uniglassAC GmbH

offers services in the consultation of glass producers and suppliers to this branch. Services extend to the education of factory staff, the analysis of primary production processes, and glass development.

Courses for factory staff have been performed for glass producers and suppliers alike. They provide recent knowledge in glass science and technology and always build the bridge to the needs of production staff.

INDUSTRY COURSES:

- energy utilization,
- raw materials,
- batch melting,
- use of thermochemical methods in glass technology,
- heat transfer,
- relaxation kinetics and melt strength,
- melt-gas interaction, emissions, flue gas cleaning,
- glass-water interaction, hydrolytic stability, bio fluid exposure, dish washing,
- design of glass composition with respect to: energy, liquidus temperature, hydrolytic stability, elastic constants.

Consultation projects comprised the topics of energy utilization optimization from planning to full-scale test campaigns with a special focus on use of raw materials, furnace performance, and high-T reactions. Another focus is the optimization of glass composition, e.g., for liquidus temperature, hydrolytic stability, elastic properties, or the use as solder glass ceramic systems.

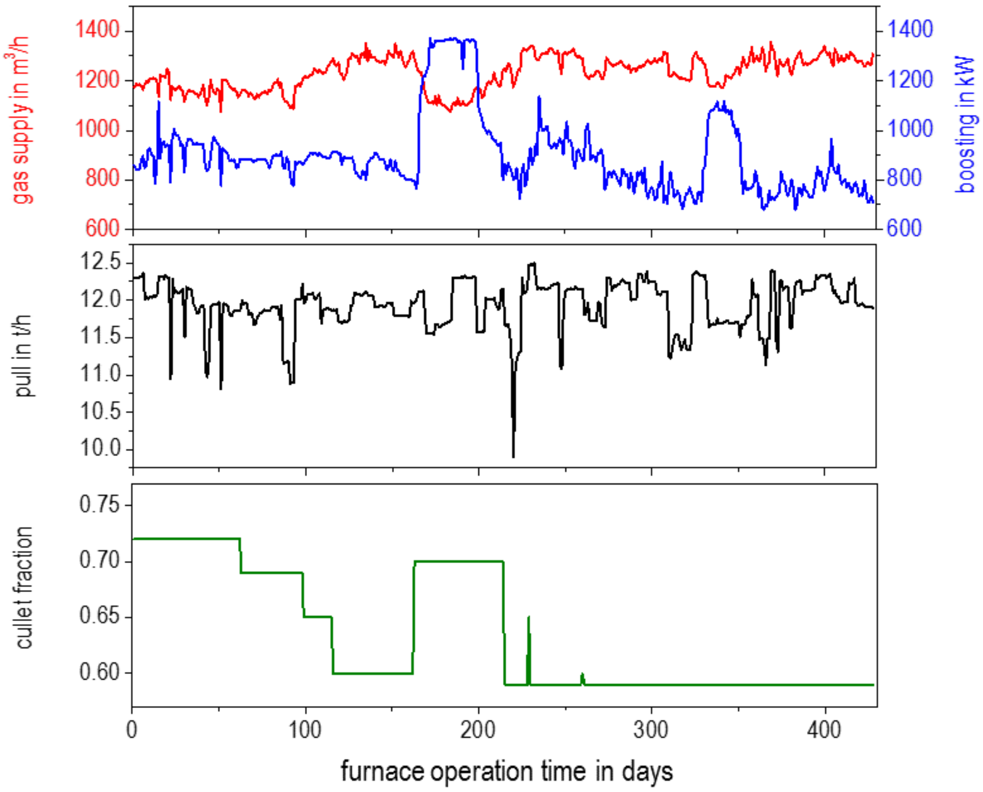
REFERENCE PROJECTS:

- furnace performance analysis, consortium with container glass sites in Australia, Austria, Germany, Japan, Mexiko, Spain, Thailand, U.S.A.; 26 cases, observation period 2 years each;
- 12 cases: container, tableware, crystal, continuous fibre, wool, soluble glass; comprising 7 campaigns with full-scale batch changes;
- support to the design of a batch pre-heater: heat transfer, bulk solid flow;
- product development and calculations of intrinsic heat demand of melting upon use of different raw materials for different
  - raw materials suppliers,
  - furnace construction companies,
  - producers of mineral insulation fibres and continuous fibres;
- evaluation of in vitro tests for health risk assessment of insulation fibres;
- optimization of clinker formation and hydration in cement industry.

INDIVIDUAL HIGHLIGHTS

Glass producers host a treasure of data of furnace operation which may be analyzed and evaluated retrospectively. Such an evaluation is the basis for the evaluation of furnace performance, and its optimization.

Example: 97 m^2 end port fired furnace, air-gas, green. The energy input, the pull, and the cullet fraction are plotted vs. time. Then, the quantities P_{in}, P_{ex}, P_{loss}, are determined and also plotted versus the pull.



FGI. 1. Primary operation data as received from industrial partner

In the energy balance, the power input P_{in} by fuel and boosting is usually well known. A lack of accurate information exists with respect to the power P_{ex} drawn from the furnace. By thermochemical methods, it can be assessed accurately for any raw material batch from $P_{ex} = p \cdot H_{ex}$, where H_{ex} is given by

$$H_{ex} = (1 - y_C) \cdot \Delta H^\circ_{chem} + \Delta H(T_{ex});$$

H_{ex} = exploited heat, p = pull rate, y_C = cullet fraction per 1000 kg of glass,)$\cdot \Delta H^\circ_{chem}$ = standard chemical heat demand of the batch-to-melt conversion (25 ↑8C, 1 bar); $\Delta H(T_{ex})$ = heat physically stored in the melt at exit temperature T_{ex}. P_{in}, P_{ex}, and hence, P_{loss} are “functions of state”; they do not depend on the actual reaction path or on furnace operation.

