce CO_2 intensity of scope 1&2 emissions with 5% p.a. (kg CO_2/€ exw revenue), equivalent to 22,5% absolute emission reduction from 2021 to 2030		**CO_2 intensity** reduced from 0,39 to 0,30 kg CO_2/€ exw revenue from 2021 R* to 2022, representing a **reduction** of **23%** Absolute **CO_2 emissions** reduced from 538 kton CO_2 to 479 kton CO_2 from 2021 R* to 2022, representing a **reduction of 11%**
	Customer and supplier engagement target covering 69% of total scope 3 emission by 2026		**19% of customers and suppliers** by emissions committed to science based Targets in 2022 **compared to 8%** in 2021 R*
	Reduce energy consumption year over year		Energy consumption was 2,225,138 MWh in 2021 R* and 2,085,534 MWh in 2022
Closure planning & biodiversity	Decrease % disturbed land on the total land managed. Targets will be determined and announced	**100%** sites have an Approved biodiversity management plan by 2030	Calculate an accurate 2022 baseline while preparing standards and developing a measurement methodology to establish a baseline

* R: Recalculated according to GHG Protocol

2. CO_2 - Challenges in glass making

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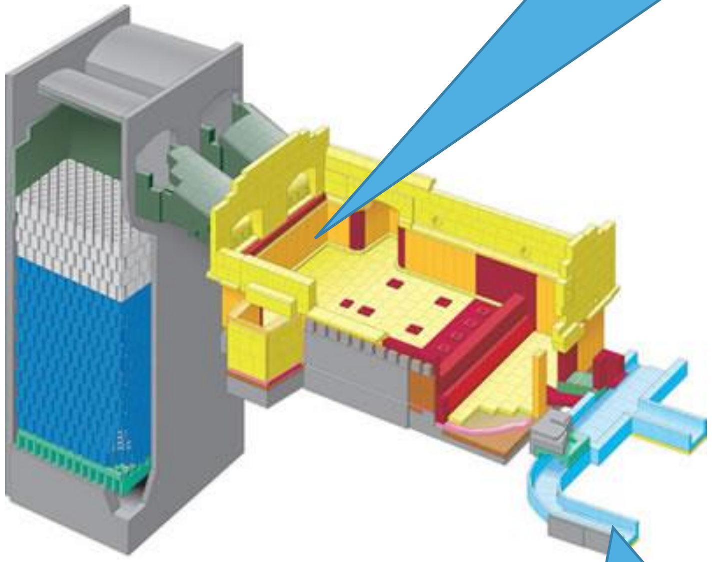
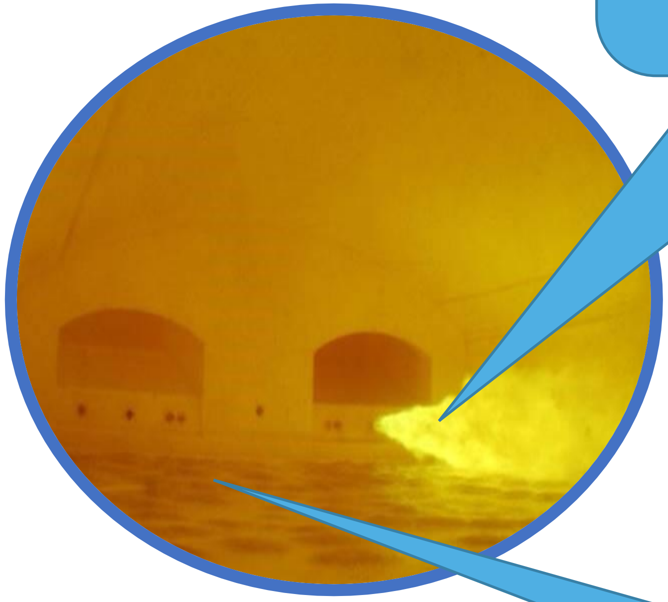
- ✓ We generate waste streams due to stringent specifications of used materials.
- ✓ **Reduction of scope 3 CO_2 emissions**

Very long residence time of glass in the furnace (1-2 days)

- Energy and CO2 intensive
- Competing alternatives with low carbon footprint





Limited possibilities to recycle ALL glass

Technological limitation to use alternative materials or materials with less stringent specifications

Direct and indirect CO2

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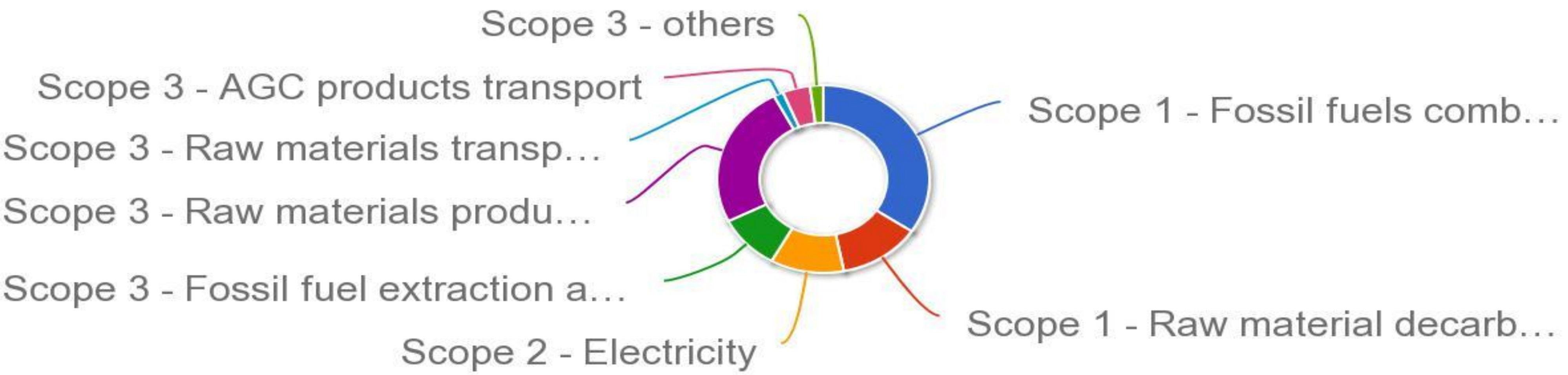
CO_2 sources float glass

(source AGC)

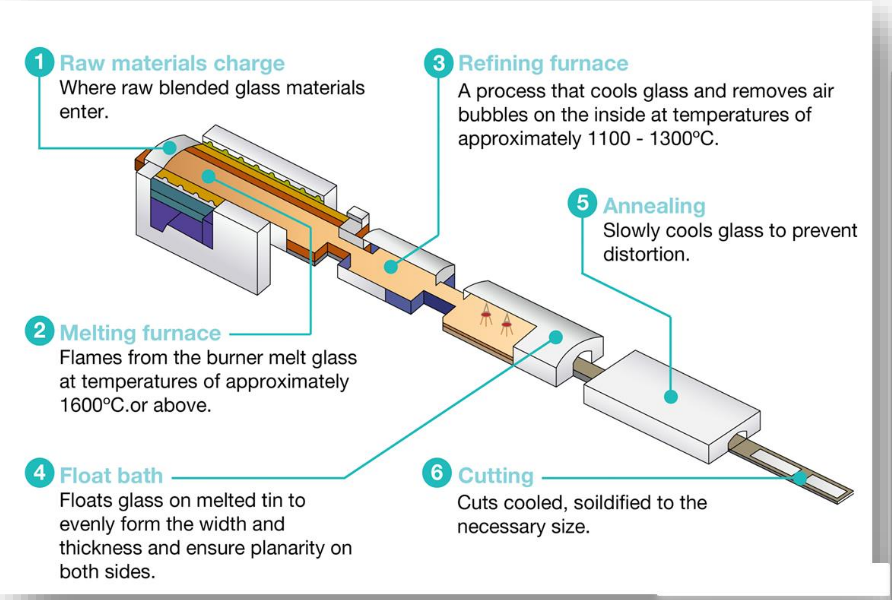
Carbon footprint breakdown

- **Raw material decarbonisation : 12.5%**
- **Raw material production (soda?) : 24.7%**
- **Raw material transport : 1.5%**
- **Total : 38.7%**



https://www.agc-glass.eu/en/sustainability/environmental-footprint/carbon-footprint

3. Float glass production line



Source. Bernhard Fleischmann (2018, DGG Journal)

Abb. 4 Prinzipieller Temperaturverlauf der (Behälter-)Glasfertigung

Some facts about energy consumption

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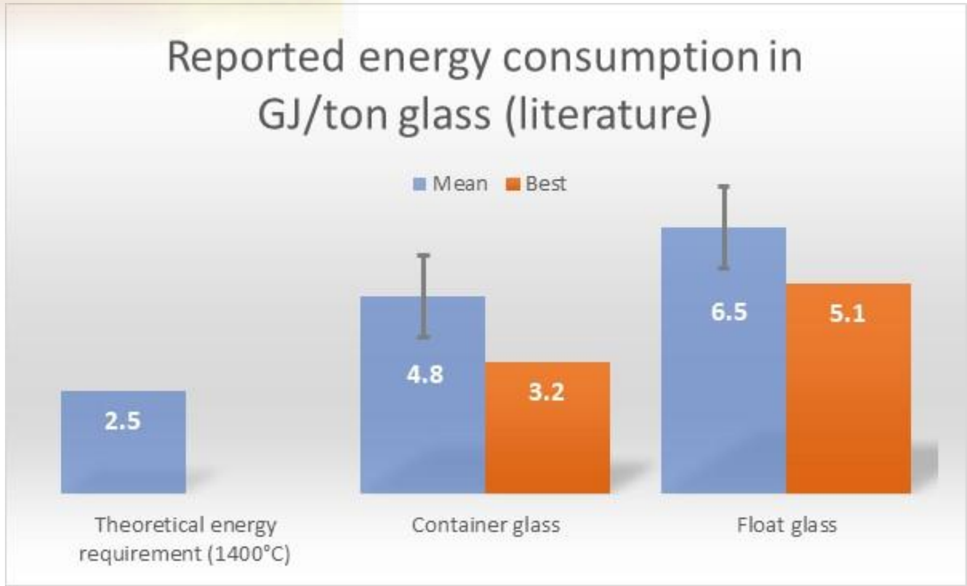
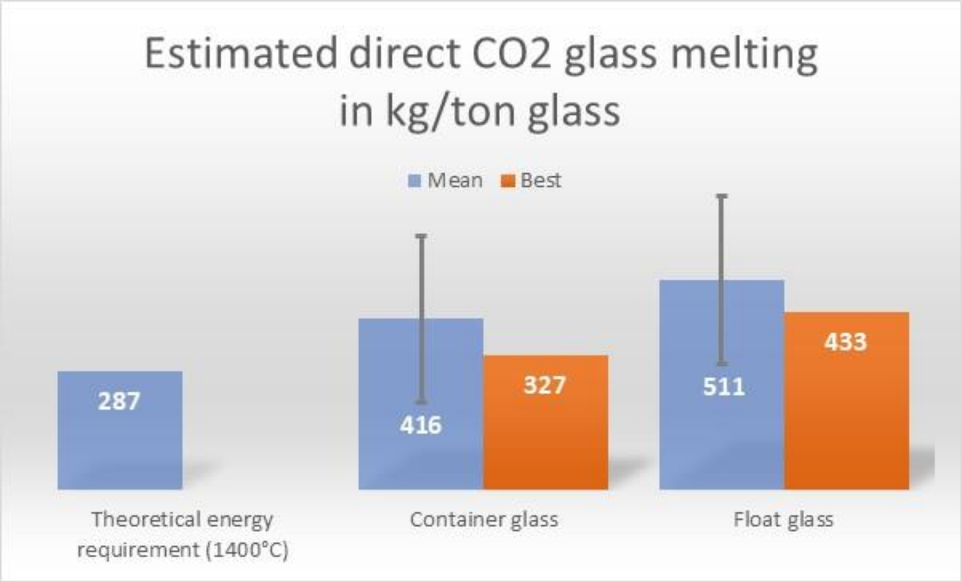
- Energy data is available in the public domain for ‘state-of-the-art’ glass melting technology.
- Air-fuel and oxy-fuel has been used, while some furnaces apply electric boosting (typically 5 – 15%).
- In Europe glass recycling is generally applied. An average container glass furnace uses 51% cullet and a float furnace 26%.





Glass melting conditions

- According ASTM-C162 glass is an inorganic product of fusion that has cooled to a rigid condition without crystallization. The temperatures that are required to form a glassy, amorphous material can be derived from thermodynamic simulations.
- According thermodynamic simulations a temperature of at least 975 to 1000 °C will be needed for a 100% conversion of a typical float glass batch into a glass melt.

