



CelSian

The contribution of thermodynamics in determining the parameters of elaboration and energy efficiency

C. Claireaux, CelSian

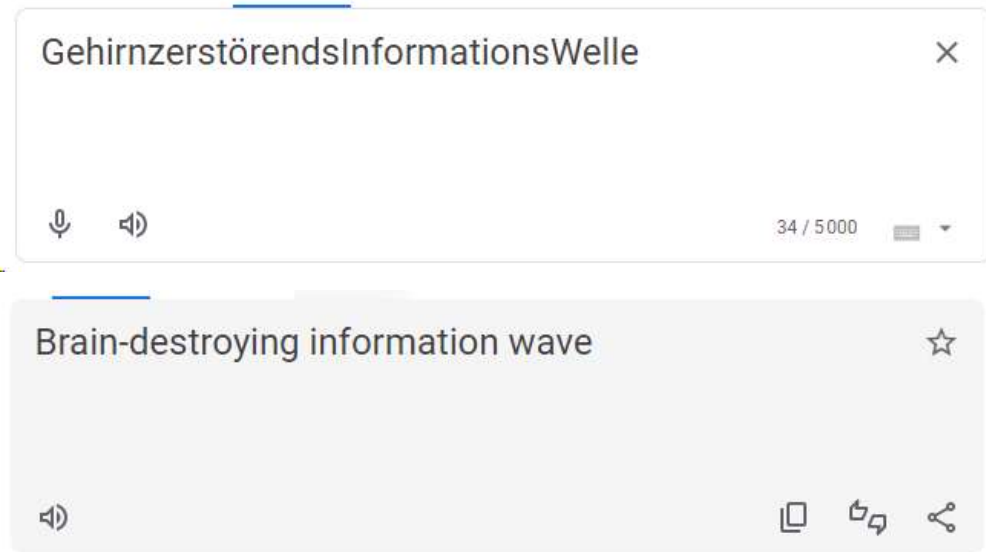


Glass for a sustainable future

April 29 – May 03, 2024, Lloret del Mar, Spain

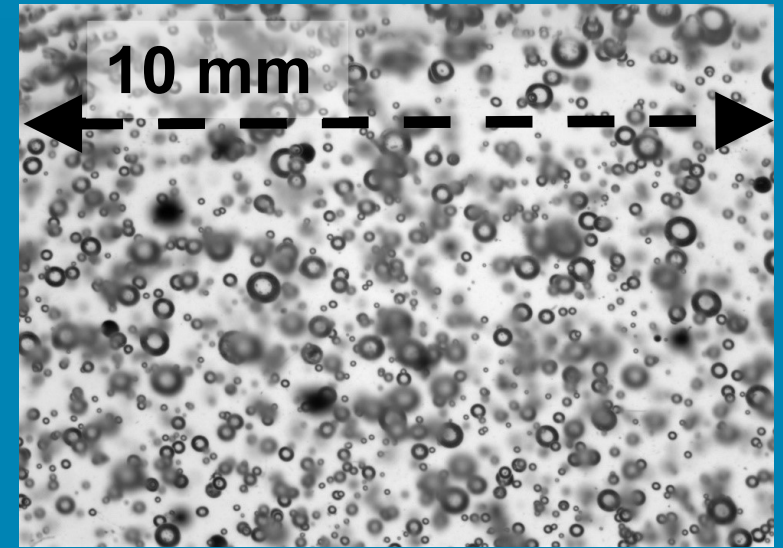
UNION
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ET LA TECHNOLOGIE
VERRIÈRES

We are not getting any younger - 2012



R Conradt, 2019. Prospects and physical limits of processes and technologies in glass melting. *Journal of Asian Ceramic Societies* 7 (4) 377-396

Real case scenario



A furnace producing amber colored bottles doesn't reach the desired pull at a satisfactory level of quality [bubbles!]



**Energy can neither
be created nor
destroyed, only
altered in form.**

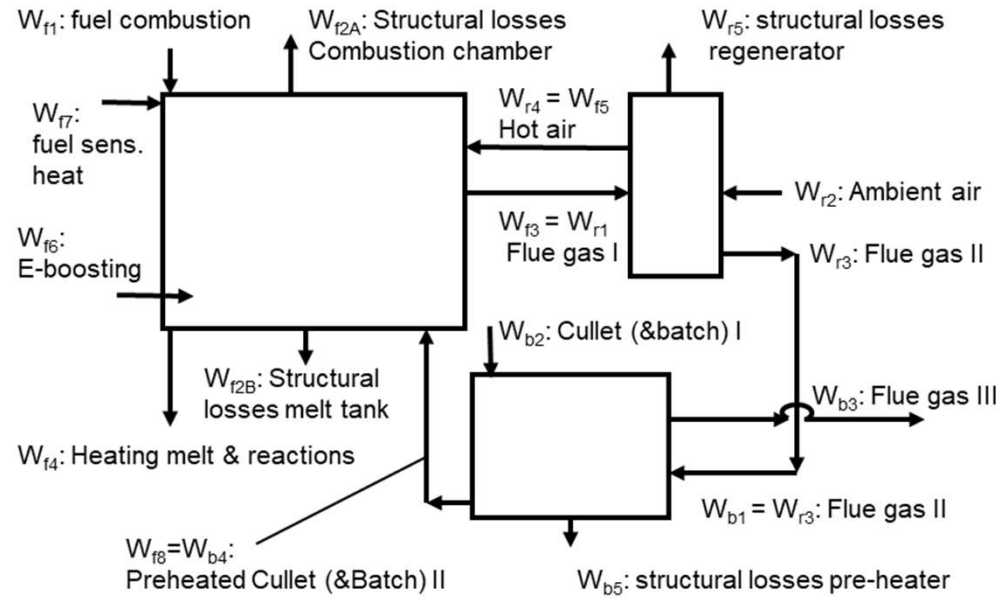


Energy balance

WHAT COMES IN

P_{in}

- Combustion
- Boosting



Reference state: 273.15 K / 0°C
 f = furnace balance
 r = recuperator / regenerator balance
 b = batch preheat balance

WHAT COMES OUT

P_{ex}

- Hot glass melt

P_{loss}

- Hot flue gases
- Structural losses

A furnace consumes energy

Power supplied to the electrical boosting [kW]