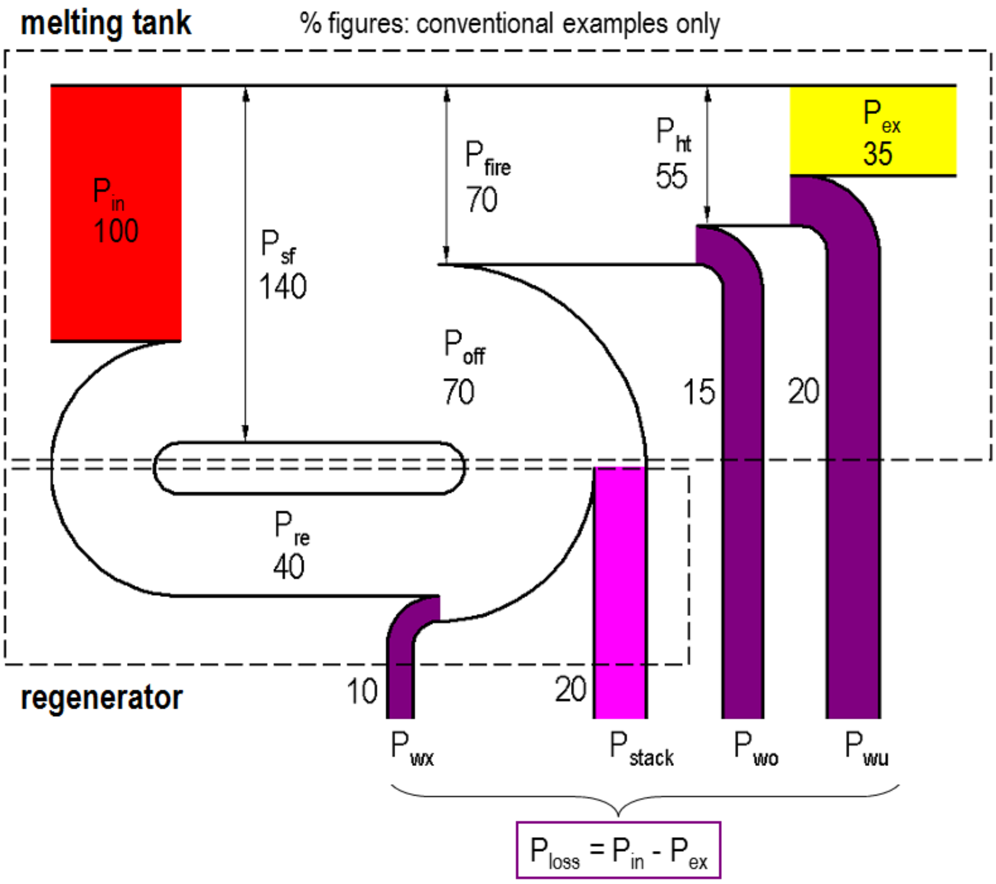


FIG. 2. Heat balance in terms of powers

The exploited heat is very different for different glass products as well as for different raw materials used to produce them. The table below gives guidelines for standard batches:

Exploited heat for different glass types, standard batches, T_{ex} = 1300 °C

glass	Hex in kWh/t
74-10-16	556,4
bottle	565,4
flacon	551,5
table	586,5
cover	801,1
low a	732,4
E	720,1
ECR	543,2
basalt	470,4
NS2.2	649,3
NS3.3	605,1
KS2.2	476,7

R. Conradt: **The industrial glass melting process.** In: The SGTE casebook – Thermodynamics at work, K. Hack, ed., CRC Press, Boca Raton 2008, chapter II.24, 282 – 303.

– " – : **Thermodynamics of Glass Melting.** In: Fiberglass and Glass Technology – Energy-Friendly Compositions and Applications. F.T. Wallenberger & P.A. Bingham, eds., Springer Verlag, Berlin 2010, chapter 9, 385 – 412.

Published oxide factor systems for the calculation of the heat $\Delta H(T_{ex})$ physically stored in the melt at exit temperature do not reach, except for simple soda lime silicate based composition, the accuracy required for an industrial heat balance.

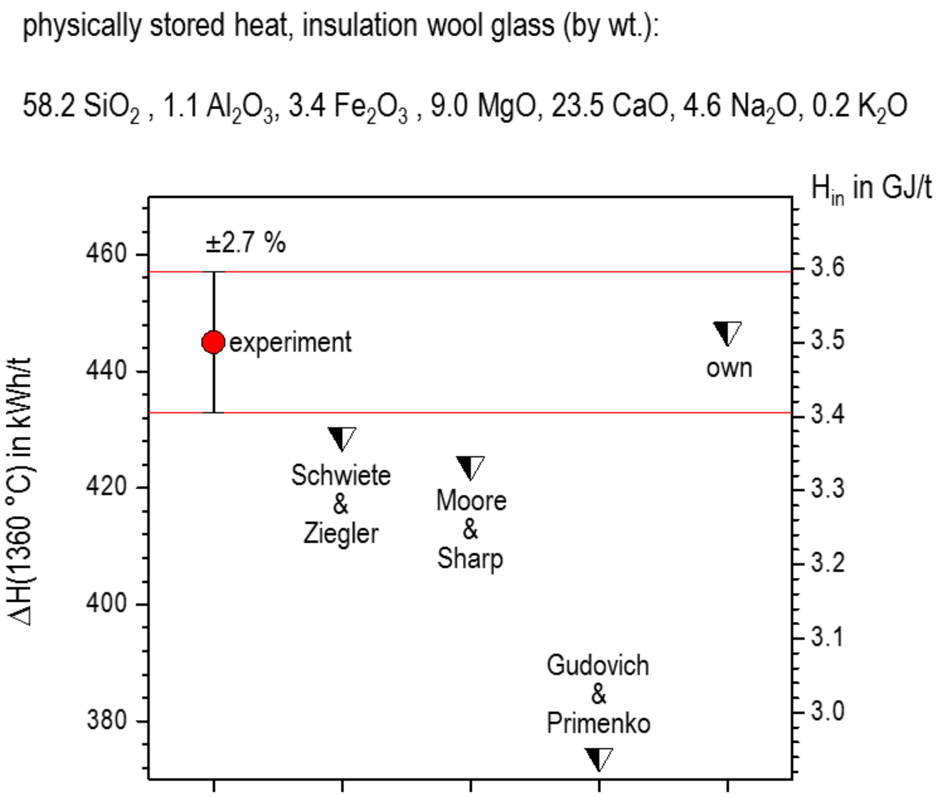


FIG. 3. Accuracy of the thermochemical approach to $\Delta H(T_{ex})$ as compared to published oxide factor systems