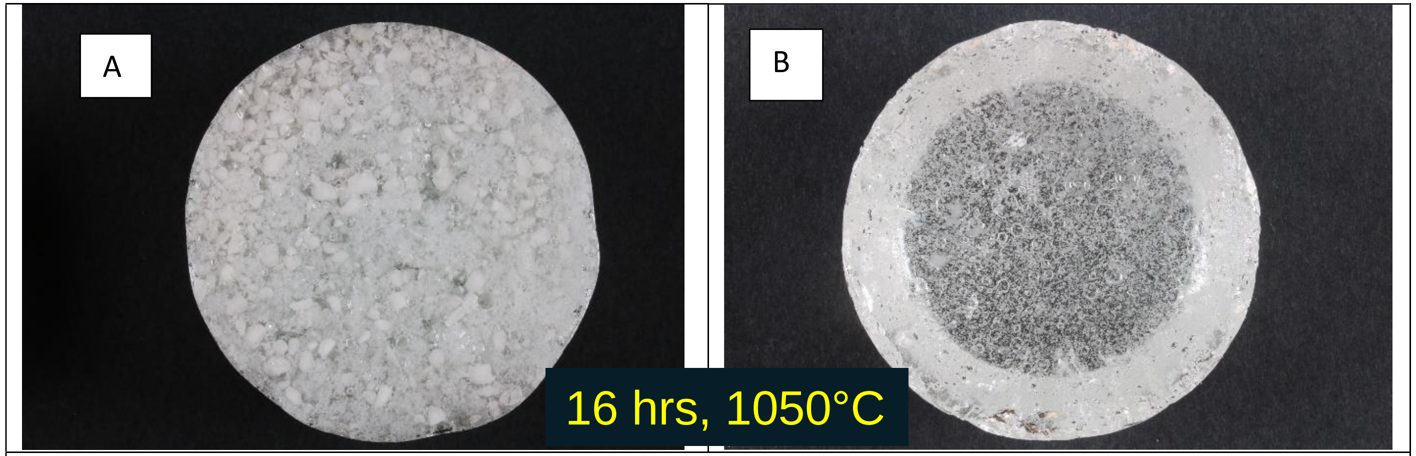


Figure 1: Top view of float glass batches heated at 1050°C for 16 hours. Figure A shows the results in case traditional raw materials with a diameter between 100 and 1500 µm are used and figure B shows the results in case activated materials are used.

Source: Van Limpt, Sibelco

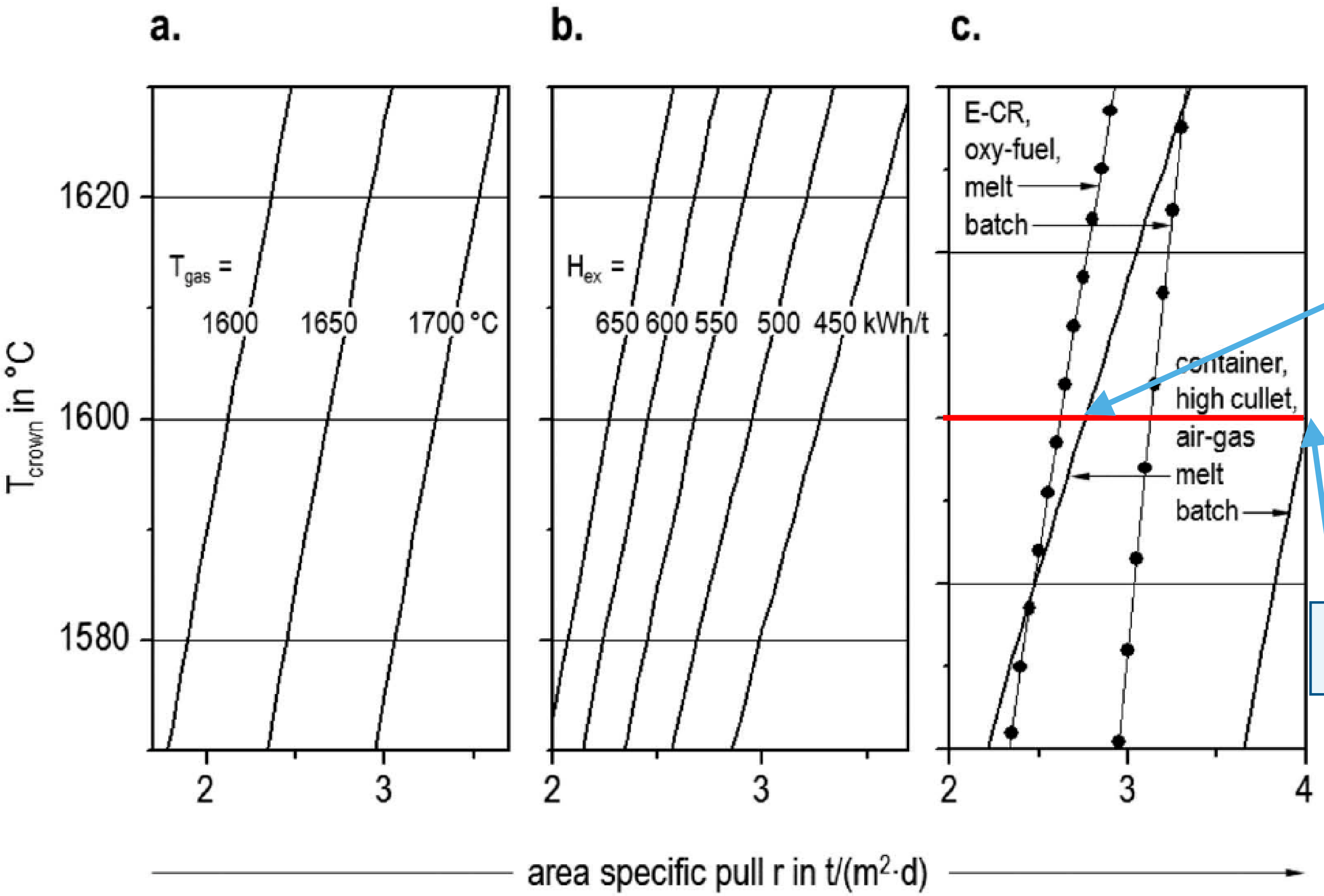
- For the time being, industrial production of high-quality glass at high pull rates is not possible at these relatively low temperatures.
- The conversion rate with traditional minerals is extremely low and even if pre-treated materials would be applied the glass melt might be full of blisters and bubbles.

Limiting factor(s) in specific pull

Source Conradt: JOURNAL OF ASIAN CERAMIC SOCIETIES 2019, VOL. 7, NO. 4, 377–396

A simplified heat transfer model for traditional fuel-fired container glass furnace has been applied to determine the limiting factor for the specific pull rate. For batch melting: T_{melt} =1250 °C and for fining T_{melt} = 1450°C. The maximum crown temperature is 1600°C.

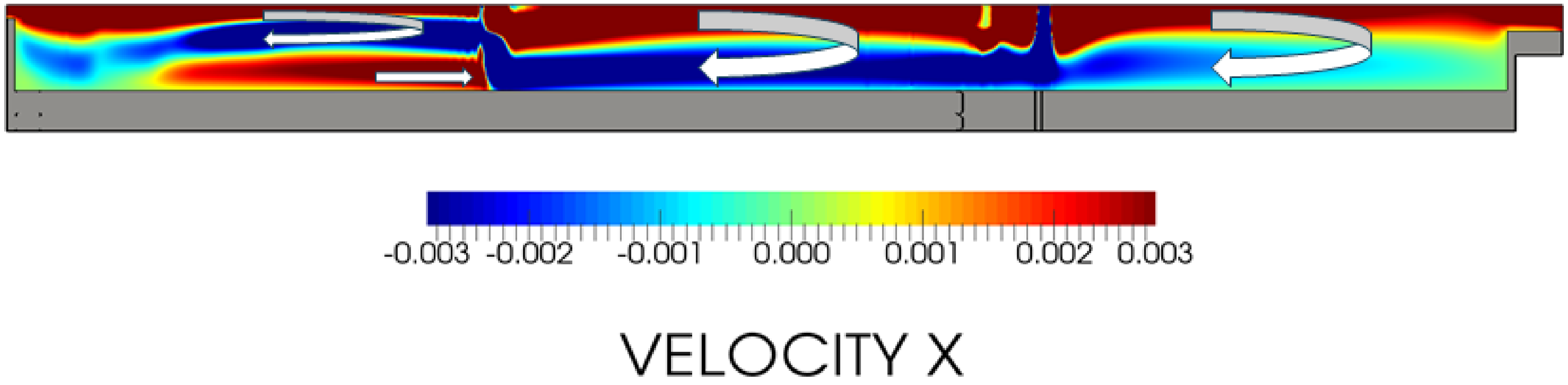
Heat transfer is not the limiting factor



Fining as limiting factor: ~2.7 ton/m²/day

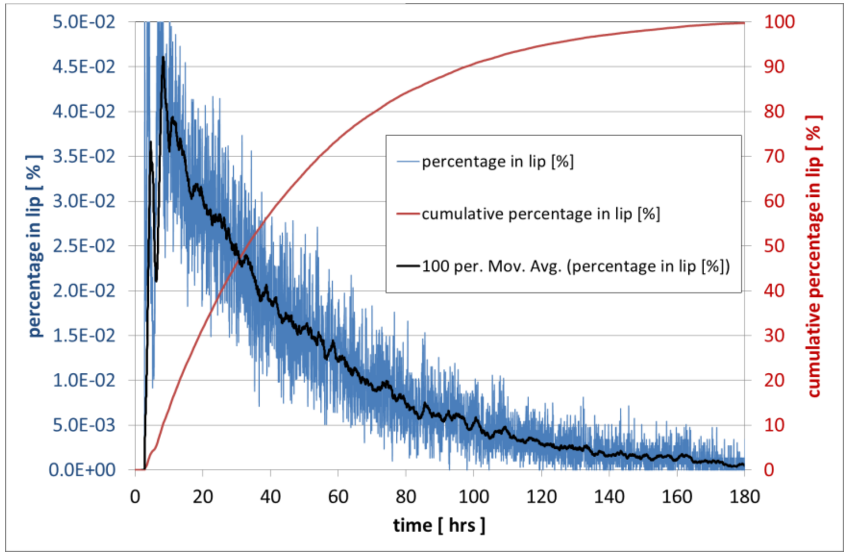
Batch melting as limiting factor: >3.5 ton/m²/day

Quality requires time !

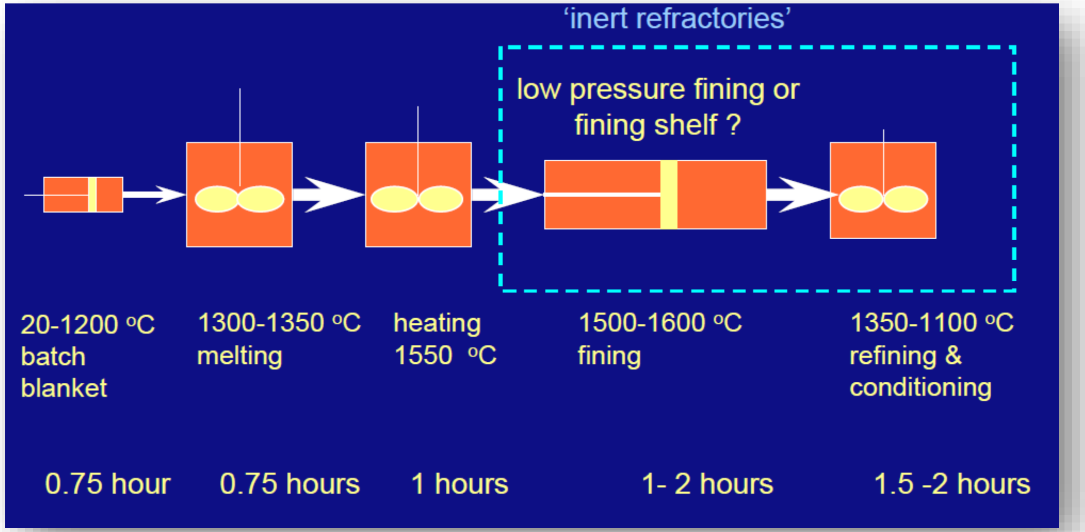


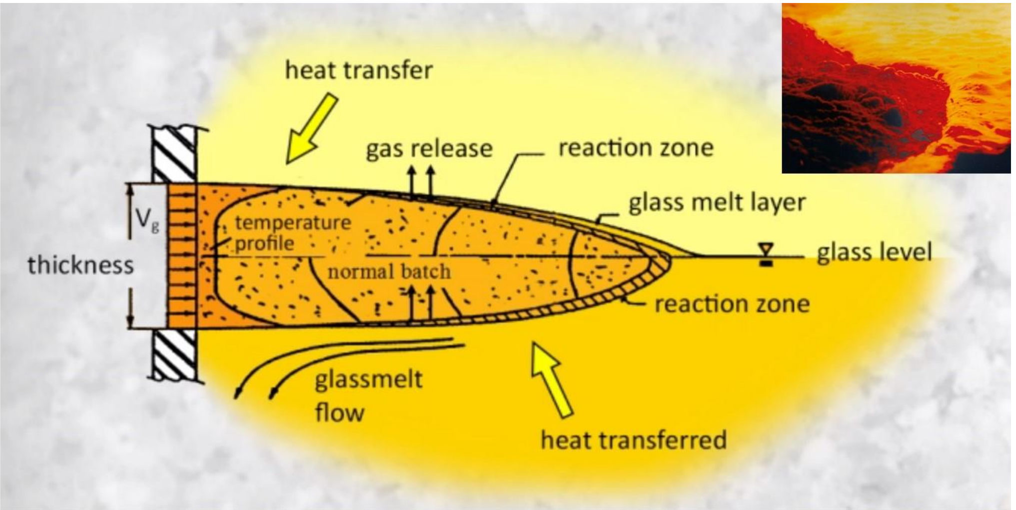
Residence Time Distribution (RTD) of the glass in the complete tank:

- t_{min} = 2.8 hrs
- t_{avg} = 48 hrs



Minerals, melting, fining & homogenization





Source: Celsian – NCNG: International Course on Glass Technology

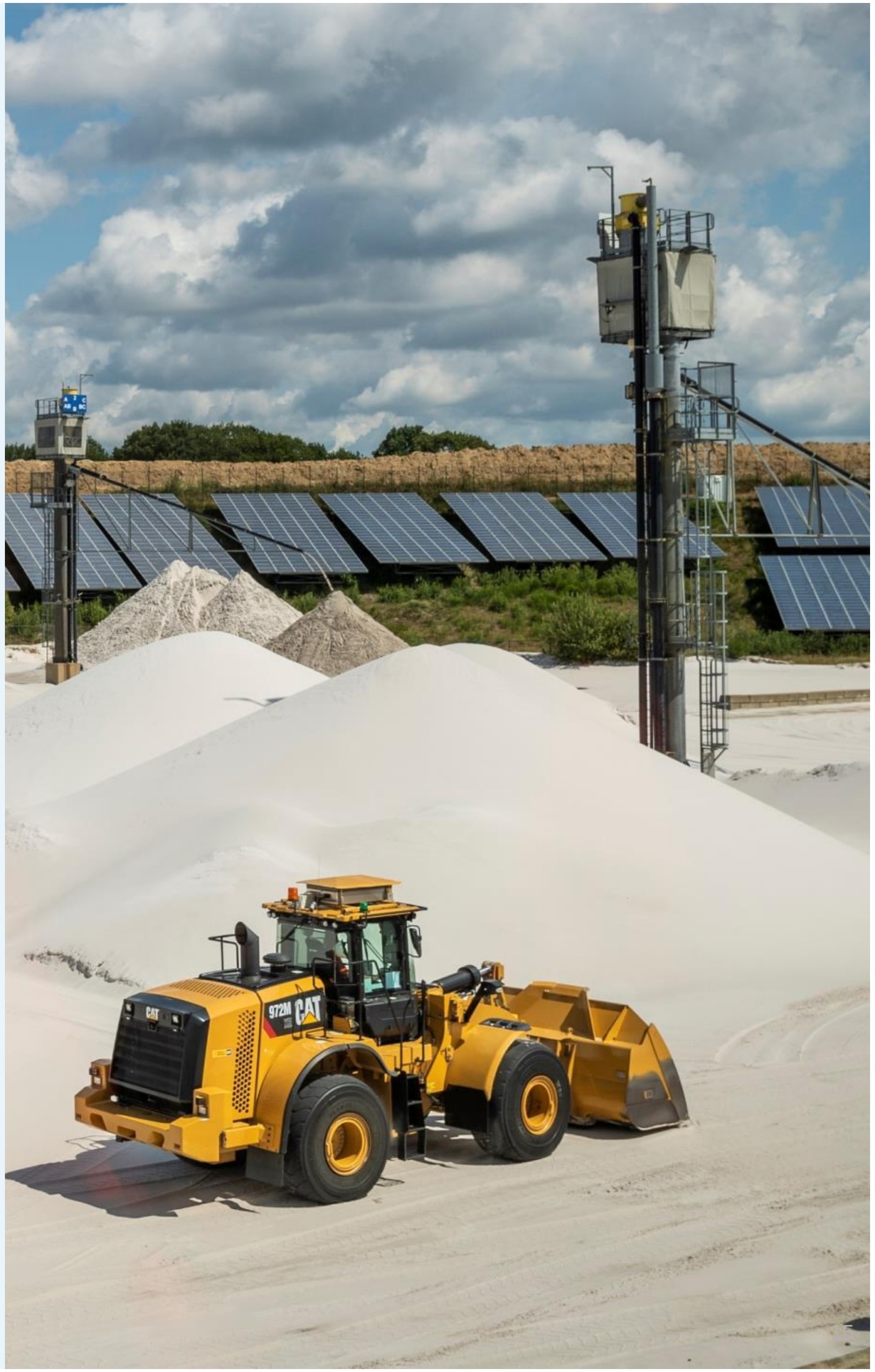
- According Beerkens concept about 6 hours is needed to form a homogeneous melt, but in the current furnace the average residence time is about 1 – 2 days !!
- The current float furnace needs **about 2 days** to homogenize the inhomogeneous primary melt formed after batch melting.

4. Raw materials

Sibelco investigates the impact of minerals on:

- **the melting behavior and**
- **homogeneity of the primary melt phases**

in order to reduce the residence time and temperatures in the glass furnace.



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Materials as key to success

- Residence (melting) time determines largely the energy consumption.
- Lab research to determine impact of materials on melting time and homogeneity glass.

Test procedure

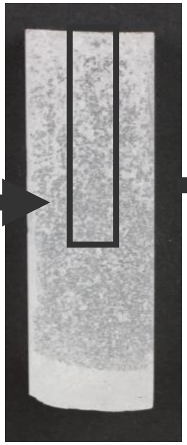
Melting

Cutting

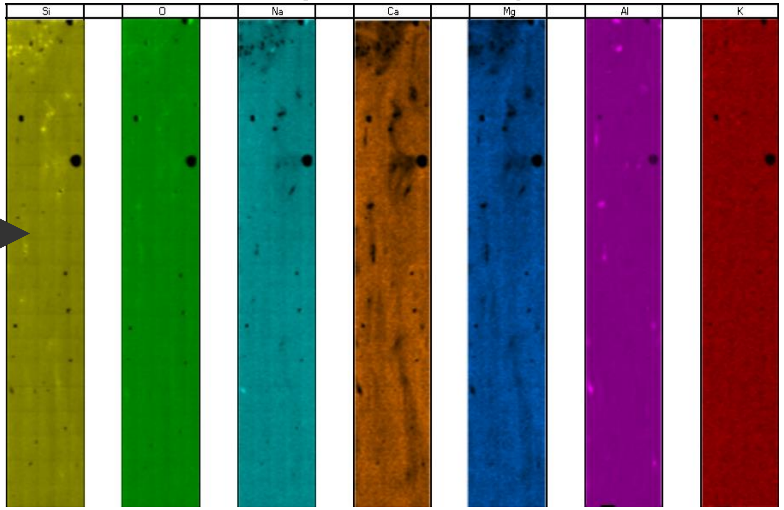
Photos

Polishing

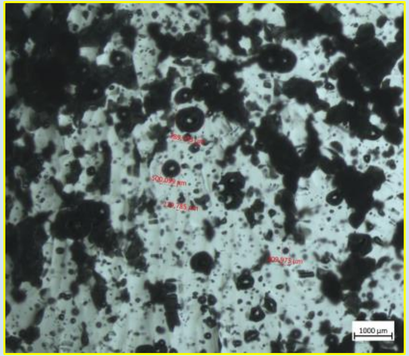
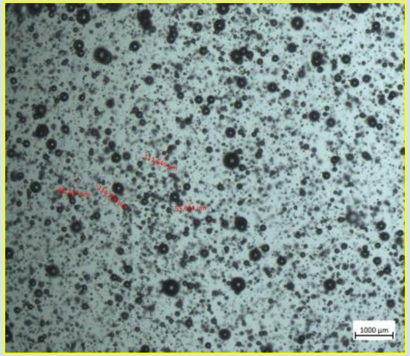
SEM-EDX



Data processing

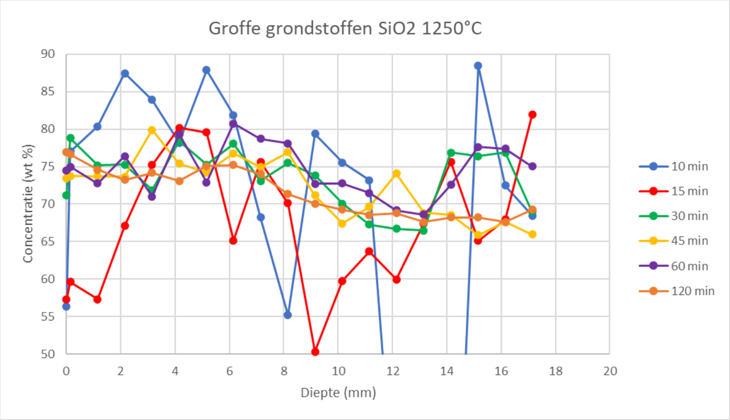
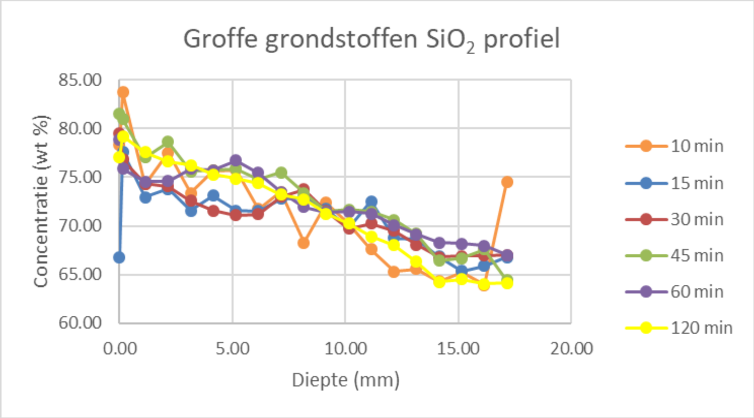
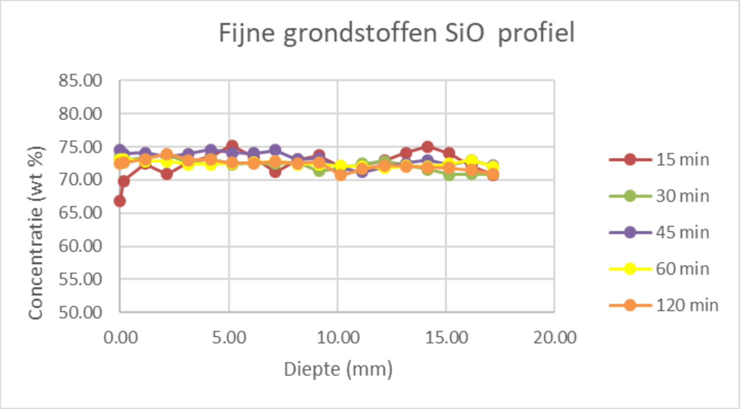
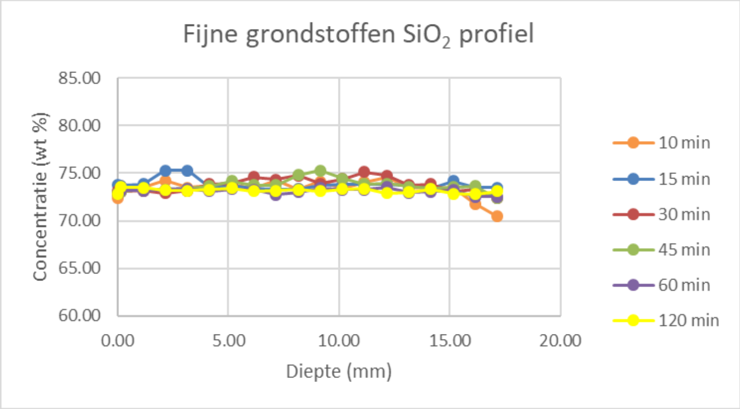