$$P_{\text{boost}}$$

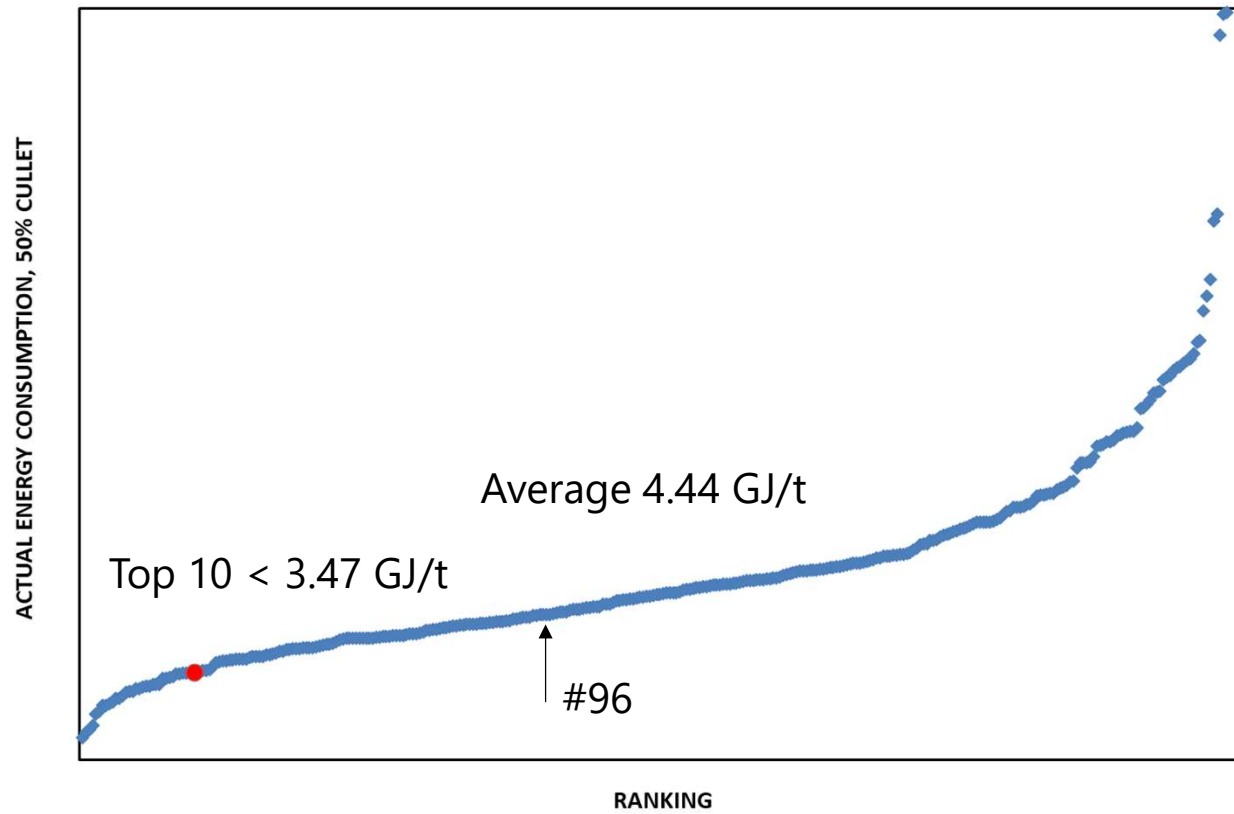
Flow of gas supplied to the burners and the composition and/or caloric value of the gas

$$P_{\text{comb}} = H_{\text{comb}} V'_{\text{fuel}}$$

→ P_{in} , the power input

$$P_{\text{in}} = P_{\text{comb}} + P_{\text{boost}}$$

Benchmark, for container furnaces



A furnace is a chemical reactor

Pull rate [tons glass per day]

Cullet fraction entering the furnace

Temperature at which the glass exits

Energy required to convert the raw materials into glass

Energy required to heat the glass to T_{ex}

→ P_{ex} , the exploited power

p

y_{cullet}

T_{ex}

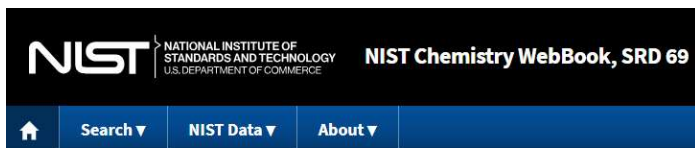
ΔH°_{chem}

ΔH

Energy demand setup

$$P_{ex} = p((1 - y_{cullet})\Delta H^\circ_{chem} + \Delta H(T_{ex}))$$

Wait, what? – ΔH and $\Delta H^\circ_{\text{chem}}$



Welcome to the NIST Chemistry WebBook

The NIST Chemistry WebBook provides access to data compiled and distributed by NIST under the Standard Reference Data Program.

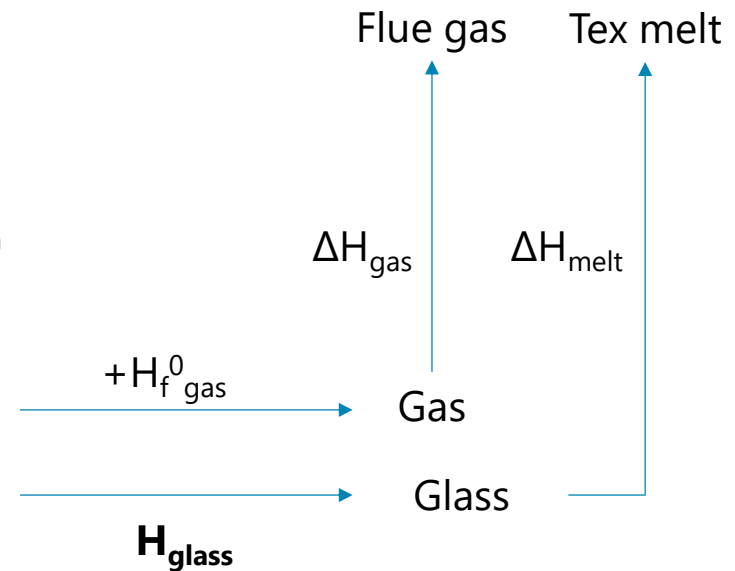
The NIST Chemistry WebBook contains:

- Thermochemical data for over 7000 organic and small inorganic compounds:
 - Enthalpy of formation
 - Enthalpy of combustion
 - Heat capacity
 - Entropy
 - Phase transition enthalpies and temperatures
 - Vapor pressure

Raw materials
 $\text{SiO}_2, \text{Na}_2\text{CO}_3$

$-\text{H}_f^0$ batch

Compounds in
reference state
 Si, Na, Ca, C, O



$$\text{H}_{\text{glass}} = \text{H}_{\text{vit}} + \text{H}_{\text{MIX}}$$

Heat of formation of the glass

75% SiO_2
 10% CaO
 15% Na_2O

35.1% $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$
 33.3% $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$
 31.6% SiO_2