The energy balance is a first approach to furnace performance only. It gives a snapshot of a specific load situation of a furnace only. The dependence of furnace performance on the pull rate p follows the theory of heat exchangers and provides a useful way of evaluation. Primarily, furnace performance is characterized by three parameters, i.e., H_{ex} (the batch used) and a, b characteristic of the specific furnace construction and fuel used

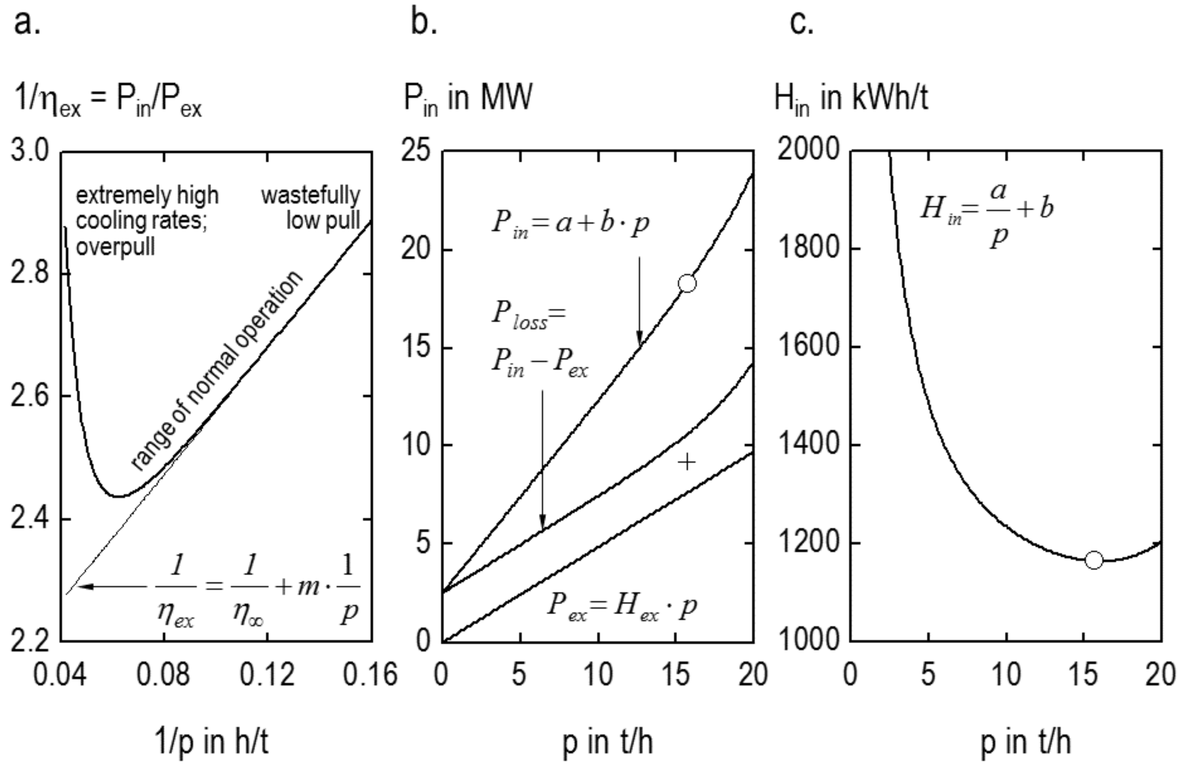


FIG. 4. Dependence of furnace operation on pull rate;
a. physical limits,
b. plot power vs. pull rate,
c. plot overall energy demand $H_{in} = P_{in}//p$ vs. pull rate;
data: end port, air-gas, 97 m^2, Cr-green containers, 70 % cullet

The following two examples refer to industrial campaigns where energy utilization was optimized via the use of a different batch

