Glass Performance Days 2025, Tampere, Finland

Sustainable melting and processing of Soda-lime-silica glasses

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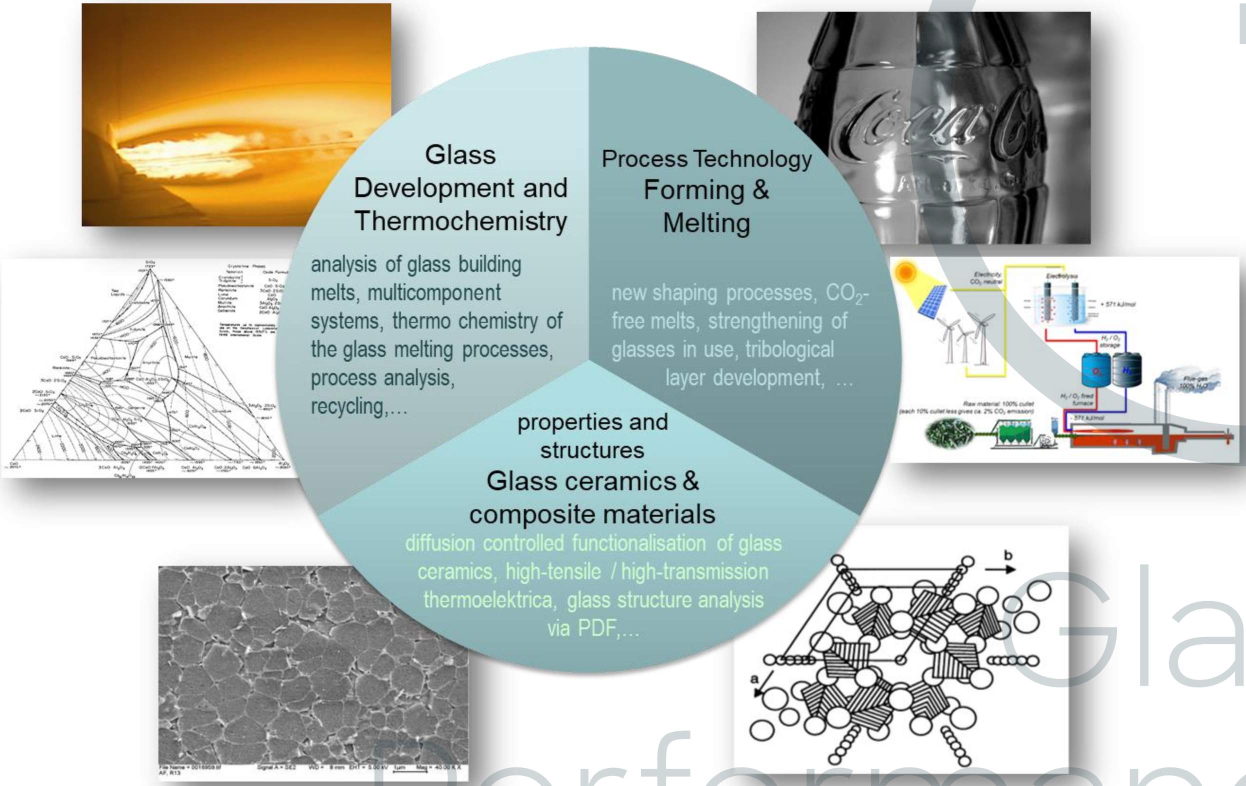

Staff

- 1 Professor
- 2 Senior engineers
- 8 PhD's
- 4 Lab / Technicians
- 2 Administration staff
- 8-10 Student assistants

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Examples for improving the sustainability of glass melting and processing

FISKARS
IITTALA

I. Intelligent glass-optimization: High-quality automated art-glass

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Soda-Lime-Silica composition for automated high-quality art-glass forming

The main specification were

- CTE and thermal shock resistance improved. Target for CTE: $8\ \text{ppm}\cdot\text{K}^{-1} < \text{CTE} < 9\ \text{ppm}\cdot\text{K}^{-1}$ but mainly relevant is withstanding of at least ΔT 60 K acc. to ASTM F2179 test.
- Mechanical resistance improved, both scratching and edge chipping.
- Dish washer resistance improved (class 2).
- Sb_2O_3 removed completely and BaO reduced + ideally no B_2O_3 (avoidance of condensates).
- All automated (centrifuge and pressing) and hand-crafted products can be manufactured from the same mass glass.

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Prof. Dr. Christian Roos
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Chair of Glass and Glass-Ceramic
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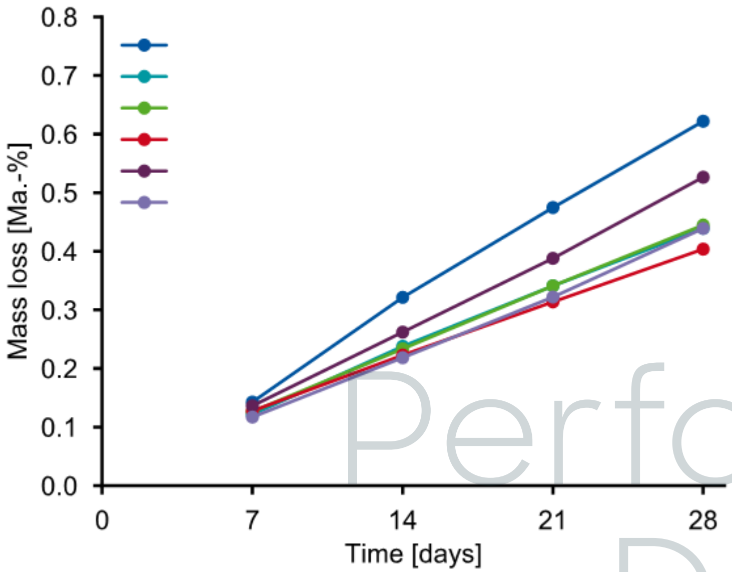
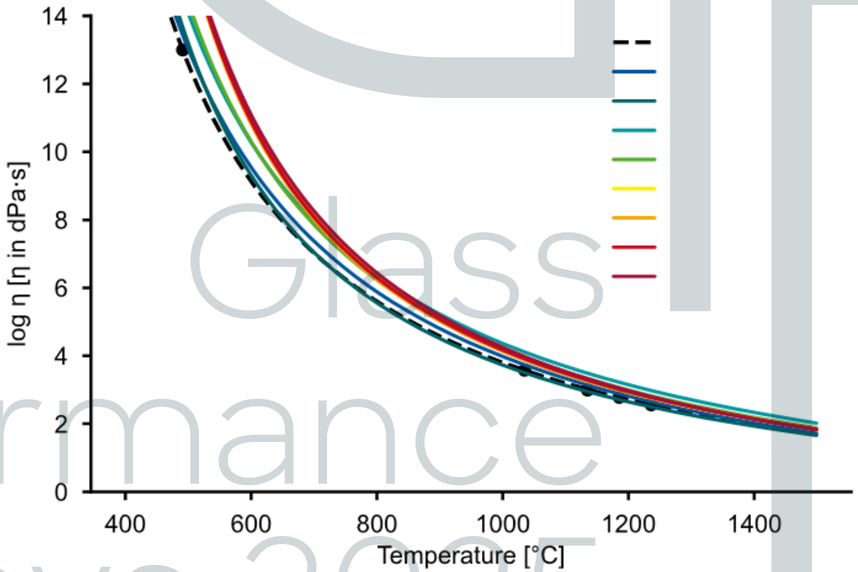
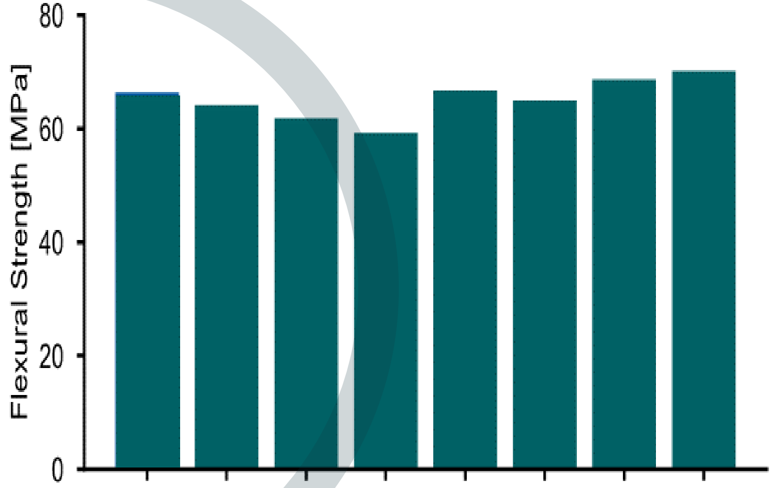
Soda-Lime-Silica composition for automated high-quality art-glass forming