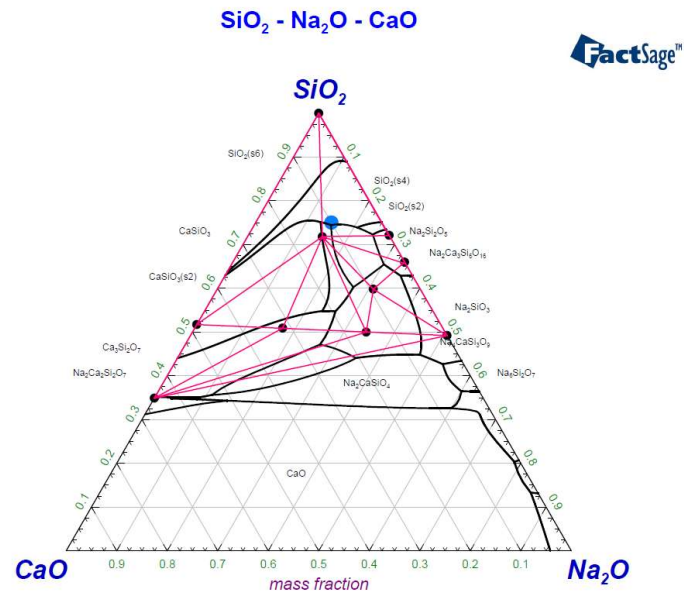


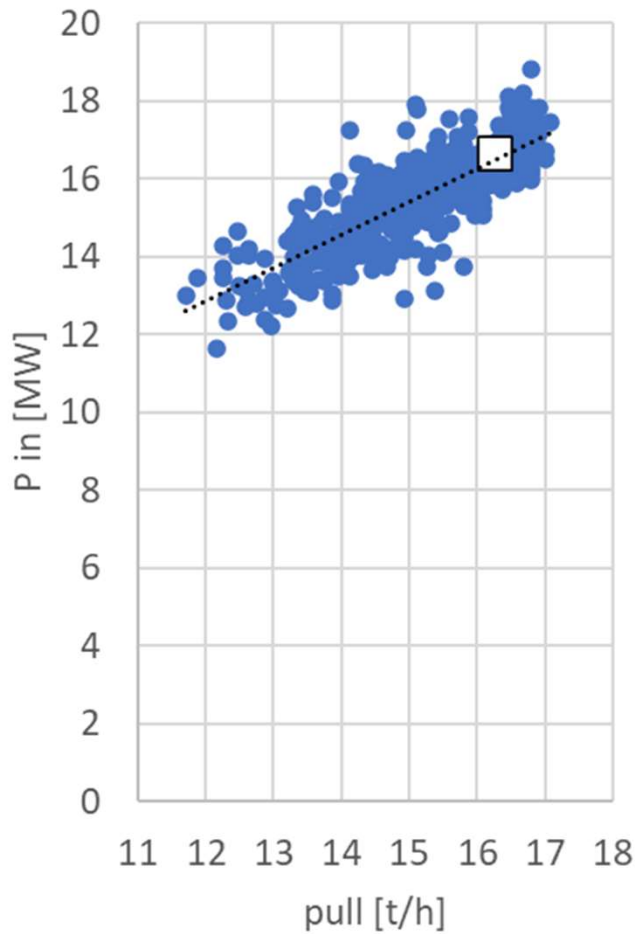
Table 5.3 (continued)

Compound	$-H_x^f$ kJ/mol	H^{vit}
$\text{CaO} \cdot \text{SiO}_2$	1635.1	49.8
$2\text{CaO} \cdot \text{SiO}_2$	2328.4	101.3
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	2473.6	29.3
$\text{Na}_2\text{O} \cdot \text{SiO}_2$	1563.1	37.7
$3\text{Na}_2\text{O} \cdot 8\text{SiO}_2$	9173.0	103.9
$\text{Na}_2\text{O} \cdot \text{CaO} \cdot 5\text{SiO}_2$	5934.0	59.8
$\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$	8363.8	141.9
$\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$	4883.6	92.5
$2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$	4763.0	92.5
SiO_2 (cristobalite)	908.3	6.9

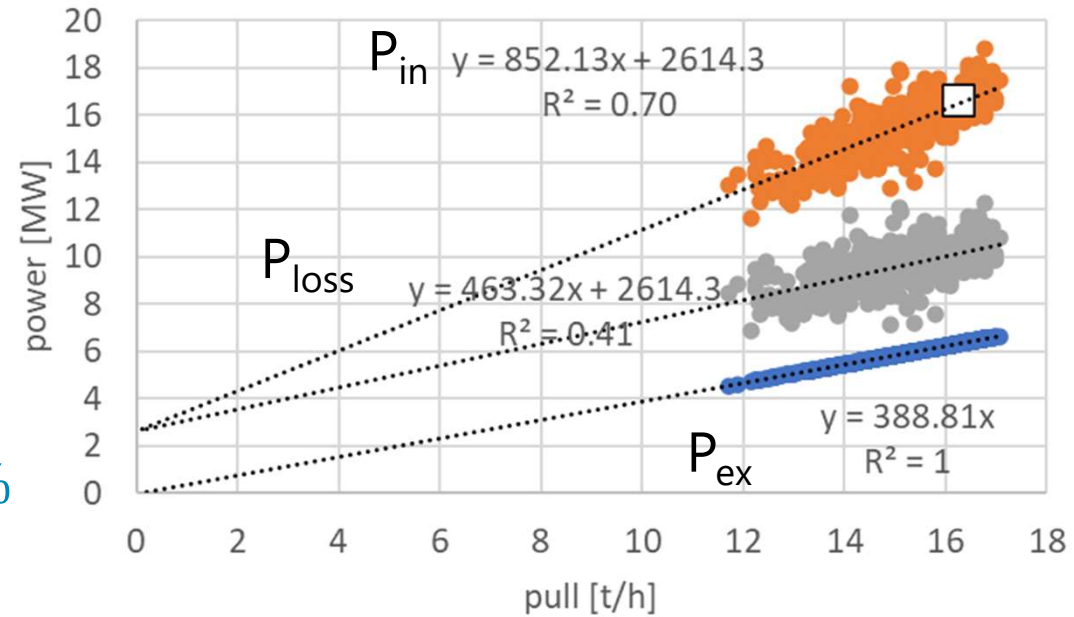
Conrad, R. (2021). Fiberglass Batch-to-Melt Process. In: Li, H. (eds) Fiberglass Science and Technology. Springer, Cham.

- Heat of vitrification of definite compounds
- Mixing energy neglectable
- Same approach for ΔH_{melt}