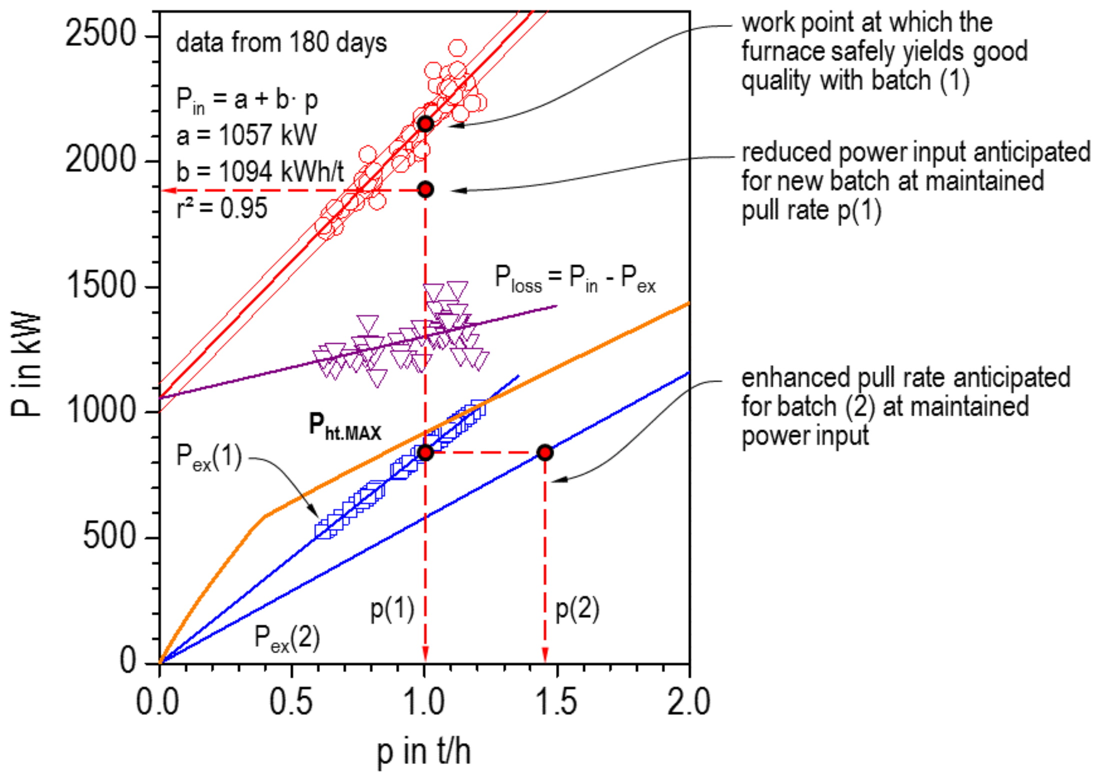


FIG. 5. Analysis of a small continuous fibre furnace; options for performance optimization by replacing batch (1) by batch (2) with less energy demand; pull rate could be enhanced by 45 %

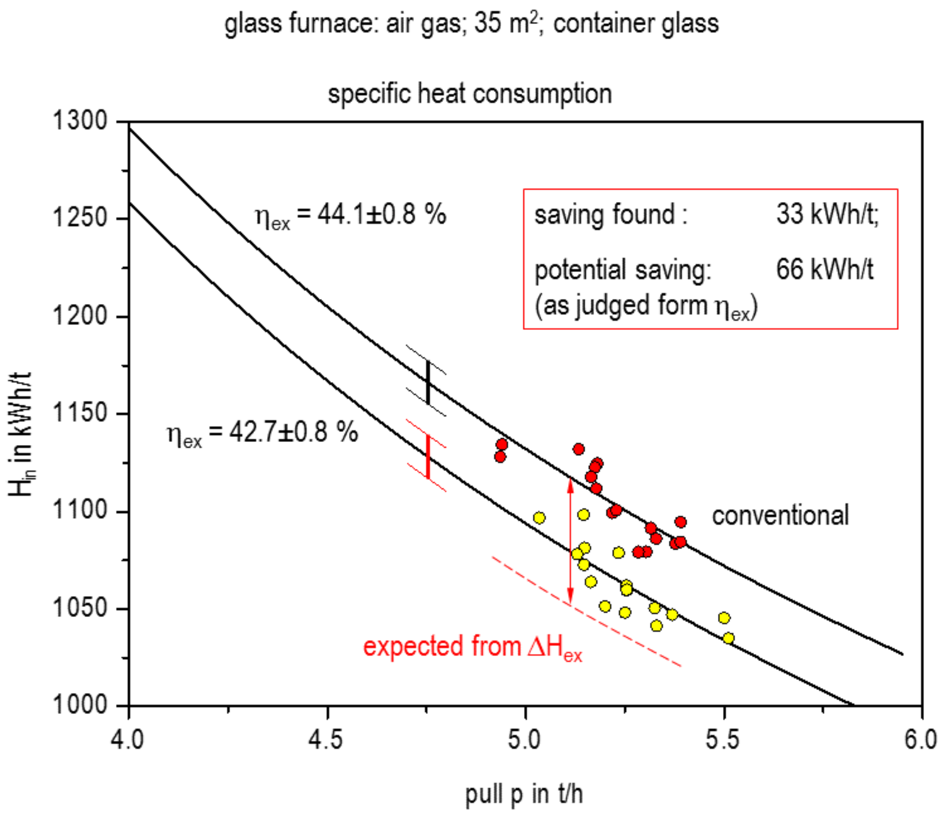


FIG. 6. Assessment of energy saving expected from the replacement of limestone by lime hydrate in a container glass batch; the campaign was extended to 7 d (conventional batch), 7 d (new batch), 7 d (conventional batch); savings actually found and savings expected long term after final adjustment to the new situation

As a result of an extended survey of container glass furnaces, the heat capacity match between the mass flow through the combustion space and the mass flow through the melting compartment was found to be a most essential figure. It is the primary influence distinguishing the overall efficiency of energy exploitation among different types of furnaces as well as of furnaces belonging to the same group. Beyond any other optimization strategies, optimizing this heat capacity match is a challenge for glass producers and furnace constructors alike.