Procedure

- Thorough process and status-quo evaluation at customer.
- Very close communication and exchange with customer, especially at process side / with the “hands-on” people.
- Thorough evaluation of the competitor land-scape.







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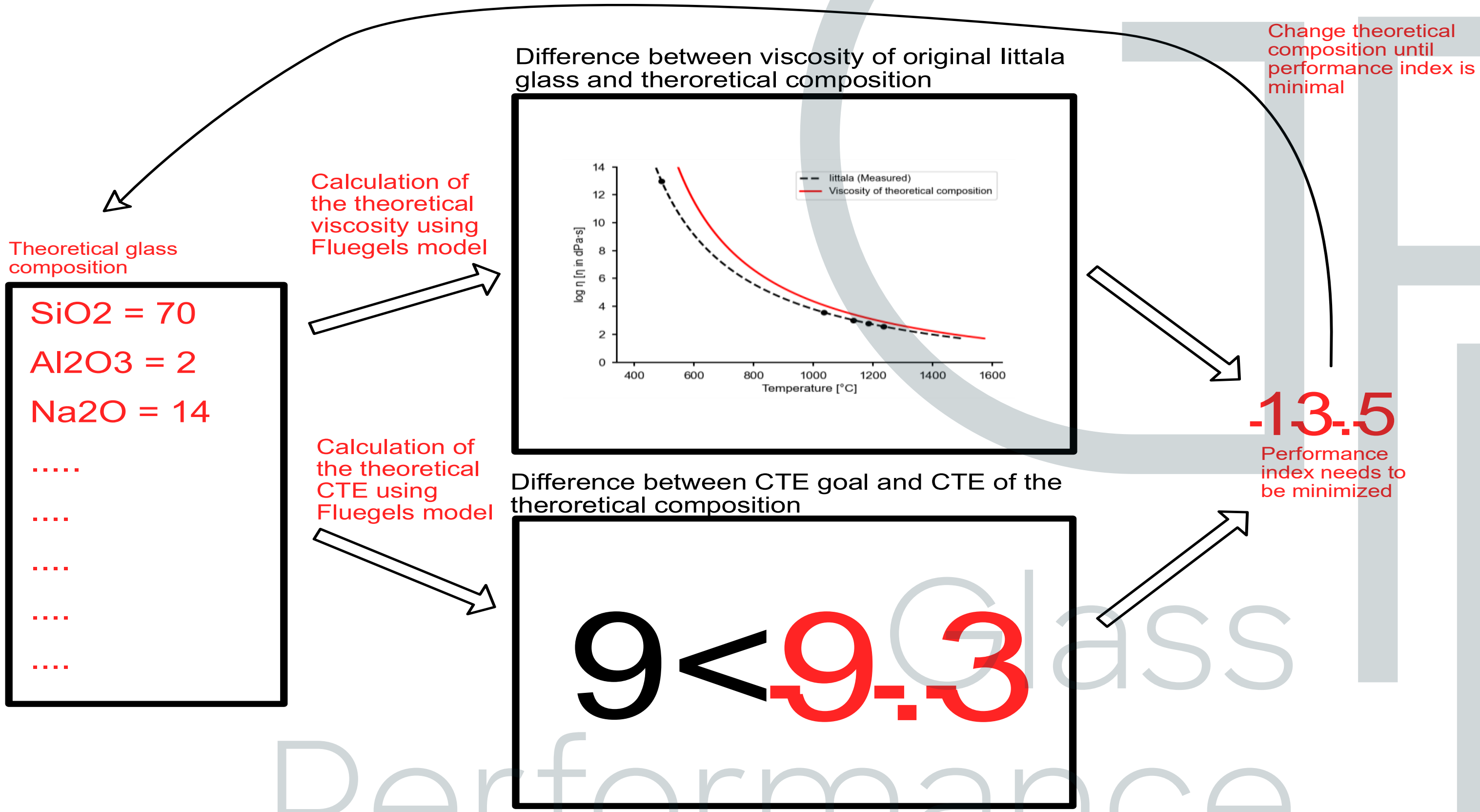
Algorithm to calculate possible glass compositions



- Where possible and especially where models (linear-incremental or non-linear incremental) yield reliable results, the respective parameters have been included in an optimization algorithm.
- Additional BFT trials to screen compositions.

- After feedback loops, compositions narrowed down to two options.