Power plot

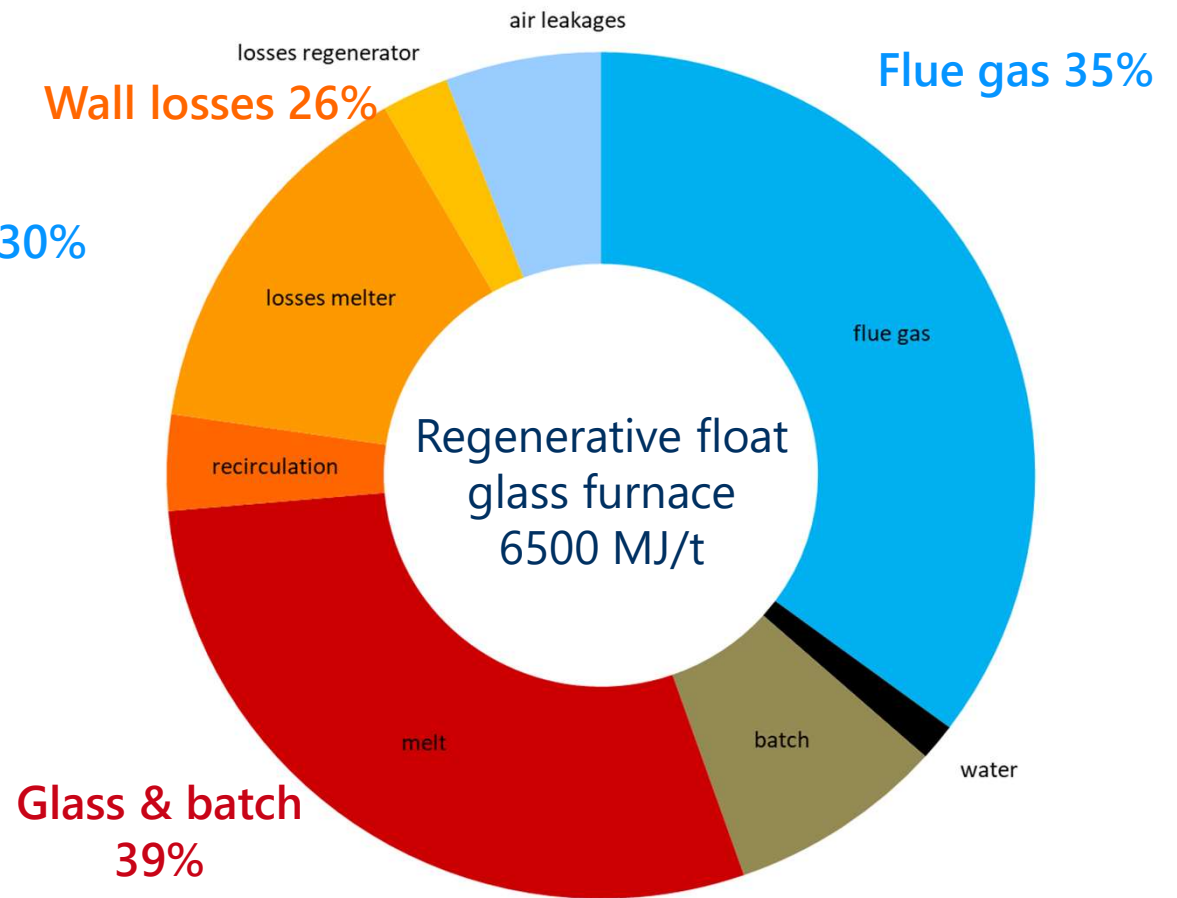
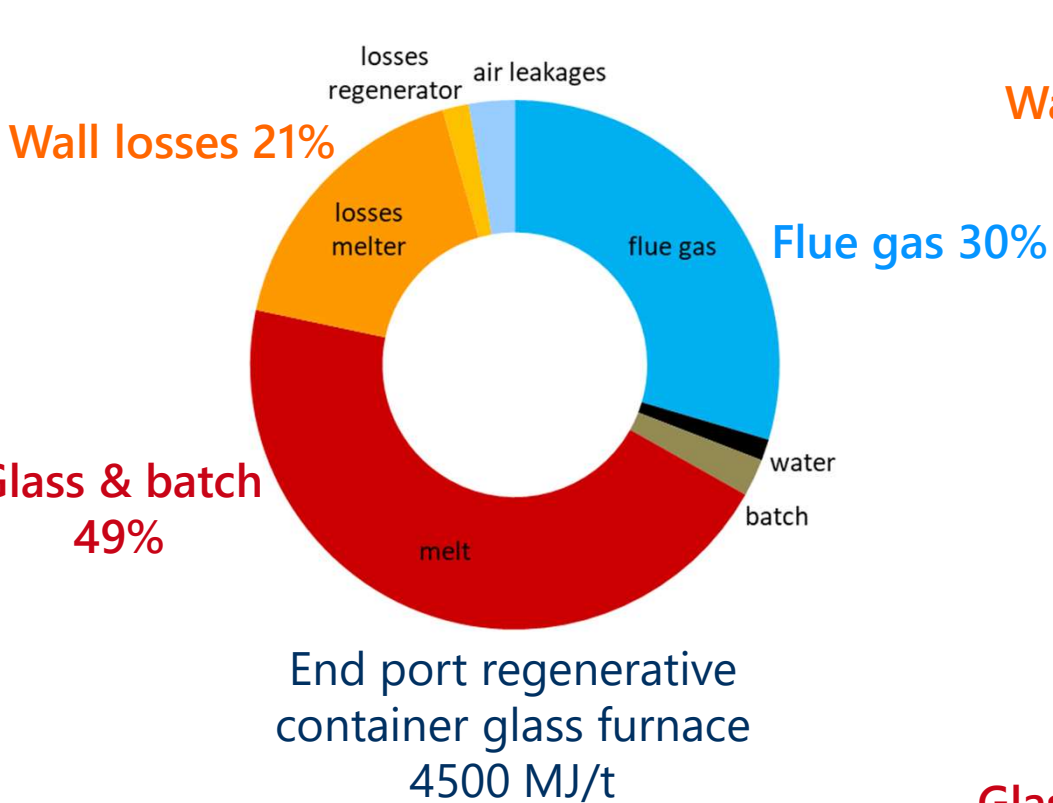


$$\eta = \frac{P_{ex}}{P_{in}} = 38\%$$



P_{loss} at 0 pull	2614 kWh
Power demand per pull unit	852 kWh/t
Exploited heat	389 kWh/t

How is the energy spent overall? Energy balance (container/float)



What can we do so far?

Boosting, combustion, pull, cullet ratio, batch composition → Energy balance and efficiency



A system at equilibrium tends to maximize its entropy.