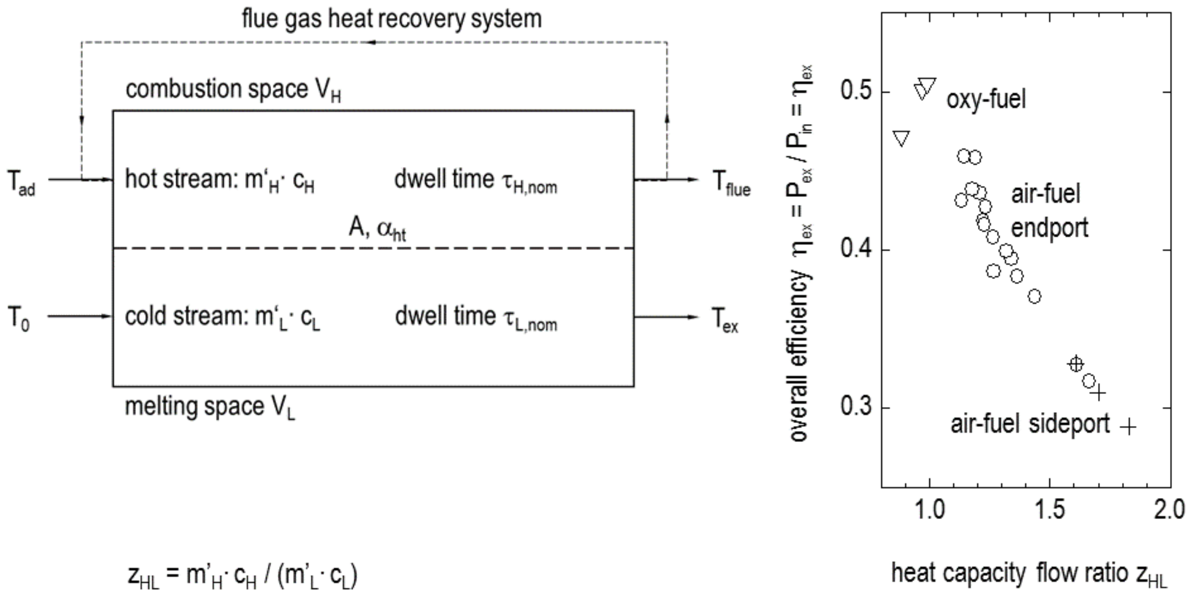
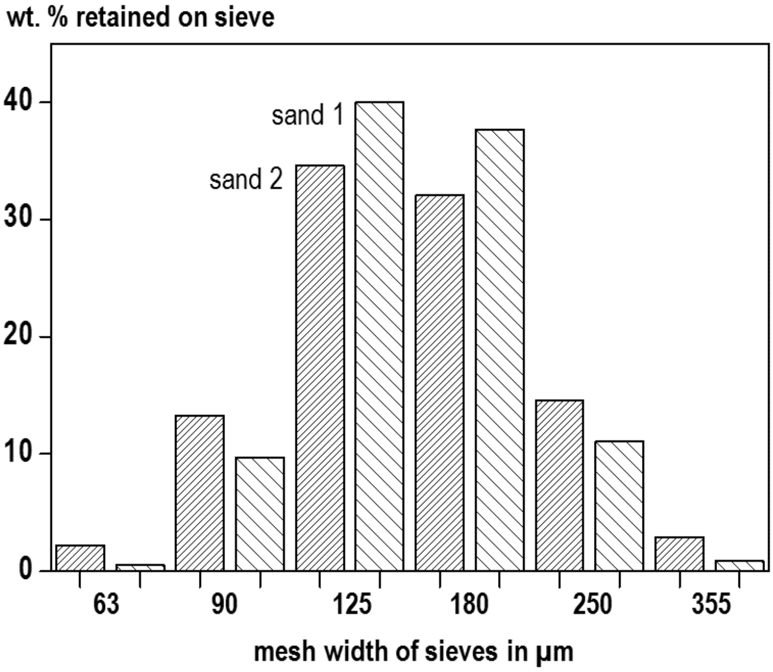


FIG. 7. Left graph: principle sketch of a furnace in its function as a heat exchanger;
Right graph: efficiency of energy exploitation of different container glass furnaces as a function of their heat capacity match z_{HL}; by construction, sideport furnaces suffer from a handicap while oxy-fuel furnaces are optimal in this respect; endport furnaces differ by construction, fuel to boost ratio, and excess of false air

In another campaign, the effect of the use of two sand qualities with different grain size distribution was analyzed with respect to sand dissolution during melting. According to the analysis, sand 2 was inferior to sand 1, which was verified by the results during production.



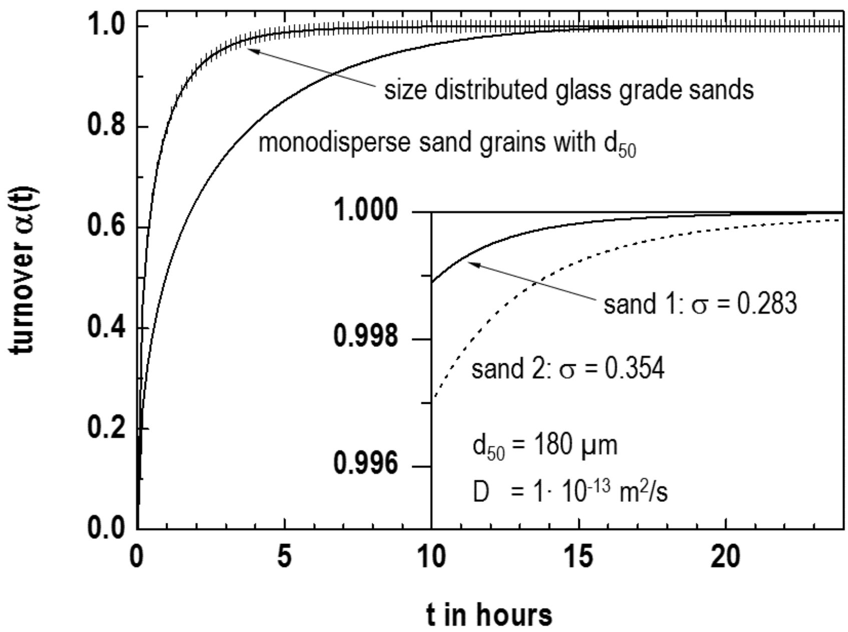


Fig. 8. Upper graph: grain size distribution of two sand qualities;
Lower graph: expected sand dissolution behavior;
sand 1 is clearly superior to sand 2, which may not be read in the same clear way from size distribution alone;
an estimate based on the median size d_{50} alone is definitely useless

Thermochemical methods are a valuable tool for a fully quantitative characterization of industrial glasses and their melts. The approach is based on the evaluation of phase diagrammes. It allows one to predict thermal and elastic properties of glasses and glass melts.