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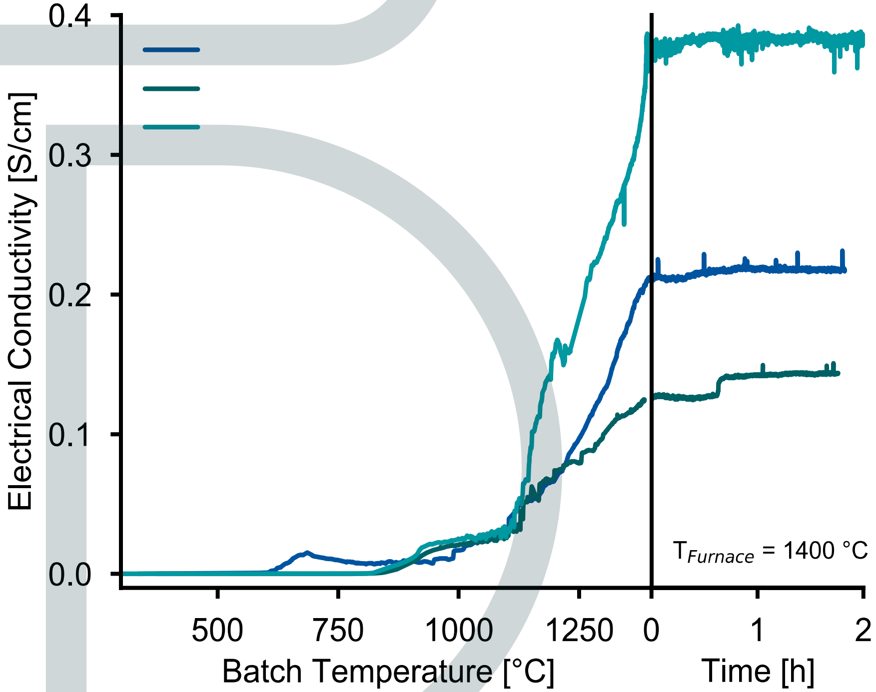
Large scale melting trials for “final” verification

- Proof of lab- and BFT trials in terms of melting-in and turn-over.
- Electrical conductivity evaluation.



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Calculation energy of the batch-to-melt conversion

$$\Delta H_{\mathrm{T,liq}} = H_{\mathrm{T,liq}} - H^{\circ}_{glass}$$

$$H_{\mathrm{T,liq}} = H_{1400°\mathrm{C,liq}} + c_{\mathrm{P,liq}} \cdot (T - 1400°C)$$

$$H_{1400°\mathrm{C,liq}} = \sum_k n_k \cdot H_{1400°\mathrm{C,liq,k}}$$

$$c_{\mathrm{P,liq}} = \sum_k n_k \cdot c_{\mathrm{P,liq,k}}$$

$$\Delta H^{\circ}_{chem} = H^{\circ}_{glass} + H^{\circ}_{gas} - H^{\circ}_{batch}$$

$$H^{\circ}_{glass} = \sum_k n_k \left(H^{\circ}_k + H^{\mathrm{vit}}_k\right)$$

$$H^{\circ}_{gas} = \sum_g n_g \cdot H^{\circ}_g$$

$$H^{\circ}_{batch} = \sum_b n_b \cdot H^{\circ}_b$$

$$\boxed{H_{\mathrm{ex}} = (1 - y_c) \cdot \Delta H^{\circ}_{chem} + \Delta H_{\mathrm{T,liq}}}$$

		Reference	Option 1	Option 2
$H°_{batch}$	kWh/t	4037.9	4417.8	4368.8
$H°_{glass}$	kWh/t	3557.7	3841.0	3841.0
$H°_{gas}$	kWh/t	300.6	426.6	392.5
$H°_{chem}$	**kWh/t**	**179.5**	**150.2**	**135.3**
$\Delta H_{gas,25\text{-}600°C}$	**kWh/t**	**23.4**	**30.3**	**27.5**
$H_{1400°C,liq}$	kWh/t	430.1	434.8	434.8
$c_{P,liq}$	kWh/(t·K)	0.361	0.382	0.382
T_3, Gob cut	°C	1137	1221	1221
$\Delta H_{T3,liq}$	kWh/t	335.3	366.4	366.4
H_{ex}	**kWh/t**	**514.8**	**516.6**	**501.7**

- In terms of chemical reaction enthalpy slight differences between the glasses in favor of option 2.
- The kinetics of the conversion (BFT trials) of option 2 however was slightly worse than option 1.
- These aspects should, in terms of melting performance, balance each other.

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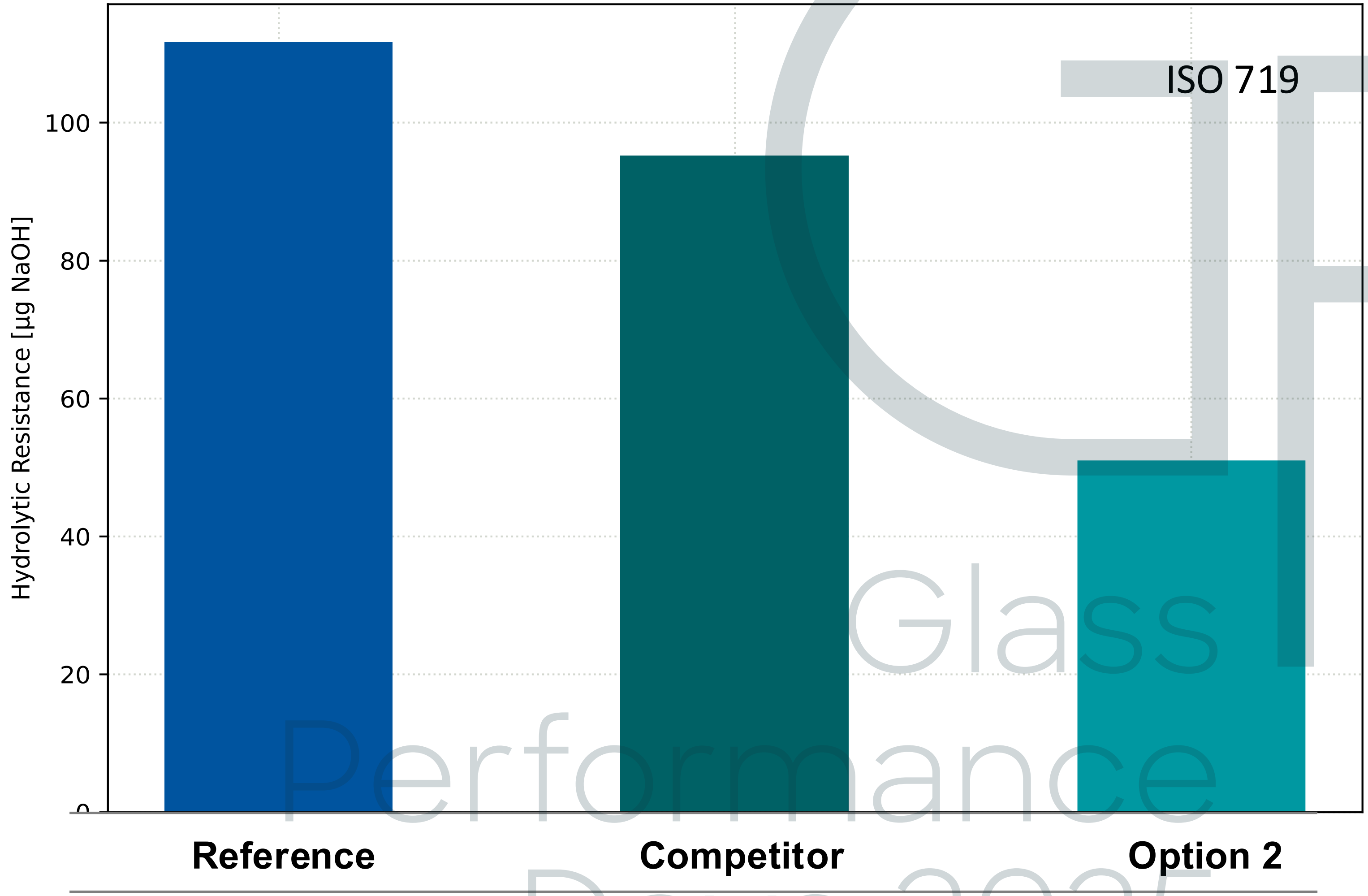
Hydrolytic resistance