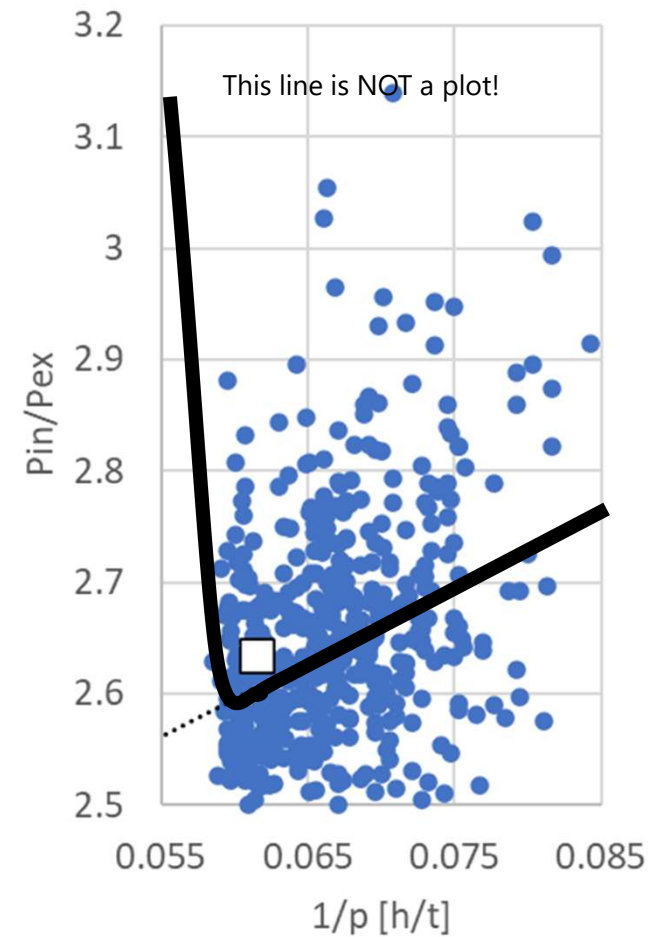
A fine balance

Heat flows from a hot body to a cooler one...
While increasing entropy

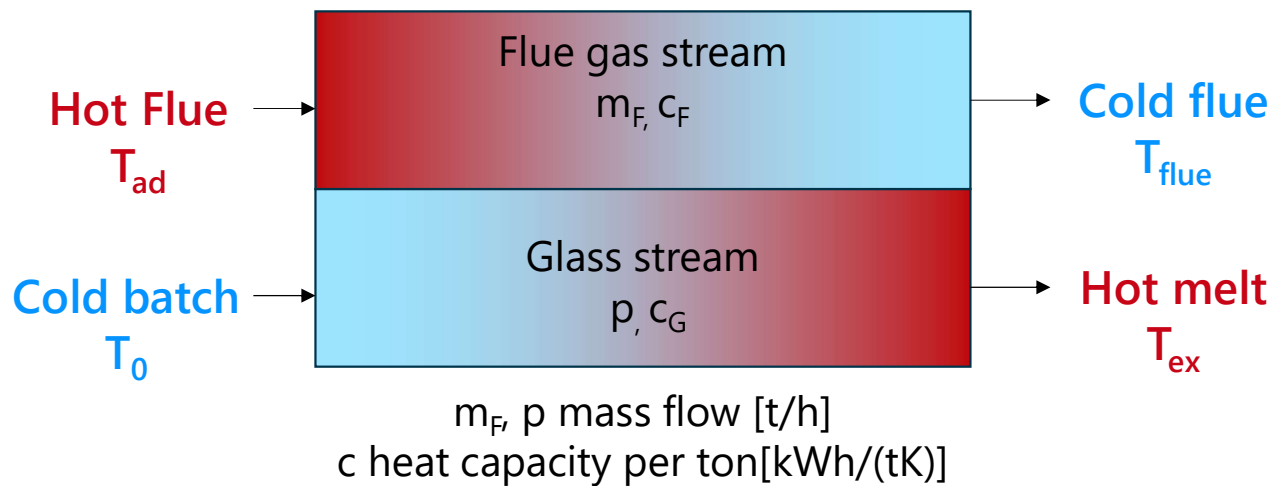
High temperature difference

- High heat transfer rate – short residence time
- High energy degradation

Chiller plot



Temperature efficiency

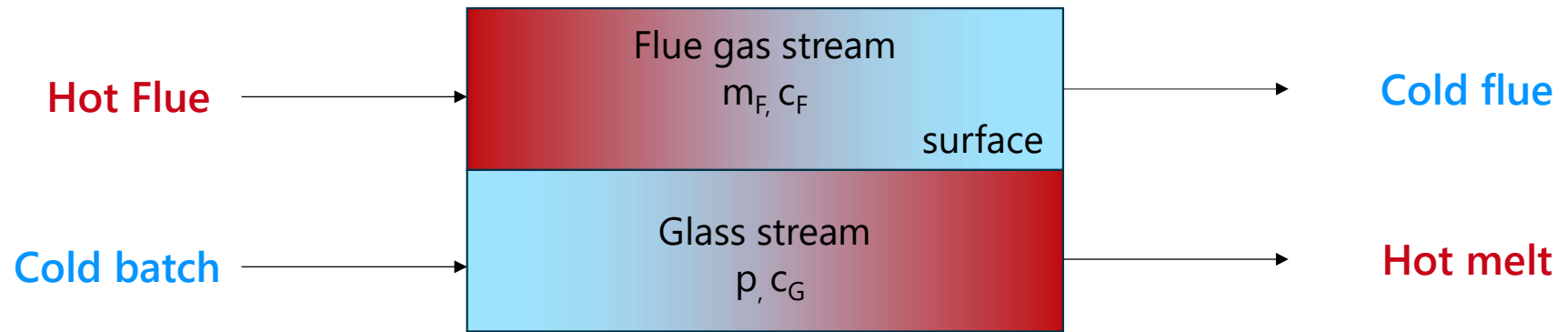


$$\zeta = \frac{T_{ex} - T_0}{T_{ad} - T_0}$$

	°C	ζ
T_0	20	
T_{ex}	1300	
T_{ad} air gas	2442	0.53
T_{ad} air oil	2520	0.51
T_{ad} oxy fuel	2780	0.46
T_{ad} oxy H ₂	3200	0.40

Glass melter = heat exchanger

Matching the power delivered to the power exploited



m_F, p mass flow [t/h]
 c heat capacity per ton [kWh/(tK)]

$$Z_{FG} = \frac{\dot{m}_F c_F}{p c_G}$$

Heat capacity flow ratio $\rightarrow 1$

Heat capacity flow ratio

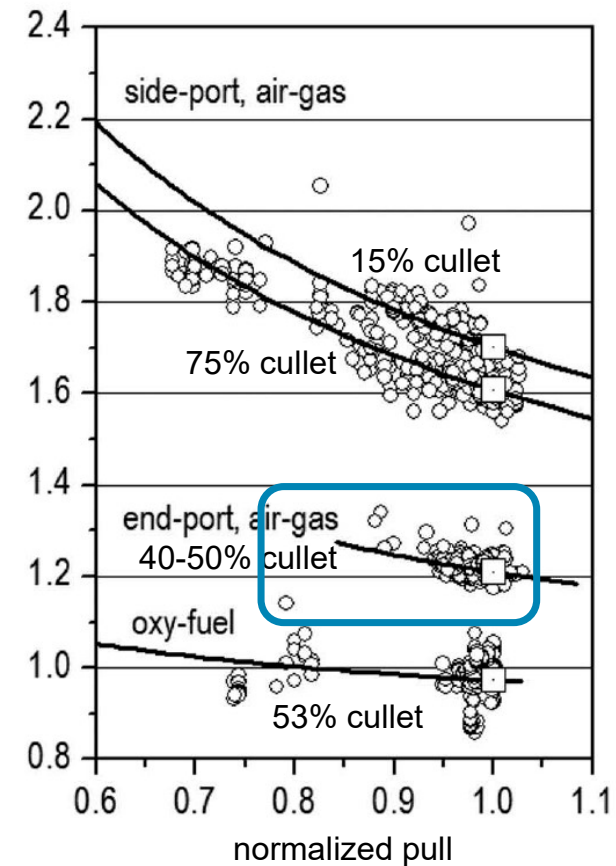
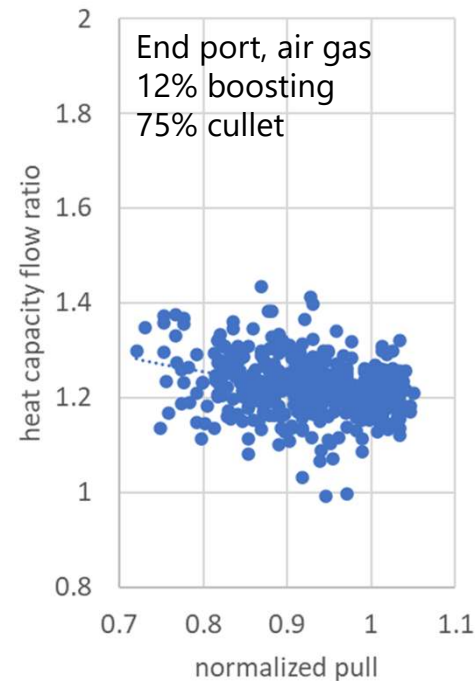
$$Z_{FG} = \zeta \frac{P_{in}}{P_{ex}} \left(1 - \frac{P_{boost}}{P_{in}}\right)$$