TABLE 1. Thermocemical analysis of a float glass composition; referernce phases mark the location of the glass composition within the phase diagramme; shorthand notation: S = SiO_2, P = P_2O_5, T = TiO_2, F = FeO, M = MgO, C = CaO, N = Na_2O, K = K_2O; G*f* = Gibbs energy of formation from the elements (as required for the assessment of hydrolytic stability), $H°_{GLASS}$ = standard enthalpy of the glass, HT = heat content of the melt; cPL = heat capacity of the melt, ΔcP = heat capacity jump in the glass transition, Svit = vitrification entropy; a_{AG} is a parameter determining the viscosity-temperature behavior of the melt

INPUT: float glass	g/100g	M(j)	n(j)	N	n(el)
SiO2	71.75	60.084	1.1942	3	3.5825
TiO2	0.14	79.898	0.0018	3	0.0053
Al2O3	1.23	101.961	0.0121	5	0.0603
Fe2O3	0.12	159.691	0.0008	5	0.0038
FeO	0.07	71.846	0.0010	2	0.0019
P2O5	0.00	141.945	0.0000	7	0.0000
MnO	0.00	70.937	0.0000	2	0.0000
MgO	4.18	40.311	0.1037	2	0.2074
CaO	6.73	56.079	0.1200	2	0.2400
Na2O	14.96	61.979	0.2414	3	0.7241
K2O	0.38	94.203	0.0040	3	0.0121
SO3	0.44	80.061	0.0055	4	0.0220
SUM	100.00		1.6843		4.8594

ENERGETICS				
G*f*	1324,5	kJ/100g	25	°C
H°Glass	3908,1	kWh/t	25	°C
HT	435,3	kWh/t	1350	°C

RHEOLOGY		
cPL	1,4001	J/(g·K)
ΔcP	0,1880	J/(g·K)
Svit	0,1007	J/(g·K)

$$a_{AG} = \frac{\Delta c_P}{S^{vit}} = 1.88 \pm 0.03$$

PHASE CONTENT	n(k)	M(k)	g/100g
C3P	0.0000	310.182	0.00
CT	0.0018	135.977	0.24
Fe3O4	0.0008	231.537	0.17
FS	0.0002	131.930	0.03
MnSiO3	0.0000	131.021	0.00
MS	0.1037	100.395	10.41
KAS6	0.0040	556.668	2.25
NAS6	0.0080	524.444	4.21
Na2SO4	0.0055	142.040	0.78
NS	0.0000	122.063	0.00
NS2	0.1884	182.147	34.32
CS	0.0000	116.163	0.00
N2CS3	0.0000	360.289	0.00
NC2S3	0.0000	354.389	0.00
NC3S6	0.0394	590.720	23.29
S	0.4045	60.084	24.30
SUM			100.00

TABLE 2. Gibbs energies of formation G^f_{el} from the elements of industrial mineral fibre glass compositions, each containing 12 different oxides

	G^f_{el} [kJ/mol]	
	experiment	calculation
glass a	-852.0	-849.6
glass b	-865.0	-867.2
glass c	-880.8	-881.8

The accuracy of thermochemical methods is also reflected by a comparison to independent viscosity measurements. For many glasses, the parameter a_{AG} (see TABLE 1) calculated via thermochemistry agrees very well with a_{AG} derived from the steepness of the viscosity curve (the “length” of a glass). Due to the quality of thermodynamic data for some reference phases, this method cannot be extended yet to all kinds of glass compositions at an accuracy required for technological application

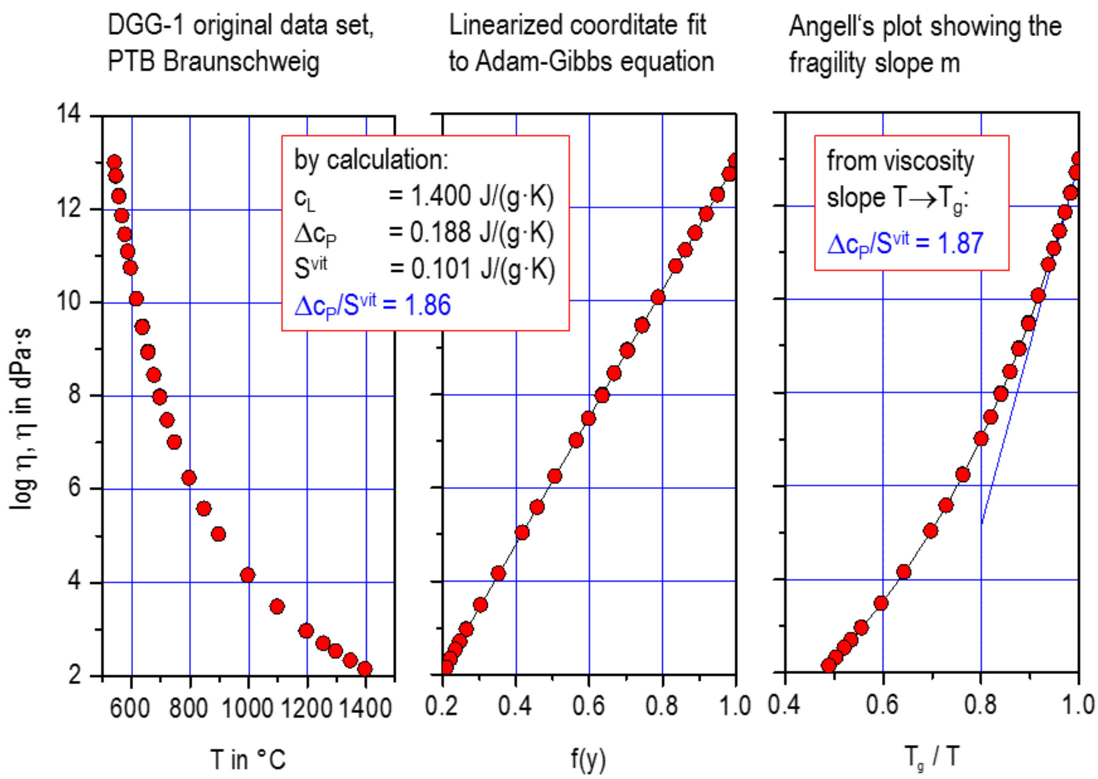


FIG. 9. Left graph: viscosity data of standard float glass DGG-1 as measured by PTB Braunschweig; VFT plot;
Center graph: evaluation of data by a linearized plot yielding the rheological parameter a_{AG} used in the Adam-Gibbs model of viscosity;
Right graph: viscosity datat plotted vs. T_g/T (Angell’s plot) illustrating the slope by which viscosity approaches T_g

As another example, an approach to the hydrolytic stability of glasses and the expected dissolution rates is presented. It is assessed by a thermochemical approach reflecting the energetic of the process combined with the analysis of the coverage of the glass surface by charged species (H^+, OH^-, Na^+) from the solution reflecting its kinetics. By this approach, glass composition may be analyzed and optimized with respect to their hydrolytic, acid, and caustic stability, to their dissolution rates, and to the differentiation of their surfaces during the process. Tha approach works is simple solutions as well as in biogentic solutions, dish washer media, etc.