Example Results – 2hrs melting @1350°C

Float glass batch	Standard materials	Fine materials
Polished glass samples, vertical cross-section		
Glass surface		
Microscopy		

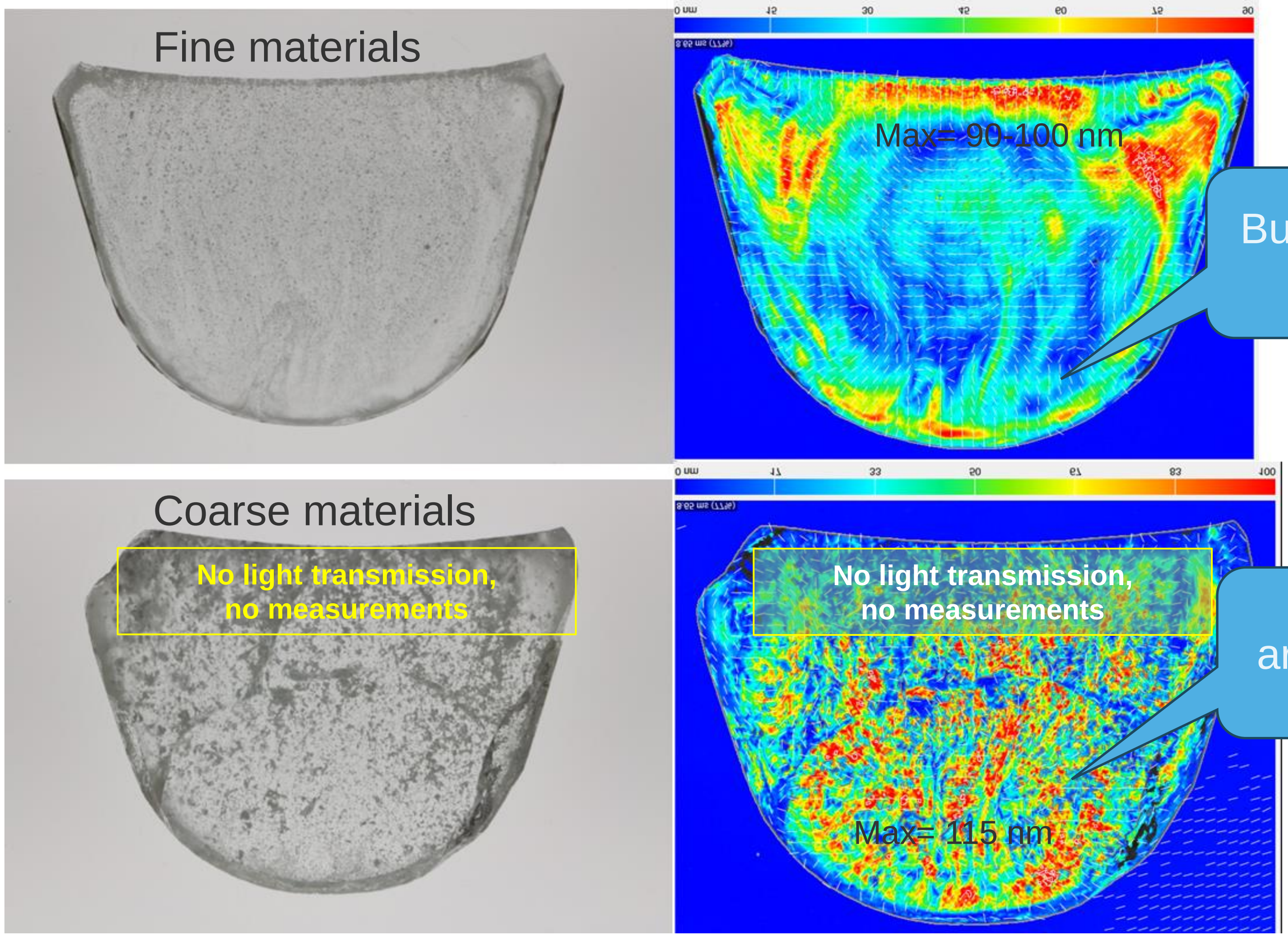
Vertical concentration gradient SiO2

- **Coarse materials** : Slow melting, inhomogeneous glass remains for hours
- **Fine materials** : Homogeneous melt @ 1250°C within 15 – 30 minutes

	1250°C	1450°C
Coarse		
Fine		

Tension in glass – Strainscope

2 hrs melting 1350°C: blue = low tension, red = high tension



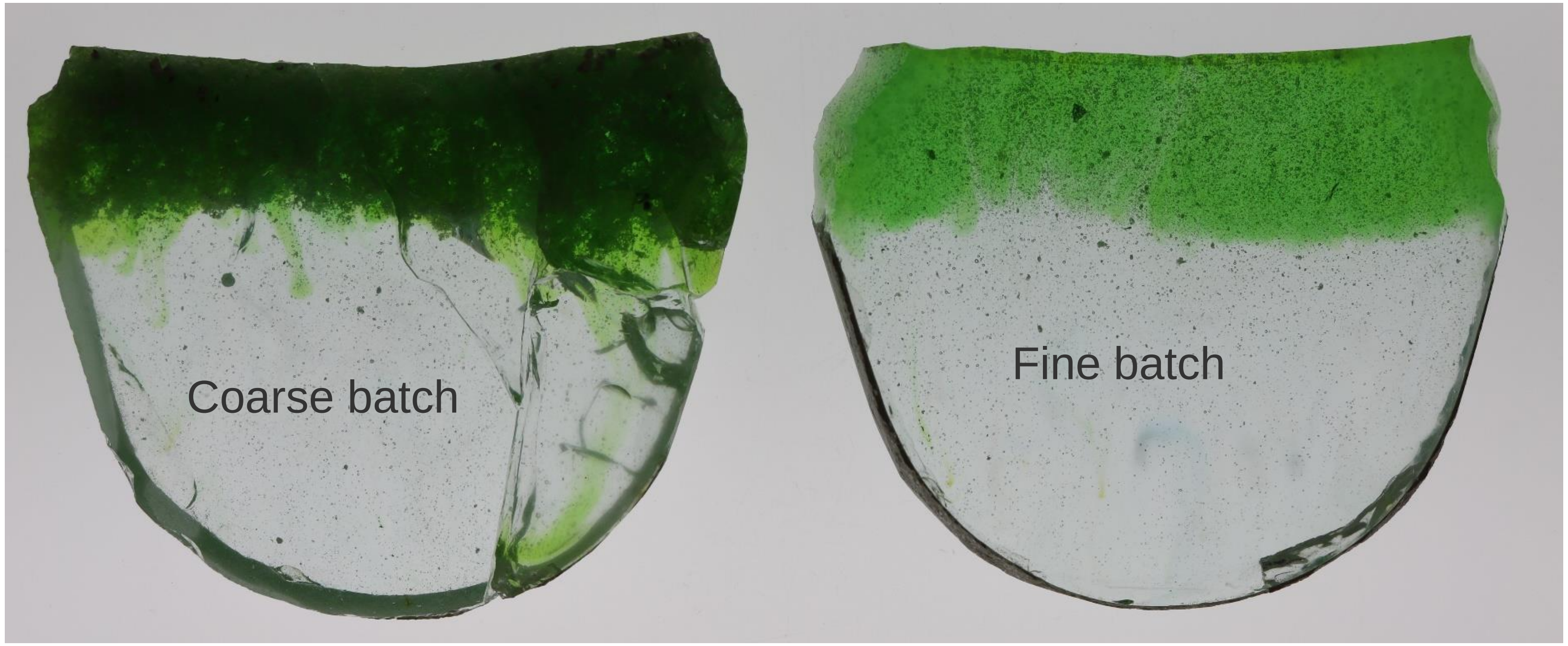
Bulk with hardly any stress

Many small areas with high tension

A strainscope can be used to visualize stresses in glass. Polarization of light is influenced by mechanical stresses. The figures shows the optical retardation.

Impact of stress

Inhomogeneous parts in glass result in stresses → cracks.



Batch is charged on top of a homogeneous melt and melted at 1150°C for 5 hrs.

The finer, the better is not always true !!

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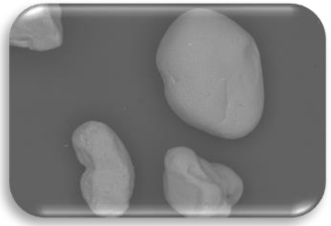
Chemical reactions affected → redox change

Standard glass-grade raw materials with difference silica sand products (particle sizes)



Silica sand (quartz)

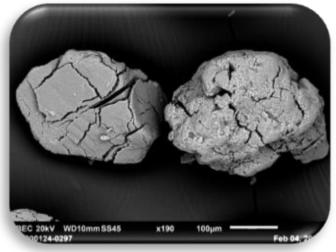
M31 | M32 | M6 | M10 | M300 | M400 | M500

SiO_2 inclusions

optimal

SiO_2 flocks/clusters

M72 | M72T | M006 | M0010 | M3000 | M4000 | M5000



Cristobalite

Sand	Coarse Flour	Fine Flour
$D_{50} \approx 250$ µm	$D_{50} \approx 30$ µm	$D_{50} \approx 5–15$ µm

What we know from the past

1944 MELTING RATE OF SODA-LIME GLASSES AS INFLUENCED BY GRAIN SIZES OF RAW MATERIALS AND ADDITIONS OF CULLET*

By J. C. Potts, George Brookover, and O. G. Burch

Journal of The American Ceramic Society

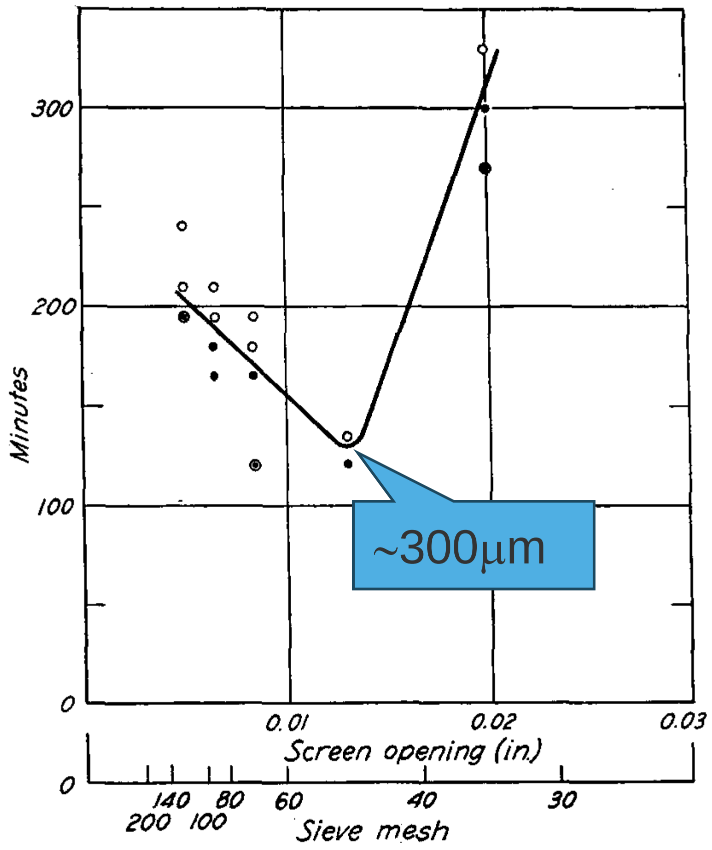


Fig. 3.—Effect of varying sand size; 40/60 soda ash and 40/60 limestone.