The optimized glass has water resistance class 2 (instead of 3).

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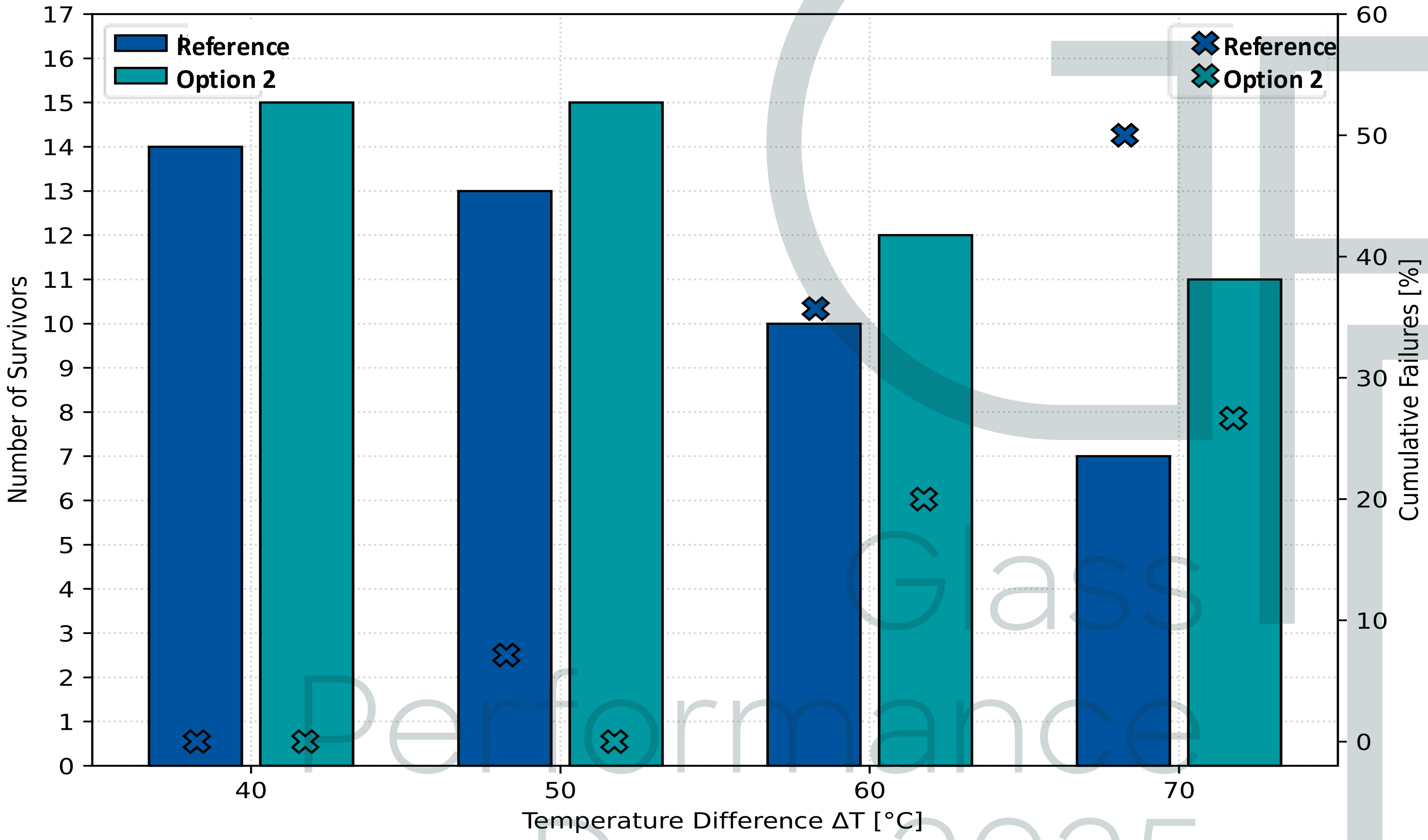
Thermo-shock resistance



Significant improvement of thermal shock resistance at all dT's.

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The results…

1. **CLAIM:** CTE and thermal shock resistance improved.
   - New glass CTE 9.2 ppm·K^{-1} (better than all competitors, including reference).
2. **CLAIM:** Mechanical resistance improved, both scratching and edge chipping.
   - Flexural strength is at a similar level for all glasses. However, edge chipping is connected to hydrolytical stability.
3. **CLAIM:** Dish washer resistance improved (class2)
   - The new glass was the only tested glass in class 2. All others tested in class 3.
4. **CLAIM:** Sb_2O_3 removed completely and BaO reduced.
   - The new glass does not contain Sb_2O_3, BaO or B_2O_3.
5. **CLAIM:** Centrifuge and pressing products can be manufactured from the same mass glass.
   - Trials showed that the glass can be used for centrifuge and pressing with similar forming parameter.

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Examples for improving the sustainability of glass melting and processing

ENERGIE- UND CO_2-EINSPAREN MIT ZEROCO2GLAS
Gefördert durch:
Bundesministerium für Wirtschaft und Klimaschutz
aufgrund eines Beschlusses des Deutschen Bundestages

II. Innovative glass-development: CO_2- and Soda-free glasses

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How to get to CO_2-free glasses?