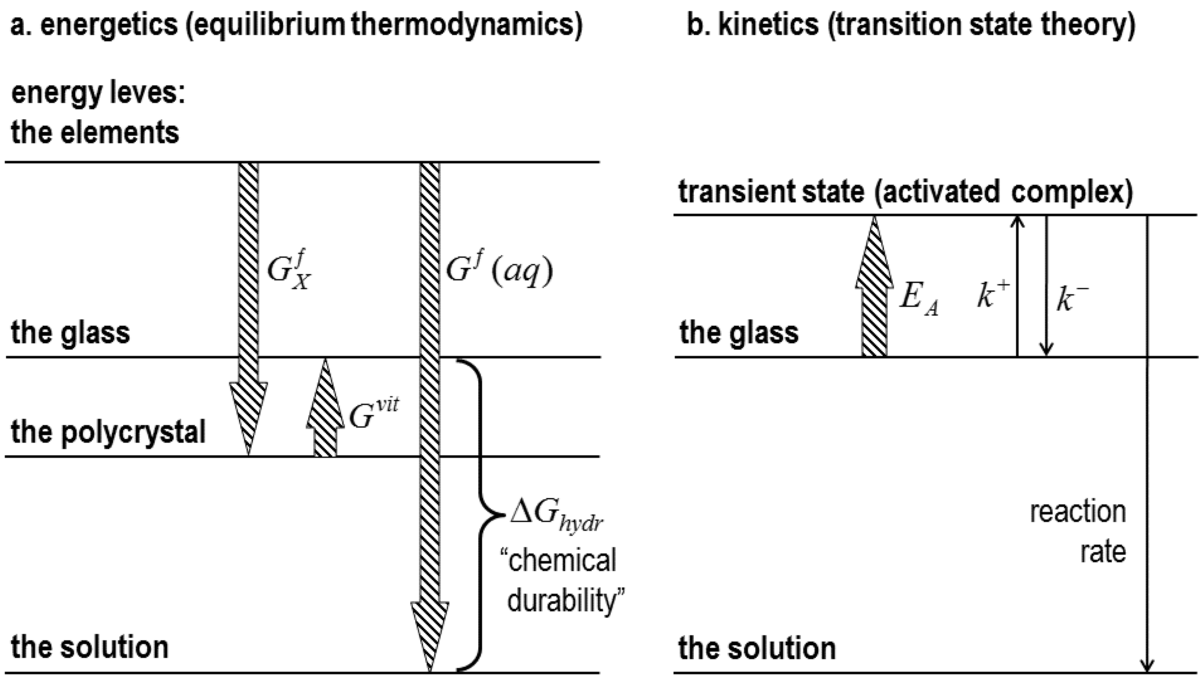


FIG. 10. Energetic and kinetic aspects involved in the reaction between a glass and an aqueous solution

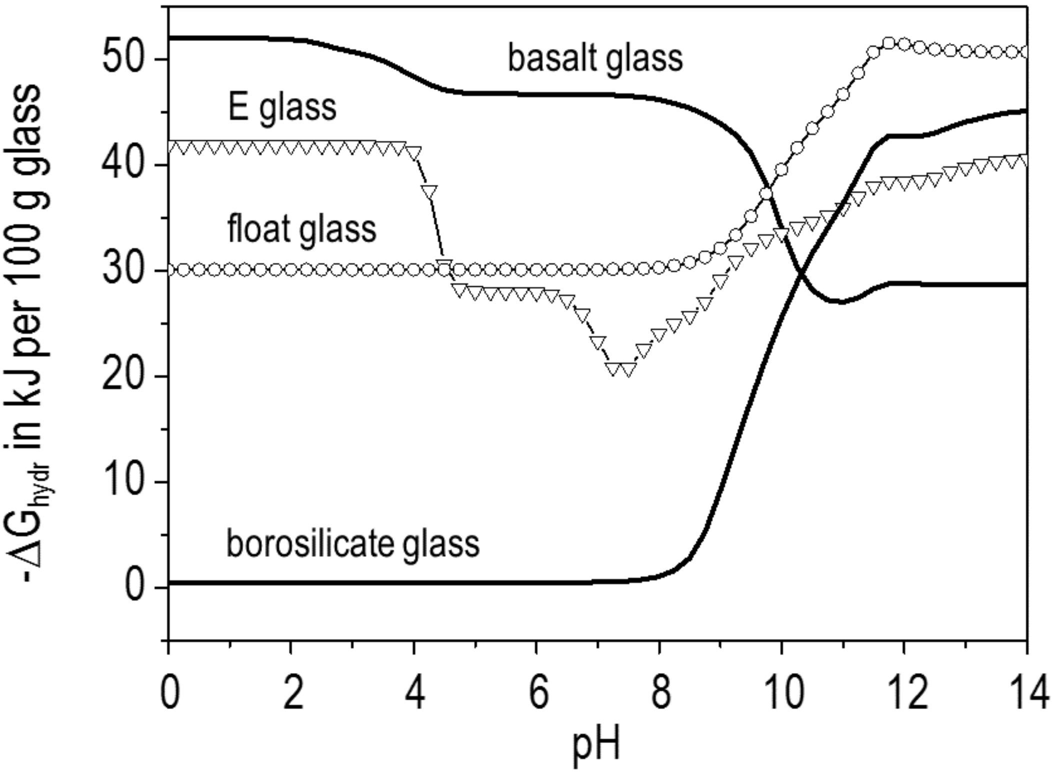


FIG. 11. Fingerprints of acid, hydrolytic, and caustic stability of different industrial glass compositions; stability decreases in vertical direction