- Batch Free Time (BFT) experiments at 1427°C.
- Particles size of minerals has been changed
- The combination of fine and coarse result in longer BFT's
- **Impact on glass homogeneity unknown**

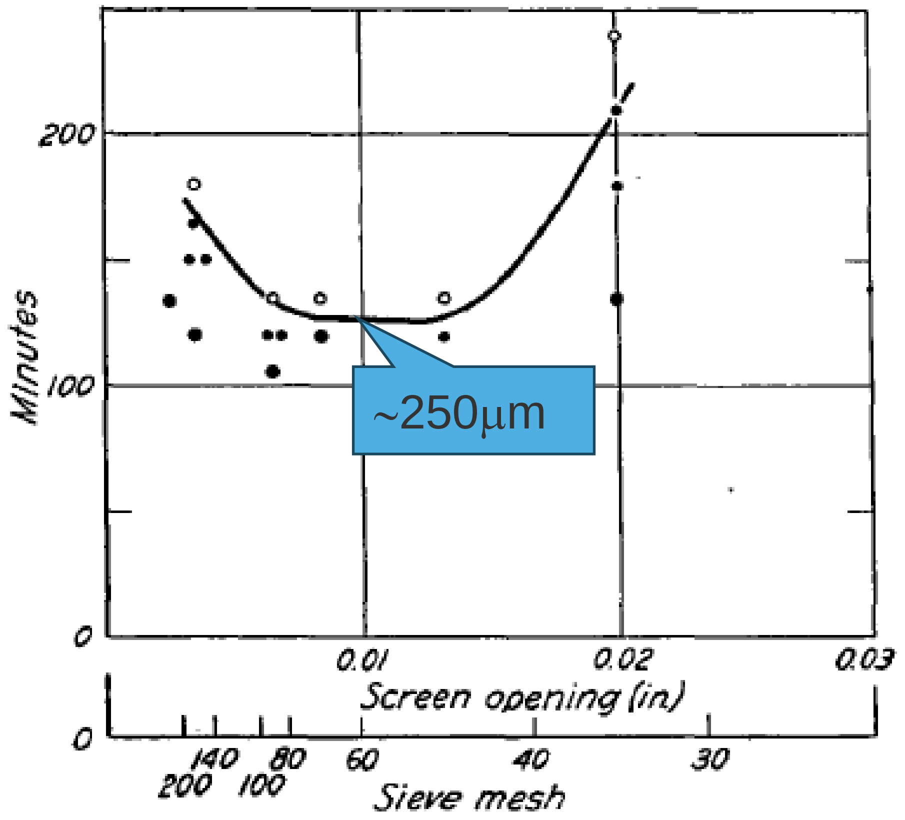


Fig. 4.—Effect of varying limestone size; 40/60 sand and 40/60 soda ash.

Importance of chemical reaction mechanisms

SLS batches are characterized by 2 main silica reactions:

1. Carbonate path

Na_2CO_3 (s) + $MgCO_3$(s) → $Na_2Mg(CO_3)_2$ (300 - 550 °C)

Na_2CO_3 (s) + $CaCO_3$(s) → $Na_2Ca(CO_3)_2$ (550 - 850 °C)

$Na_2Ca(CO_3)_2$ (m/s)+ 2 SiO_2(s) → Na_2SiO_3 -$CaSiO_3$ + 2 CO_2 ↑ (600 - 800 °C)

2. Silica path

Na_2CO_3 (s) + 2SiO_2 (s) → $Na_2Si_2O_5$+ CO_2 ↑ (700 - 860 °C)

For standard glass batches:

- Silica path is supposed to be predominant.
- Remaining silica, MgO and CaO particles slowly dissolve in the primary melt phase.
- This two-step process results in phase separation and the formation of a viscous silica-rich top layer.

Thermodynamics Na-Ca-Si glass

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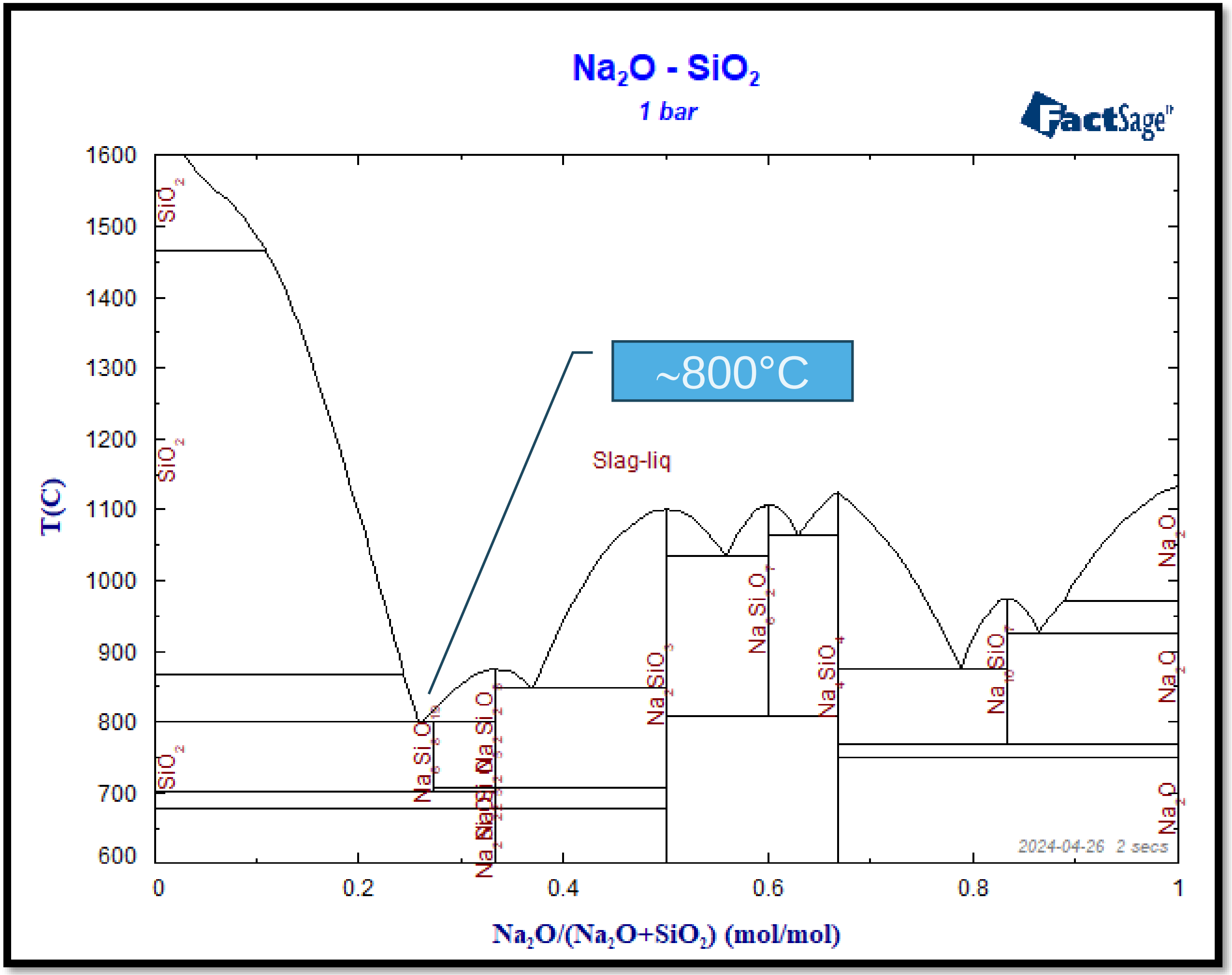
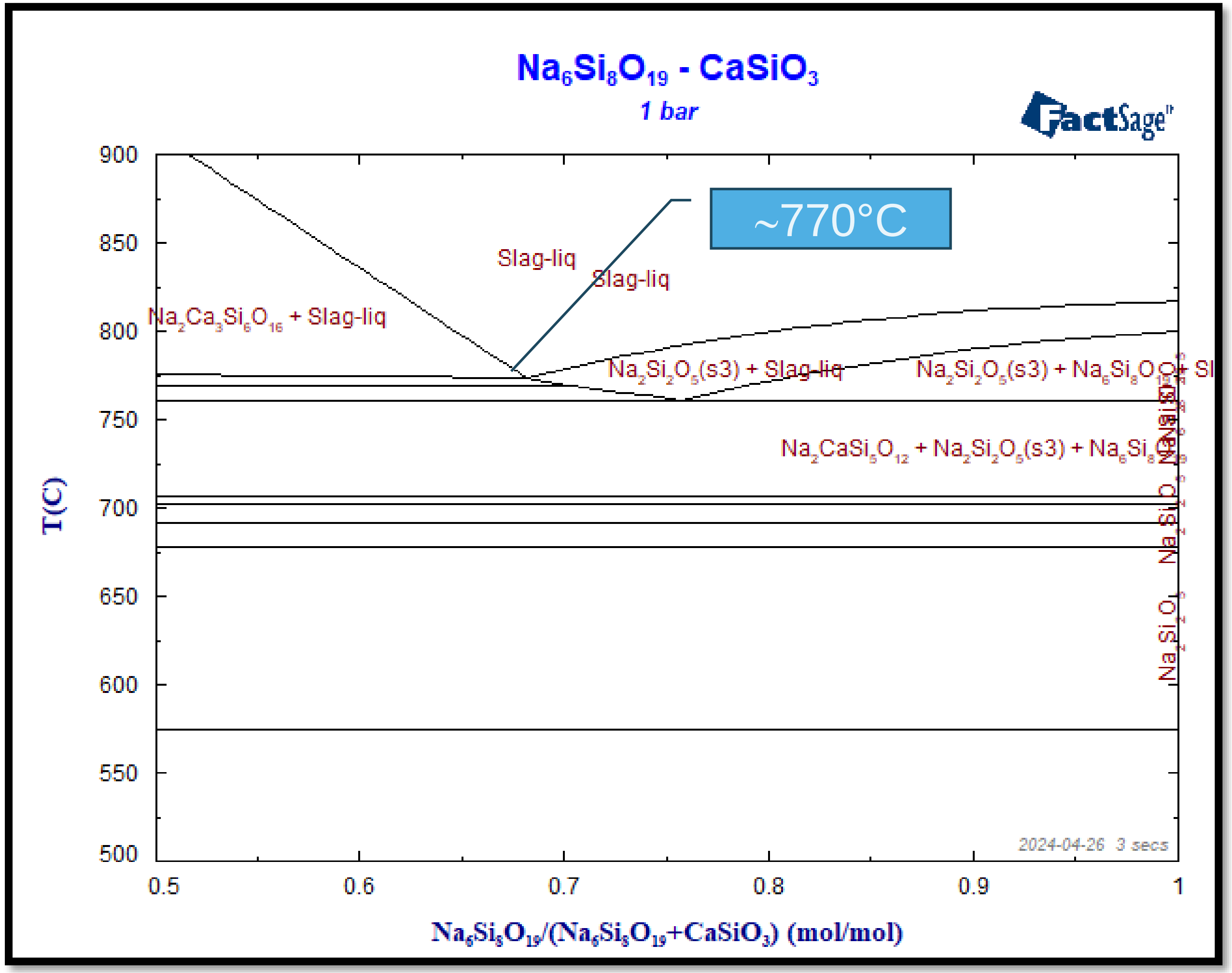
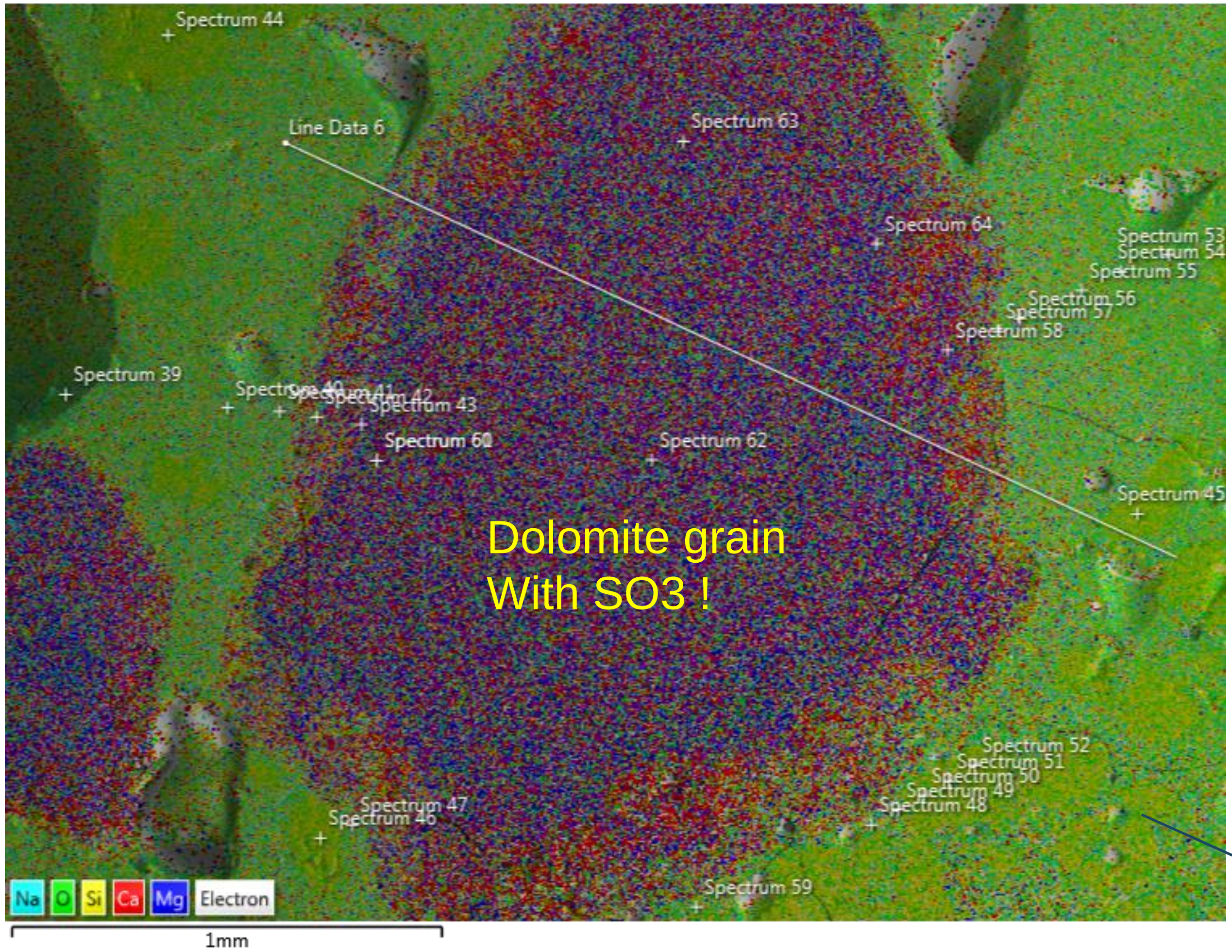