Electrolysis-H_2 ?

TCR-NH_3 ?

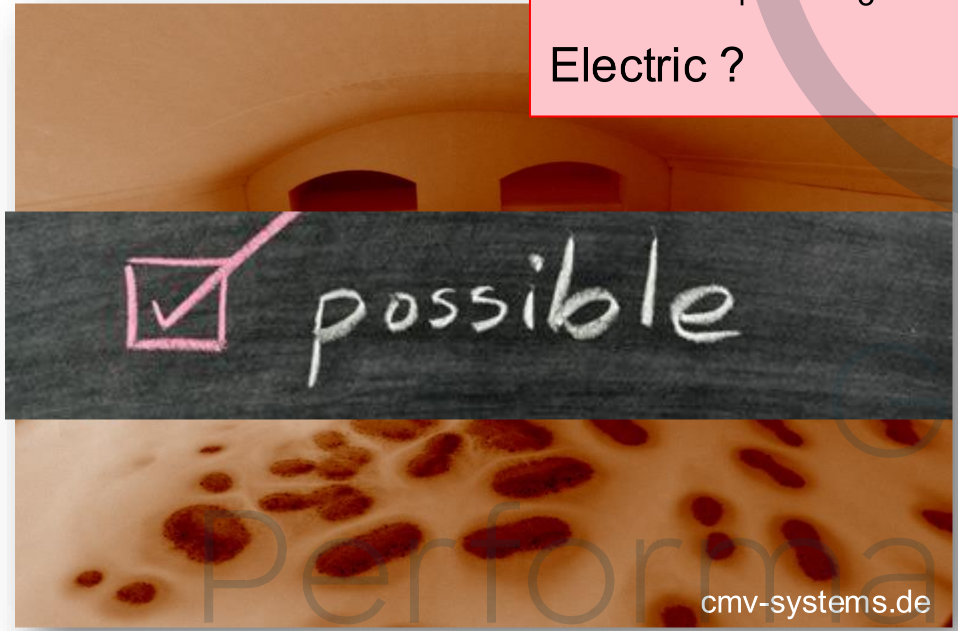
TCR CH_4 / CH_3OH ?

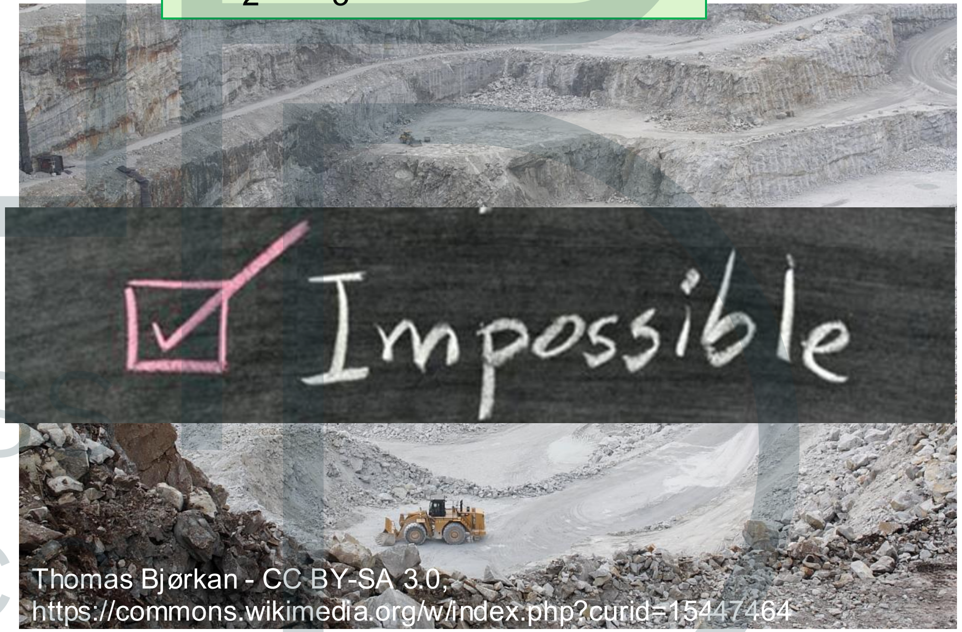
Electric ?

$CaCO_3$?

$MgCO_3$?

Na_2CO_3 ????????????





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Soda-free glasses

Simple math:

20 - 30 % of the total CO_2 comes from the batch itself, depending on cullet (e.g. 27 % at 60 % cullet).

Options for Carbonate-free batches

→ Cullet ratio?
→ calcinated raw-materials?
→ Get rid of Soda!

E-glass based composition without soda / sodium coming from other raw materials

	REF	Xa	Xc	Ya1	X	Xb	Y2	Ya2
	IST	IST	IST	IST	IST	IST	IST	IST
SiO2	73,27	60,7	60,06	58,94	61,15	58,88	60,50	61,08
Al2O3	1,56	14,17	15,02	14,17	13,34	16,53	12,81	11,61
CaO	9,12	17,45	17,43	17,73	20,75	17,53	22,44	17,94
MgO	2,58	1,27	1,27	2,68	1,43	1,22	2,93	2,52
Na2O	11,97	5,17	5,01	5,21	2,09	5,09	0,09	5,51
K2O	0,93	0,48	0,43	0,49	0,48	0,14	0,48	0,51
Fe2O3	0,2	0,25	0,23	0,26	0,29	0,23	0,24	0,29
TiO2	0,05	0,34	0,33	0,35	0,35	0,17	0,33	0,38
SO3	0,27	0	0,09	0,11	0,06	0,07	0,05	0,08
B2O3	0	0	2,00*	0	0	2,00*	0	0