Normalized pull

$$p_{86} = \langle p \rangle + \sigma_p$$

$\langle p \rangle$ average pull rate

σ_p standard deviation



Radiative heat transfer from the combustion space is key

95% heat flux combustion → glass

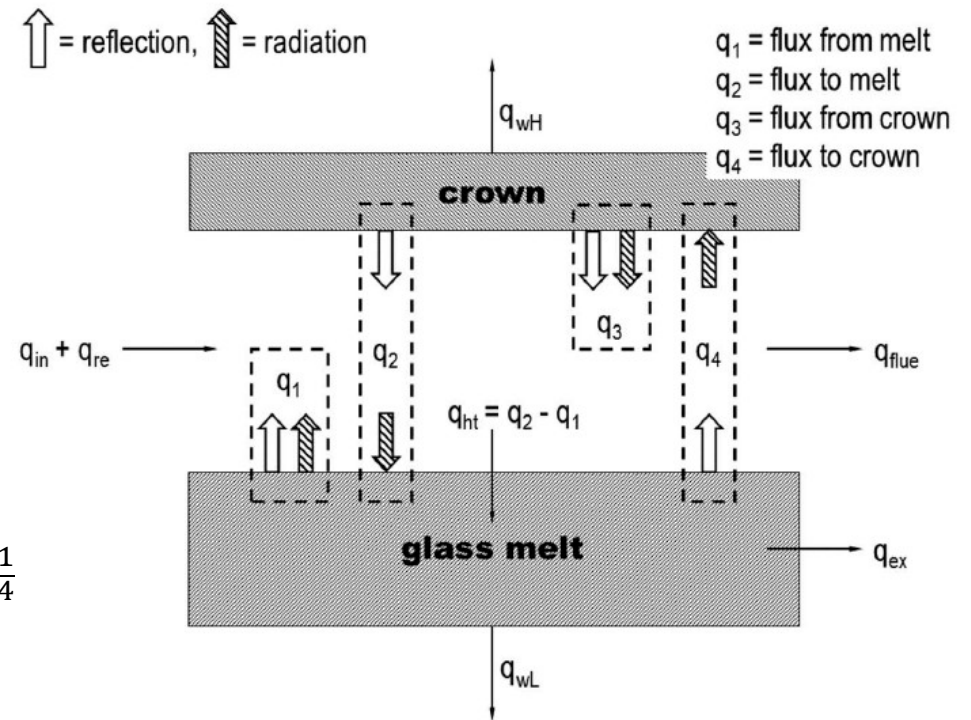
Grey radiation model

Emissions = $\epsilon\sigma T^4$ [kW/m²]

Balance of heat fluxes q [kW/m²]

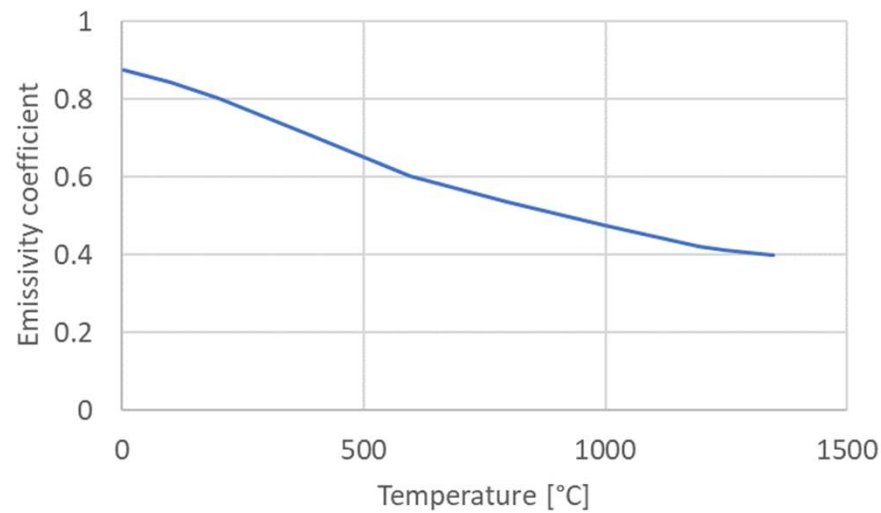
a, b, c functions of ϵ gas, melt, crown

$$T_{crown} = \left[\frac{c}{b} (q_{loss} + rH_{ex}) - \frac{a}{b} T_{gas}^4 + \left(1 + \frac{a}{b} \right) T_{melt}^4 \right]^{\frac{1}{4}}$$



Emissivity of the crown

For most oxide-based materials $\epsilon \approx 0.4$



Unless coated with high emissivity paints

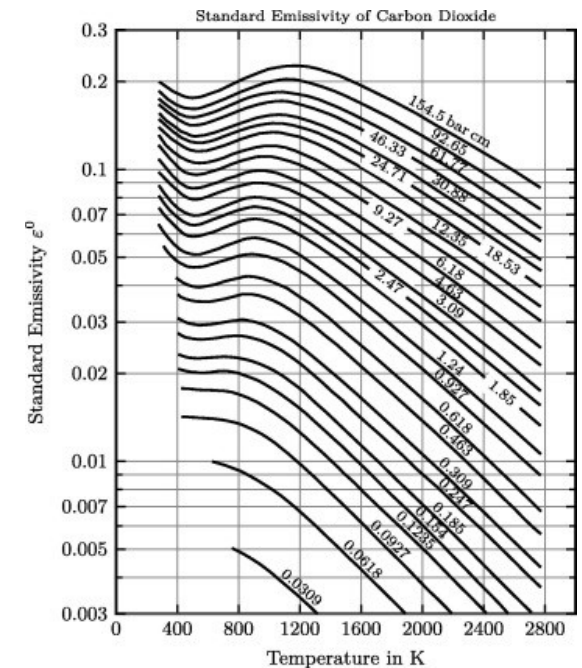
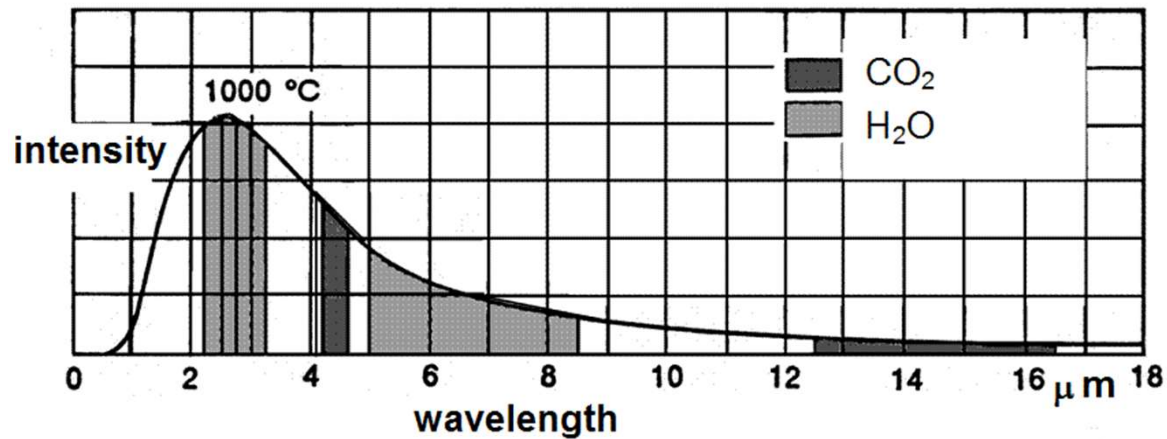
Emissivity of the combustion space