Eutectic composition:	
Na2O	= 26.8 wt%
CaO	= 0 wt%
SiO2	= 73.2 wt%

Eutectic composition:	
Na2O	= 25.7 wt%
CaO	= 3.9 wt%
SiO2	= 70.5 wt%

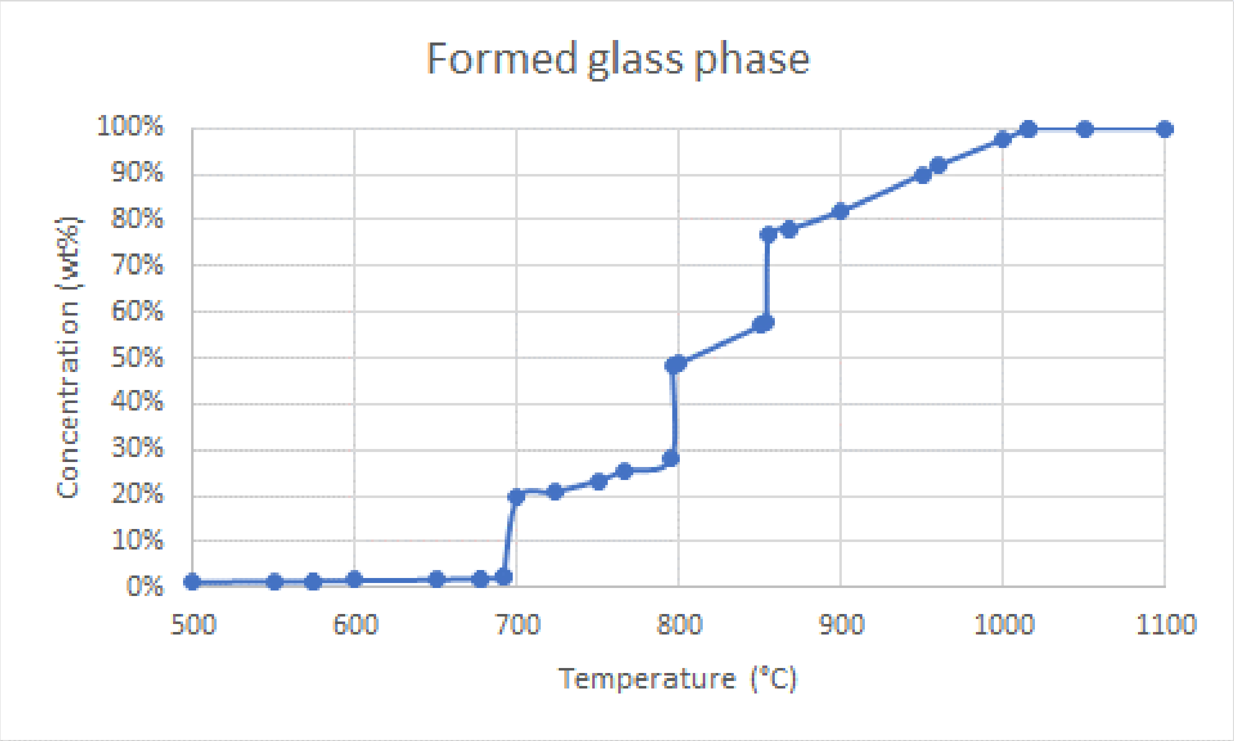
Dissolving dolomite – $MgCO_3.CaCO_3$

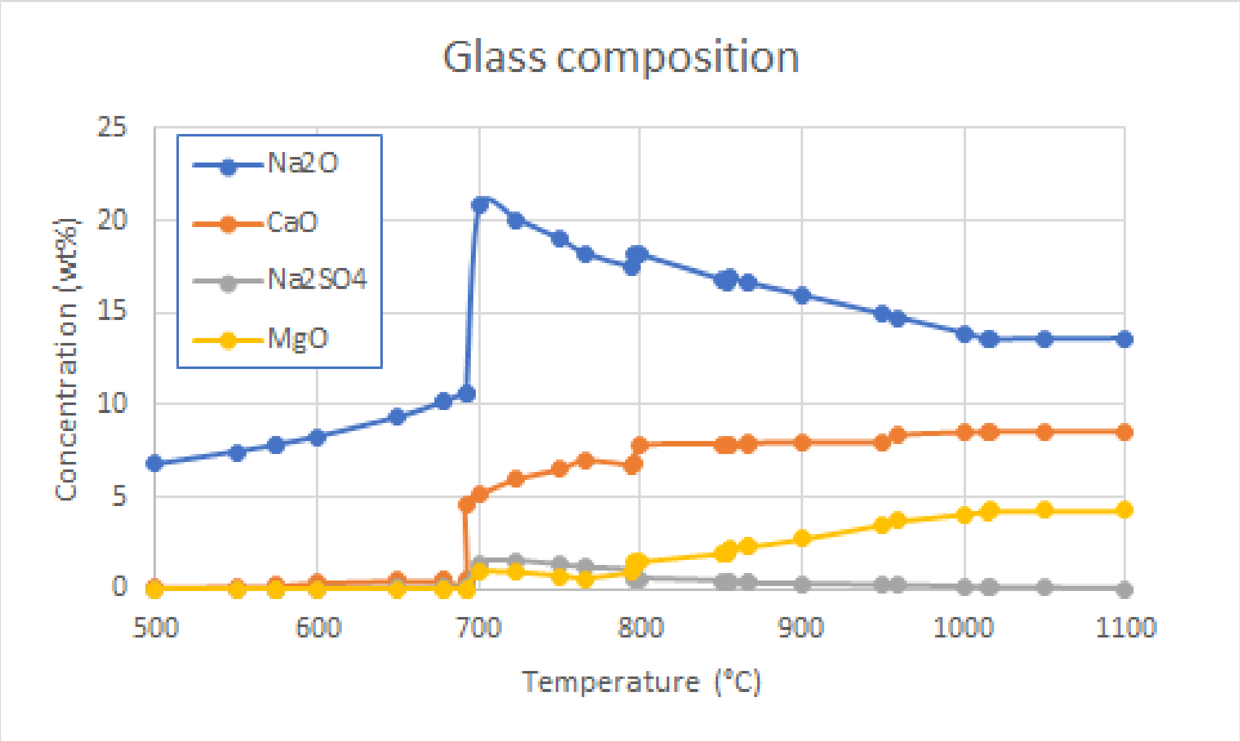


Spectrum Label		Na2O	MgO	Al2O3	SiO2	SO3	K2O	CaO
Spectrum 39		22.07	3.99	0.58	66.75	0.23	0.29	6.08
Spectrum 40		19.95	8.02	0.61	57.39	0.42	0.26	13.36
Spectrum 41		17.28	16	0.61	53.66	0.4	0.26	11.65
Spectrum 42		3.50	30.33	0.19	22.85	0.68		42.08
Spectrum 43		1.78	42.16		6.61	1.59		47.86
Spectrum 44								
Spectrum 45								
Spectrum 46								
Spectrum 47		8.64	18.91	0.46	37.02	0.4	0.14	34.43
Spectrum 48		18.20	7.96	0.53	61.22		0.33	11.77
Spectrum 49		17.34	8.1	0.75	61.33		0.33	12.15
Spectrum 50								
Spectrum 51								
Spectrum 52								
Spectrum 53		19.54	3.94	0.92	67.67		0.41	7.53
Spectrum 54		17.35	3.47	0.93	69.94	0.32	0.44	7.54
Spectrum 55		20.77	5.38	0.55	62.7	0.28	0.34	9.97
Spectrum 56		16.70	11.33	0.66	54.72	0.5	0.26	15.69
Spectrum 57		18.47	11.89	0.6	59.36	0.47	0.5	8.71
Spectrum 58		1.68	41.2		2.26	0.86		54.01
Spectrum 59		11.52	0.81	18.05	64.14		2.74	1.83
Spectrum 60			45.67		1.76			52.57
Spectrum 61			47.04					52.96
Spectrum 62		1.27	51.15		0.93	1.23		45.42
Spectrum 63		1.30	43.91		1.46	1.08		52.26
Spectrum 64		1.30	51.29		1.65	0.95		44.81

Yellowish parts represent dissolving silica grains

Again thermodynamics

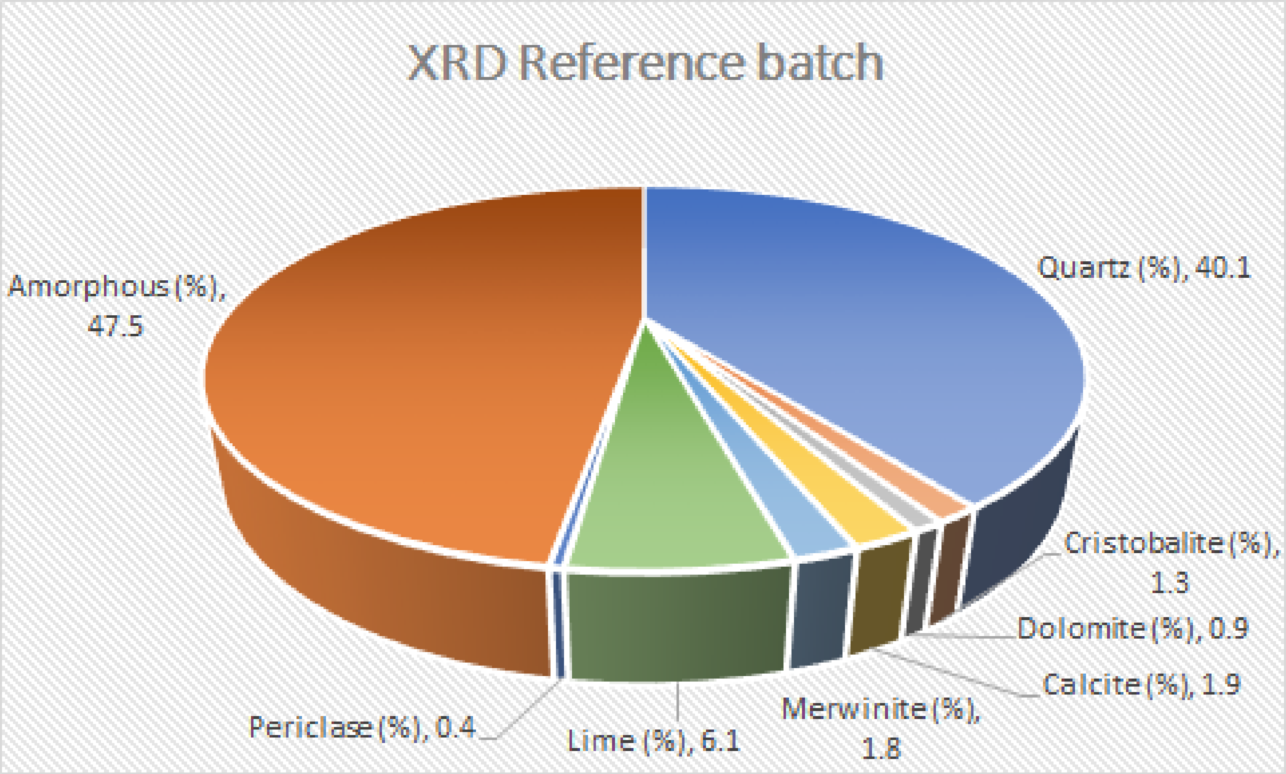




- Primary Na2O-rich melts / salts attack the porous dolomite grains.
- MgO and CaO are selectively dissolving.
- **Less aggressive sodium-compounds remain for dissolution of silica grains.**