EP 22 179 847.3
C. Roos, R. Conradt, F. Güclü

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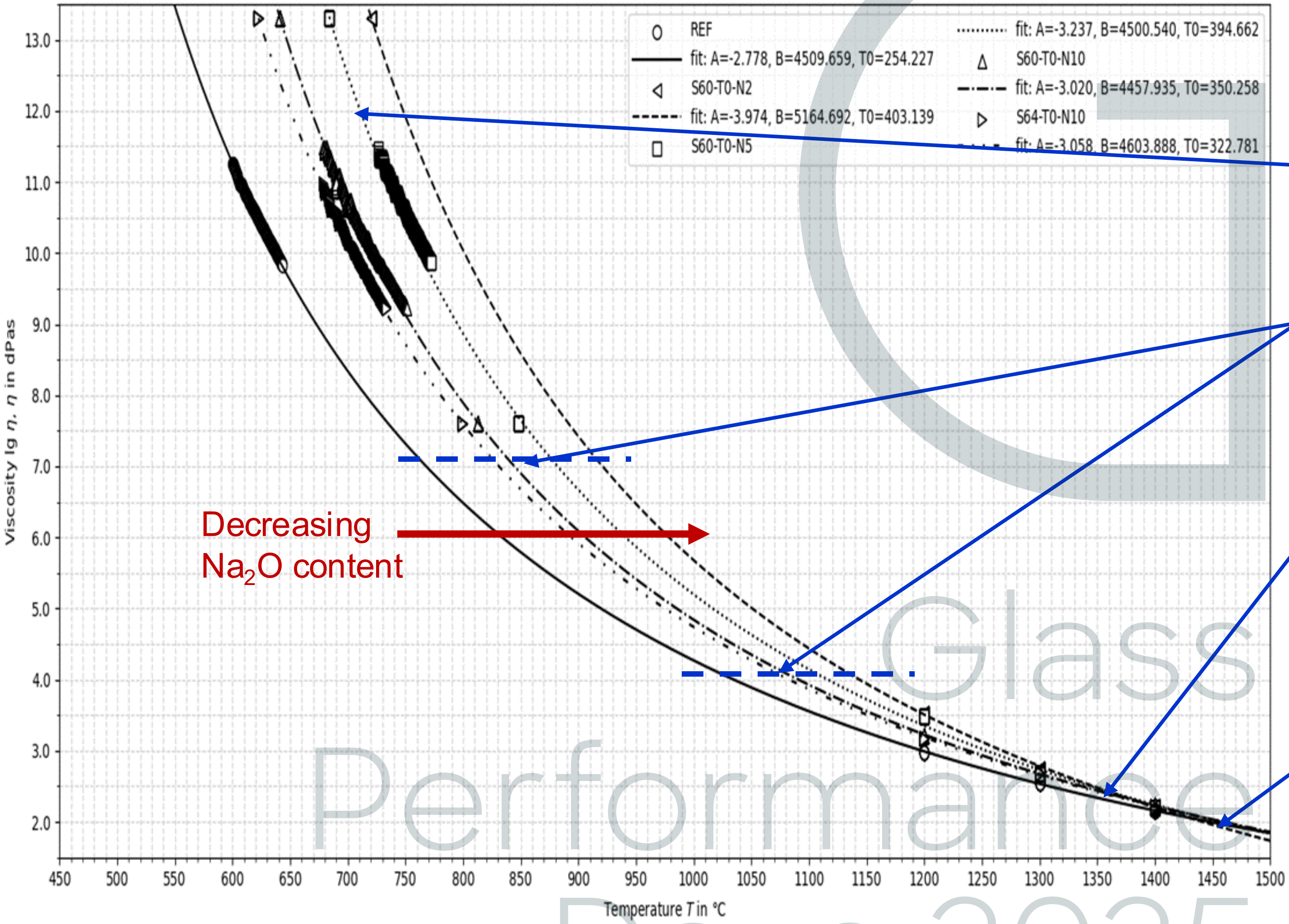
Meltability of Soda-free glasses - viscosity



Annealing is crucial, as dT is much higher than conventional lehrs can handle + much shorter times required.

Forming is crucial (higher T, material heat load)

Electrical heating in lower T-zones (Feeder) may be crucial (Na ↔ Ca + higher η)

Meltability seems to be „no“ problem

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CO_2 and Soda-free glasses

IPGR
International Partners in Glass Research

Department of Glass and Glass-Ceramic | RWTH AACHEN UNIVERSITY

IOB Institut für Industrieofenbau und Wärmetechnik | RWTH AACHEN UNIVERSITY

HORN GLASS INDUSTRIES

Wiegand-Glas

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Efficiency of combustion an relation to flame temperature

Chambadal–Novikov efficiency:

$$\eta_\infty = 1 - \sqrt{\frac{T_0}{T_{ad}}}$$

Leads to a combustion efficiency (NTP, if applicable: non-stoec.) of

	T_{ad} / K	Efficiency
CH_4-Air	2.233	0.65
Heavy Oil-Air	2.375	0.66
NH_3-O_2	2.380	0.66
CH_4-O_2	2.599	0.68
H_2-O_2	2.792	0.69

- In reality the process is never adiabatic.
- In the high temperature of the flame there may be product dissociation and other reactions in addition to the main combustion reaction.
    - ➢ Therefore, the highest temperature does not necessarily mean stoichiometric combustion.
- Usually λ slightly < 1, yielding better ignition and flame stability due to higher flame speed.
- For comparison: 1 eV e^- equals roughly 11.600 K

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Some simple math….

Data taken from:
VDI-Wärmeatlas
Perry's Chemical Engineers' Handbook
Ullmann's Encyclopedia of Industrial Chemistry

	Calorific value		Calorific value			„CO2-Efficiency“ (primary)
	lower	upper	lower	upper	CO2-release	CO2 per 1 kJ "Hex"
	[MJ/kg]	[MJ/kg]	[kJ/mol]	[kJ/mol]	[kg/kg]	[g/kJ (Hu)]
H2	120,00	141,86	241,92	285,99	0,00	0,00
CH4	50,00	55,50	802,15	890,39	2,74	54,86
C2H6	47,50	51,90	1.428,33	1.560,63	2,93	61,62
C3H8	46,30	50,40	2.041,69	2.222,49	2,99	64,67
C4H10	45,60	49,50	2.650,45	2.877,14	3,03	66,42
C2H4	47,20	51,30	1.324,15	1.439,17	3,14	66,47
C3H6	45,80	48,90	1.927,31	2.057,76	3,14	68,50
C2H2	48,20	50,20	1.255,03	1.307,11	3,38	70,13
CH3OH	19,60	22,70	628,02	727,35	1,37	70,08
C2H5OH	26,80	29,70	1.234,65	1.368,25	1,91	71,29
NH3	18,60	22,50	316,77	383,19	0,00	0,00
CO	10,10	0,00	282,90	0,00	1,57	155,56
H2S	15,00	18,60	511,14	633,81	0,00	0,00
Zr	19,00	0,00	1.733,26	0,00	0,00	0,00
C4N2	59,94	0,00	4.558,88	0,00	2,31	38,61

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Thank you very much for your attention

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Examples for improving the sustainability of glass melting and processing

III. Sustainability in forming-process: Avoidance of glass-contact lubricants

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A new approach to glass contact interactions

Describe a highly

- non-Arrhenius
- non-isothermal
- non-static
- non-isochemical
- non-Newtonian (?)
- non-ideal surface situation…