Flame emission coefficient = $f(T, [\text{CO}_2], [\text{H}_2\text{O}], \text{flame thickness}, [\text{soot}])$

Luminous, sooty flames $\epsilon = 0.25$

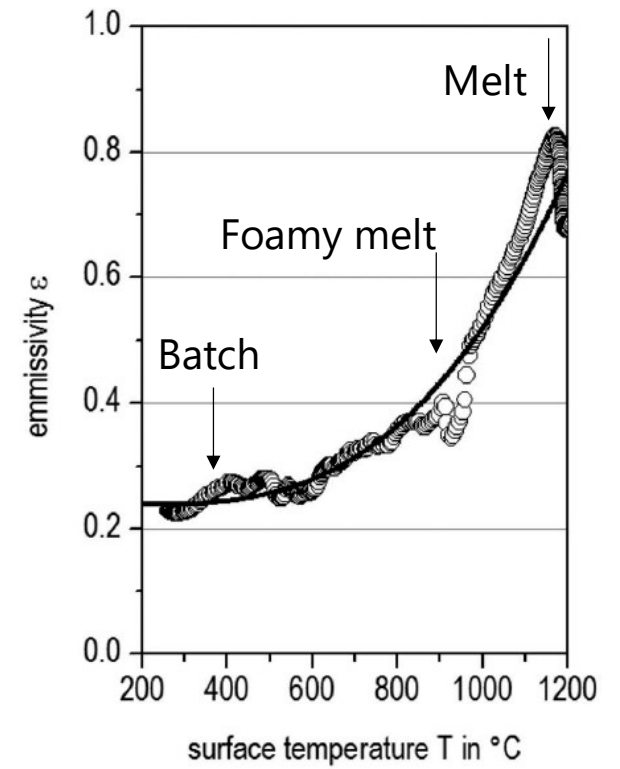
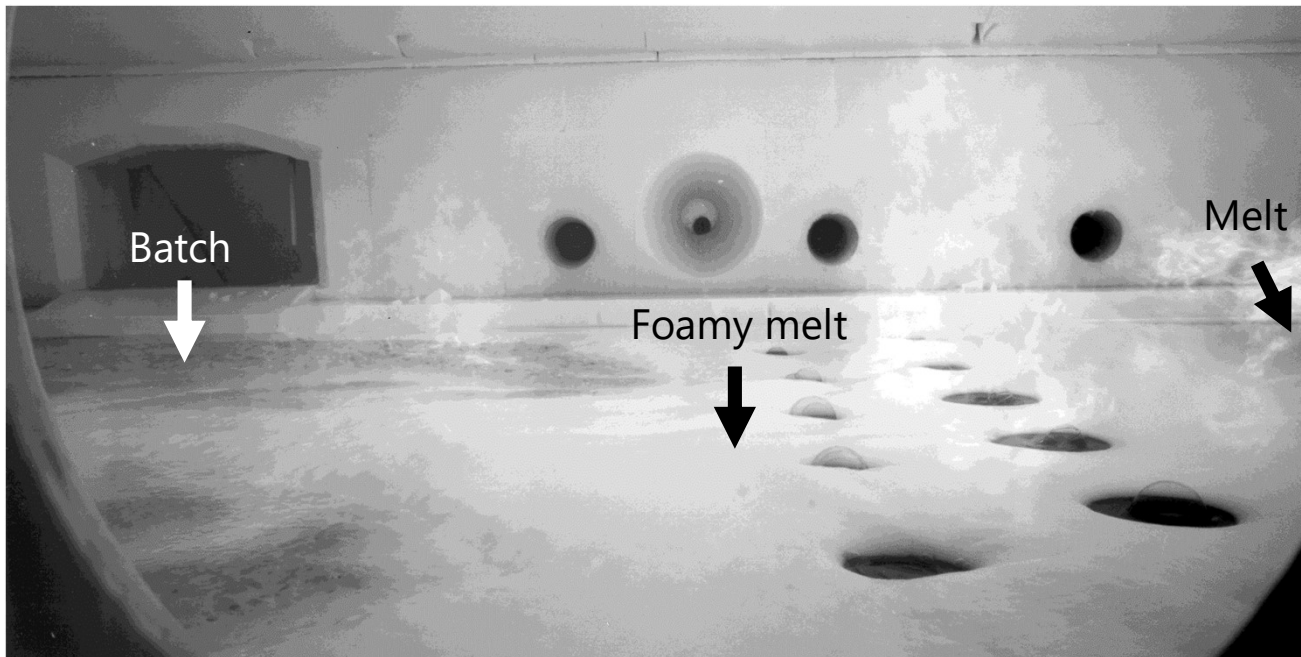
Non sooty flames

Air gas $\epsilon = 0.12$ / Oxy-fuel $\epsilon = 0.4$



Hottel's charts

Emissivity of the glass



And in reality?

ϵ melt (clear)	0.6
ϵ crown	0.4
ϵ gas (luminous air gas)	0.25
T melt	1350°C
T gas	1573°C
T crown	1570°C
q boosting	8 kW/m ²
q losses	78 kW/m ²
H ex	389 kW/m ²

$$P_{ex} = p((1-y_{\text{cullet}})\Delta H^{\circ}_{\text{chem}} + \Delta H(T_{\text{ex}}))$$

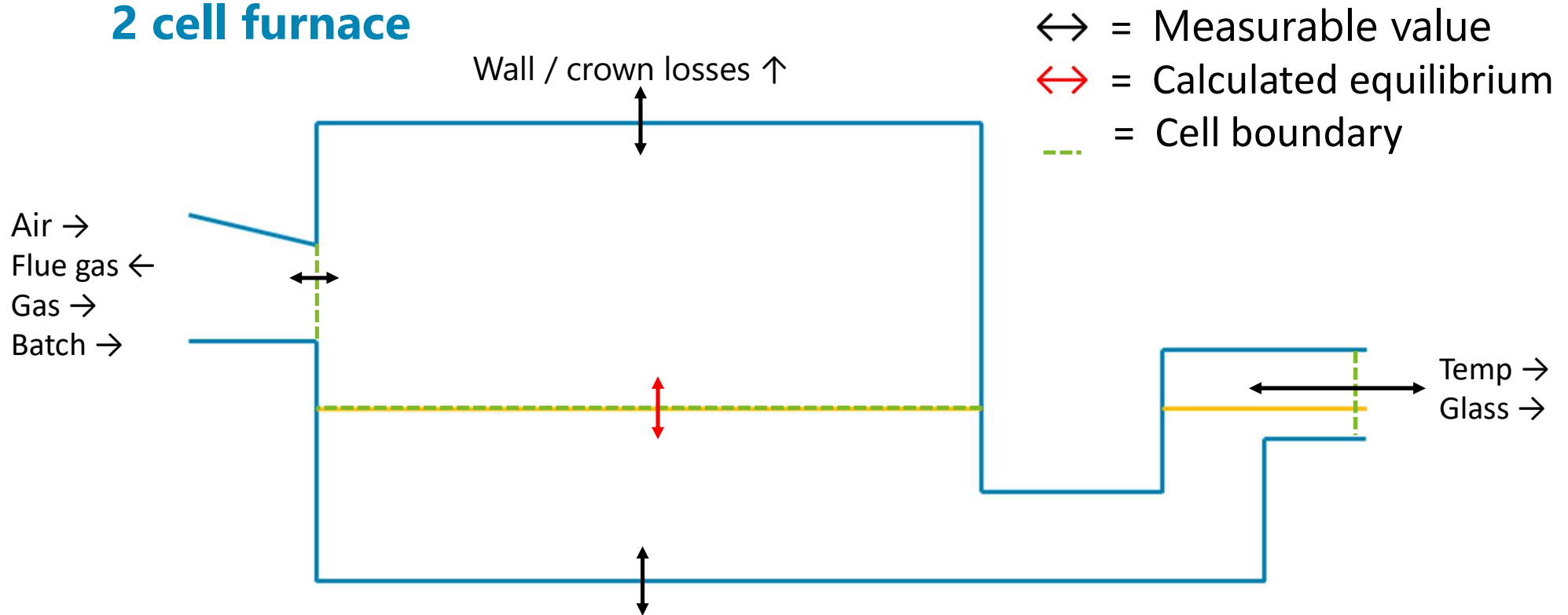
Theoretical specific pull rate
3.12 t/m²/day