Impact of different minerals on primary melt phase

- Melting trials with SLS batches using different Ca, Mg and Na minerals
- T=1200 °C & t = 10 minutes

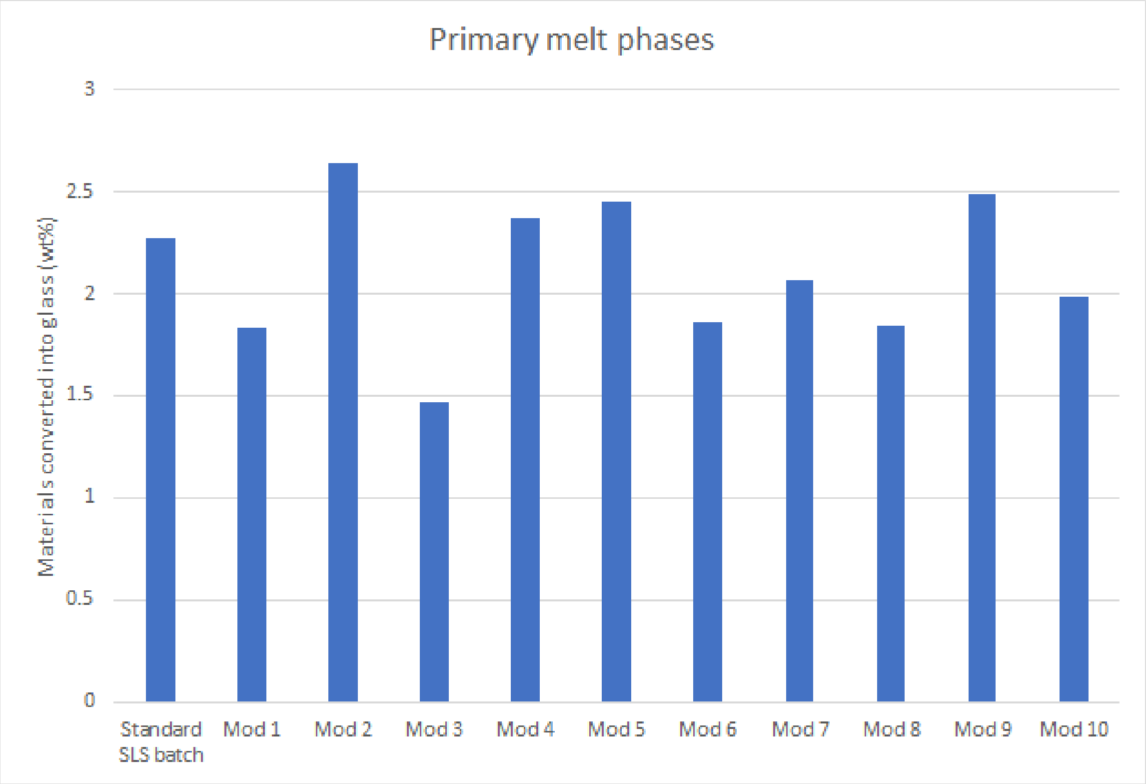


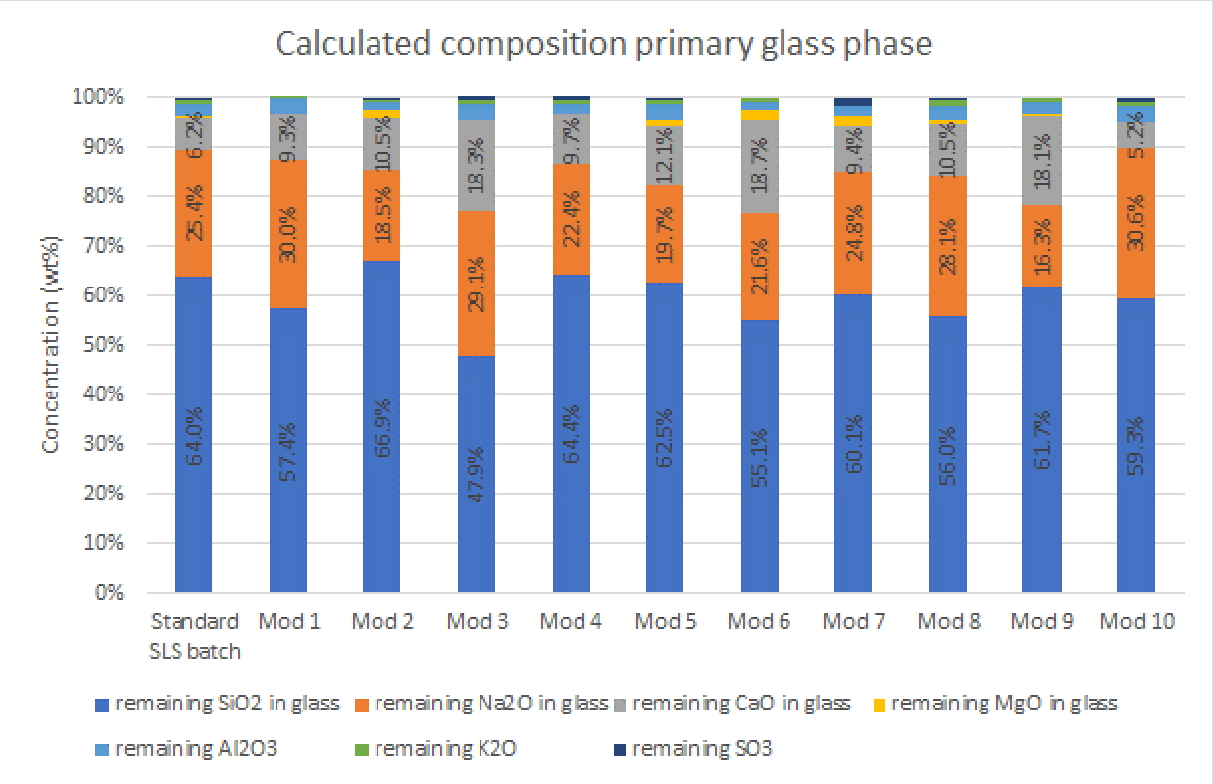
The reference batch contains among others:

- Limestone
- Dolomite
- Soda ash

Impact of alternative minerals / materials

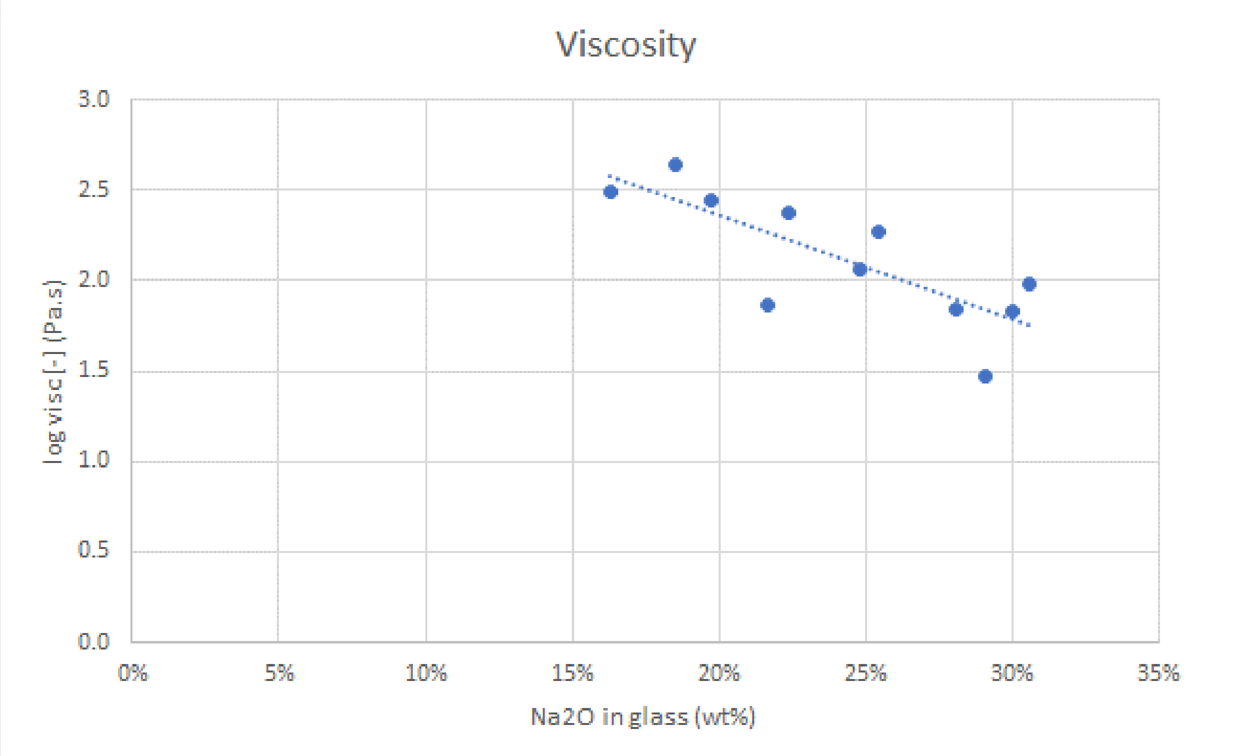
Amounts of primary melt phases AND compositions change.

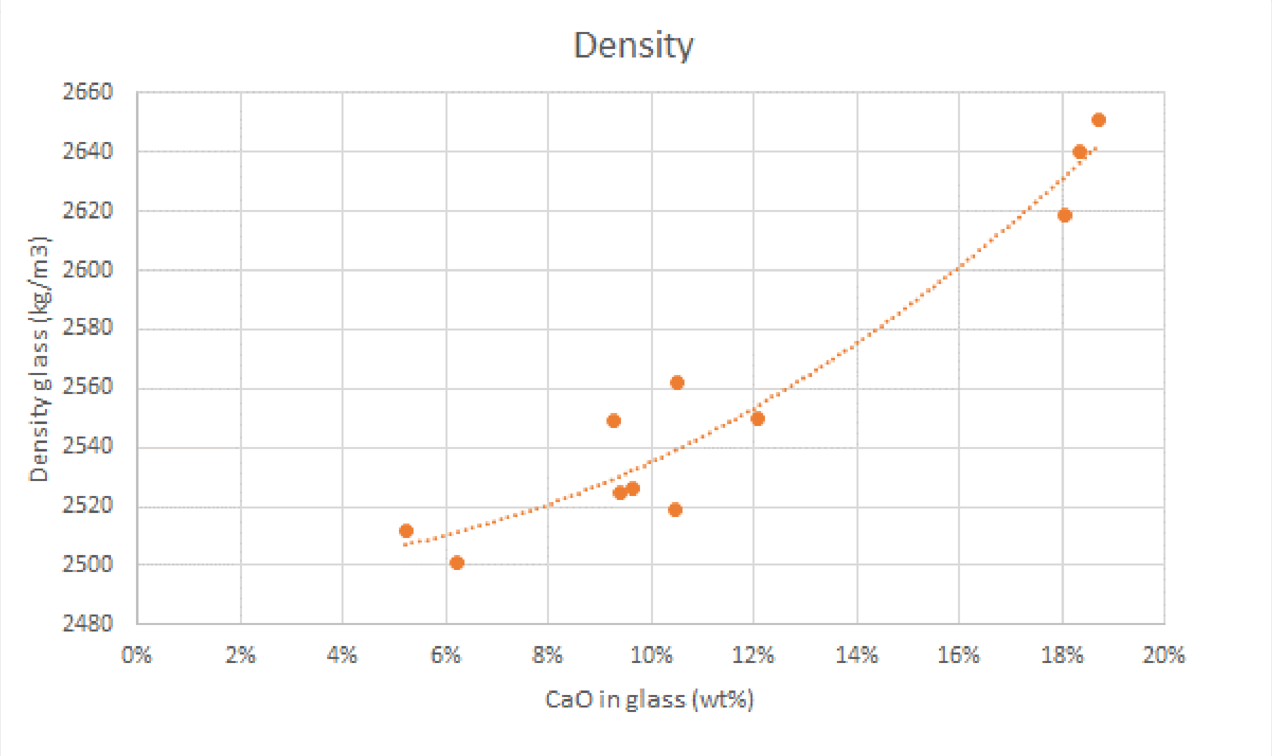




Impact of alternative minerals / materials

Properties of the primary melt phases are very different.