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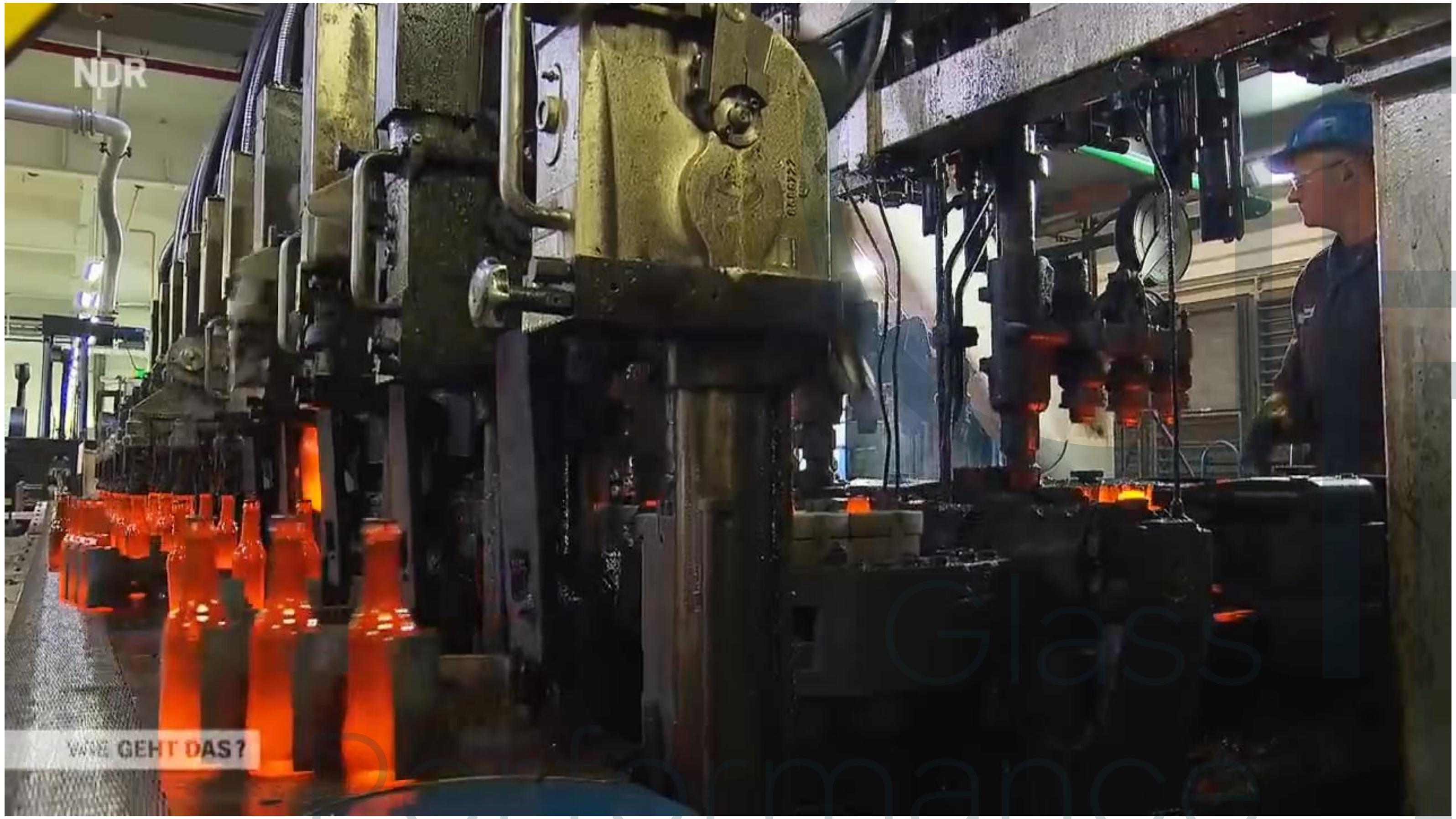
A new approach to glass contact interactions



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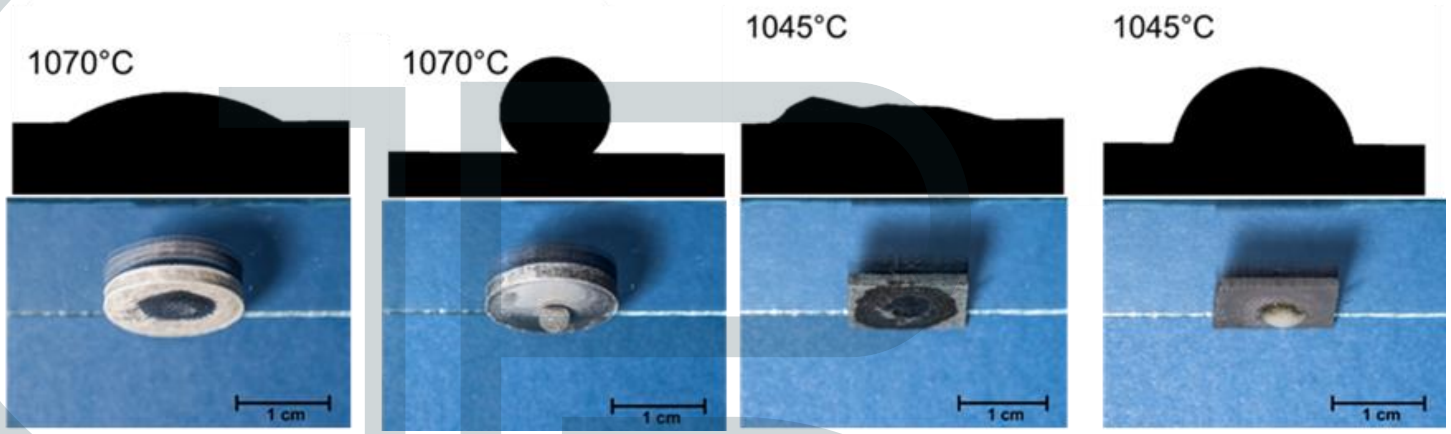
A new approach to glass contact interactions

- Optimize system for non-isothermal conditions
- Evaluate multiple materials (materials-combinations)
- Calculate adhesion forces based on Van-der-Waals approach (adhesion force depends on London and Debye forces)



$$\omega(r)_{Debye} = -\frac{u_{01}^2 \cdot \alpha_{02} + u_{02}^2 \cdot \alpha_{01}}{(4\pi\epsilon_0\epsilon)^2 \cdot r^6}$$

$$\omega(r)_{London} = -\frac{3}{2} \cdot \frac{\alpha_{01}\alpha_{02}}{(4\pi\epsilon_0)^2 \cdot r^6} \cdot \frac{h \cdot \nu_{01}\,\nu_{02}}{\nu_{01} + \nu_{02}}$$