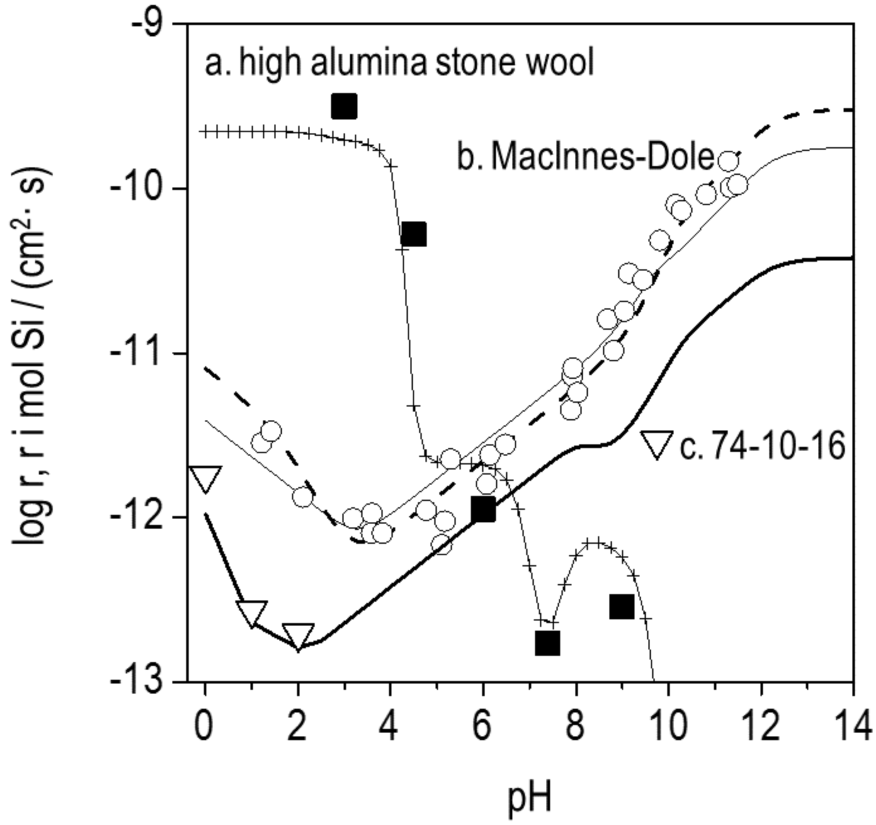


FIG. 12. Dissolution rates of different glasses in aqueous solutions as a function of pH value; calculated values and experiments; the dashed line for the MacInnes-Dole glass takes into account the early precipitation of a calcium hydrate silicate phase

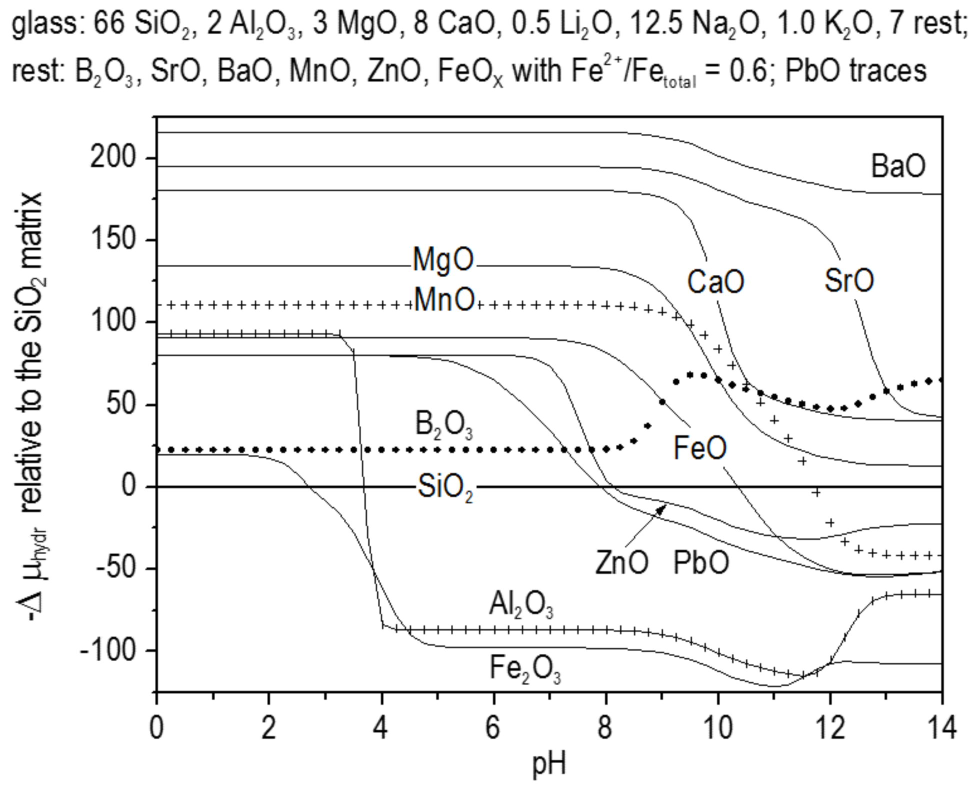


FIG. 13. Stabilities $\Delta\mu_{hydr}$ of different oxides in an insulation fibre glass relative to the silica network; stability decreases in vertical direction; oxides above the SiO_2 line are preferentially leached out while oxides below this line are enriched in the glass surface