Same glass, different melting behavior

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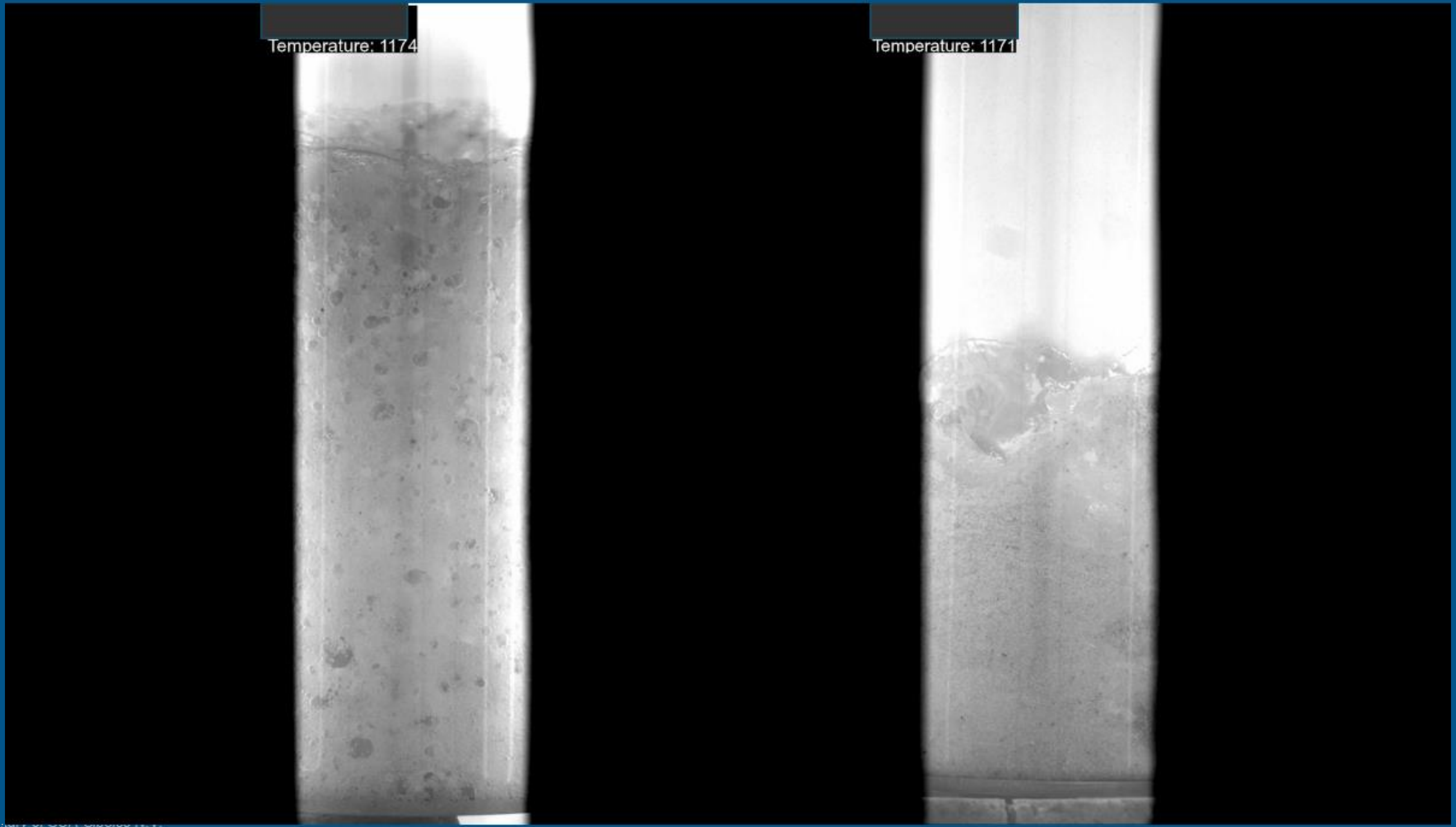
Standard batch with soda, limestone and dolomite:

Long-lasting foam → viscous silica rich top layer with slowly dissolving dolomite is formed

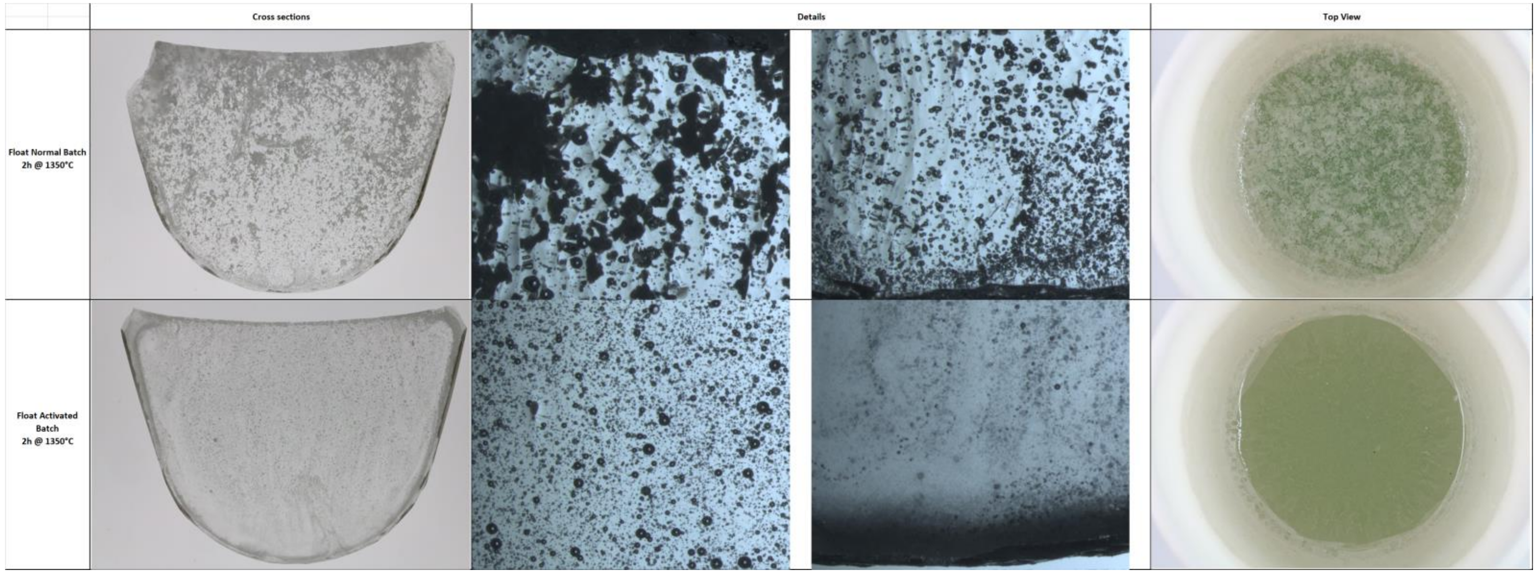
Alternative Batch:

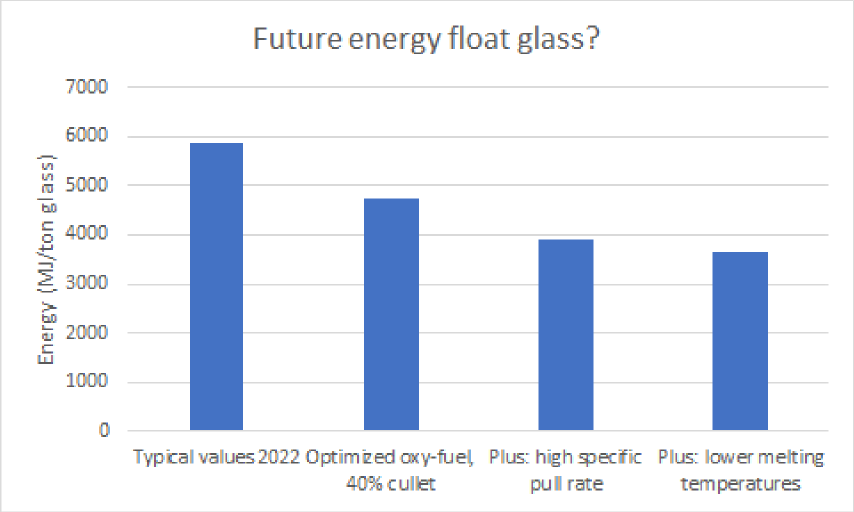
Limited foam → less phase segregation

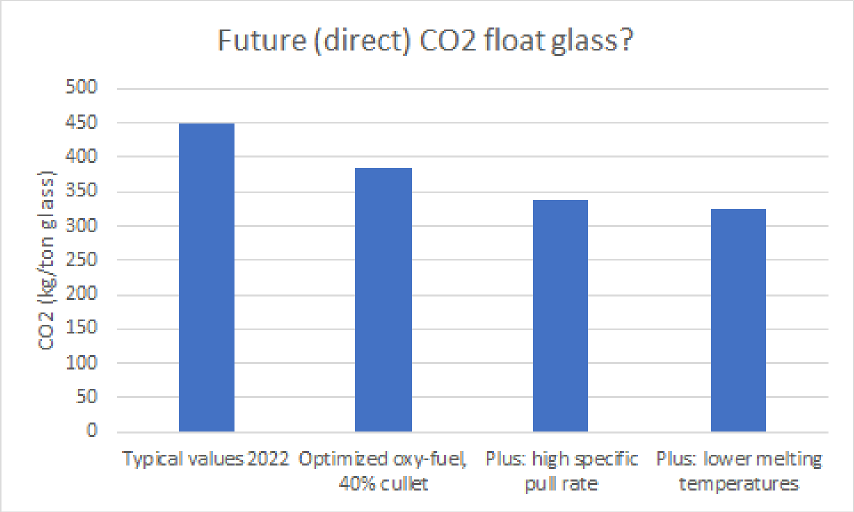


Future of glass melting?

Alternative materials may allow shorter residence times & lower temperatures.

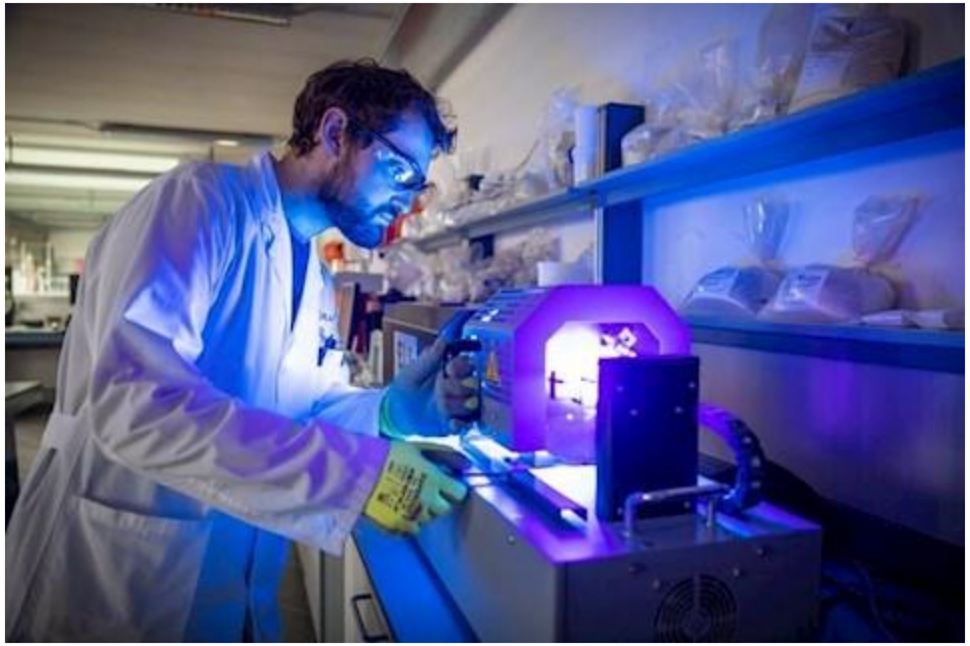






Outlook

- The choice of raw materials will largely determine the final homogeneity of the glass.
- In addition, the choice of material will also determine the risks of unmelted raw materials and solid inclusions in glass.
- High melting rates combined with the production of homogeneous, high-quality glass can only be produced in a **furnace with intense mixing, without short-cut flows and with pre-selected raw materials**.
- This combination will result in a break-through in energy efficiency and carbon footprint.



- Glass Research is high on our agenda.
- Interested to become member of the team?

Contact hans.van.limpt@sibelco.com

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