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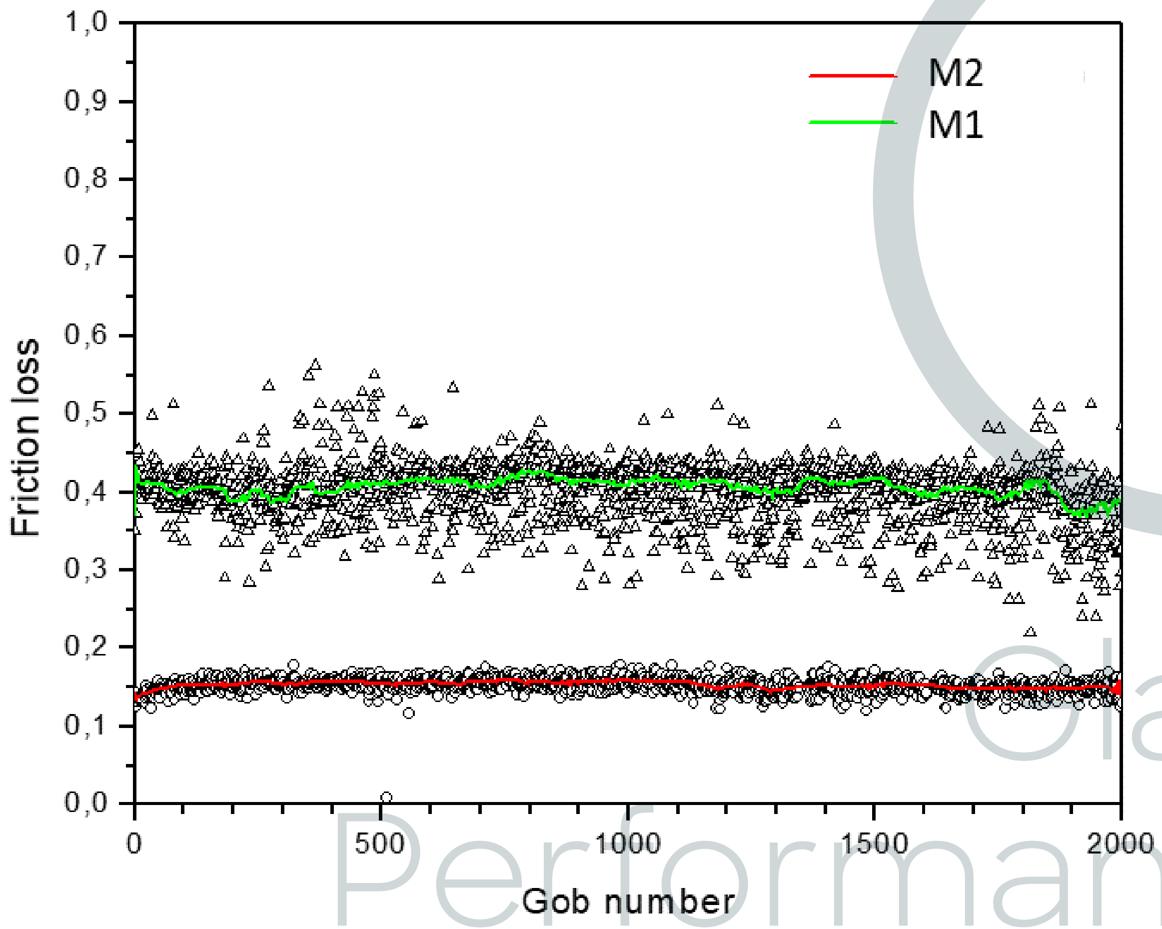
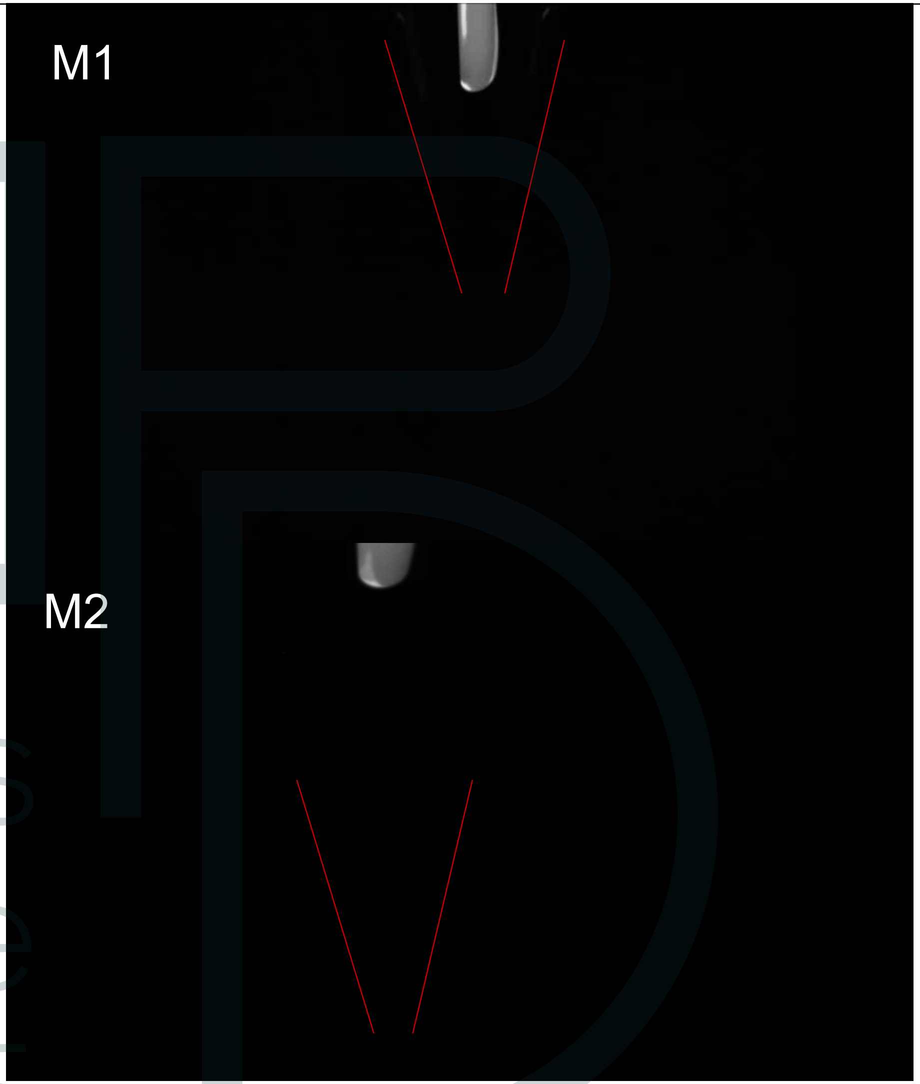
A new approach to glass contact interactions





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