Actual specific pull rate
3.12 t/m²/day

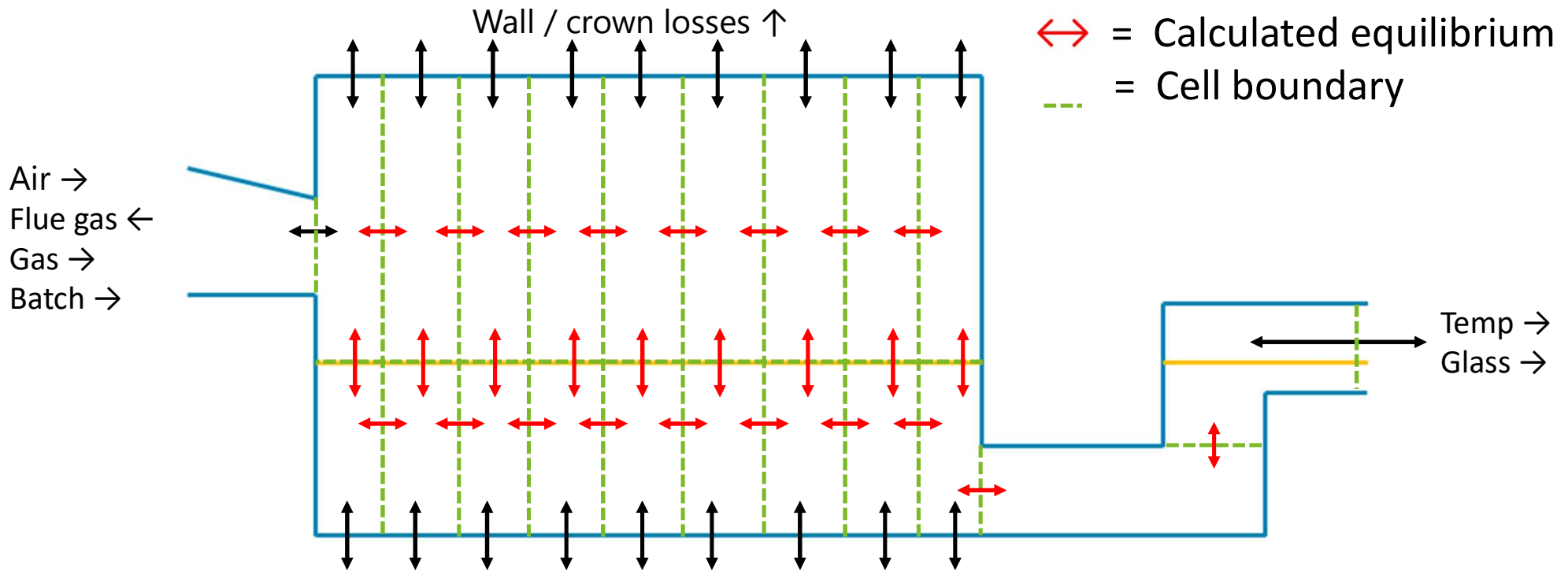
What can we do now?

Quantify the influence of the heat transfer on the efficiency and combine everything to estimate the achievable pull rate

2 cell furnace

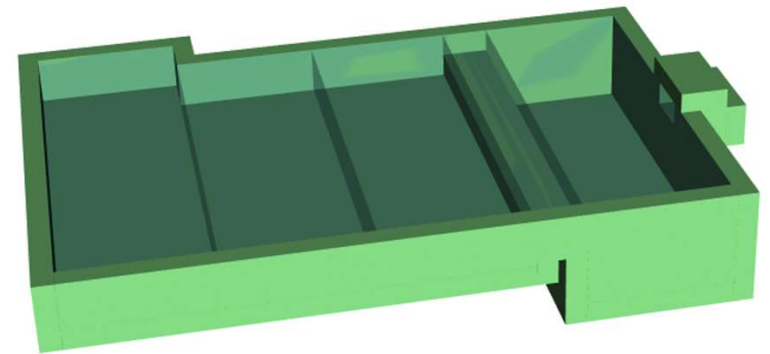
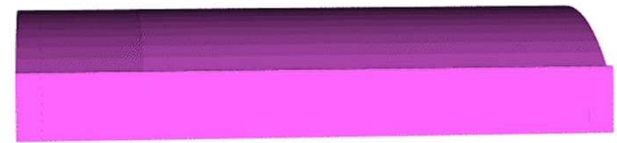


20 cell furnace



Energy Balance Model

- “Fast” (1-2 min) calculations
- Potential energy savings and CO₂ reduction potential
- Detailed picture where to save energy
- Quantify impact of implementing energy saving-measures
- Training tool !



Have we solved the problem?

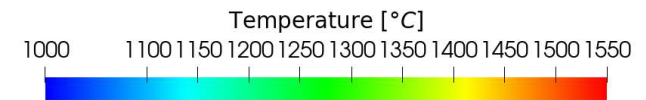
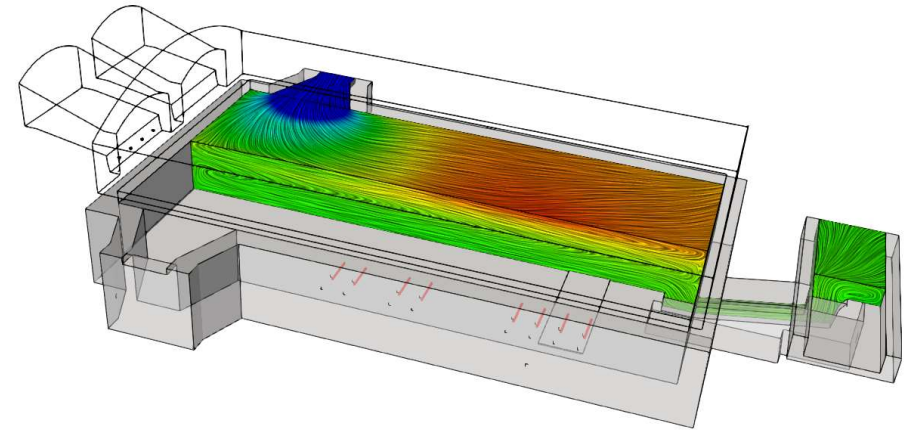
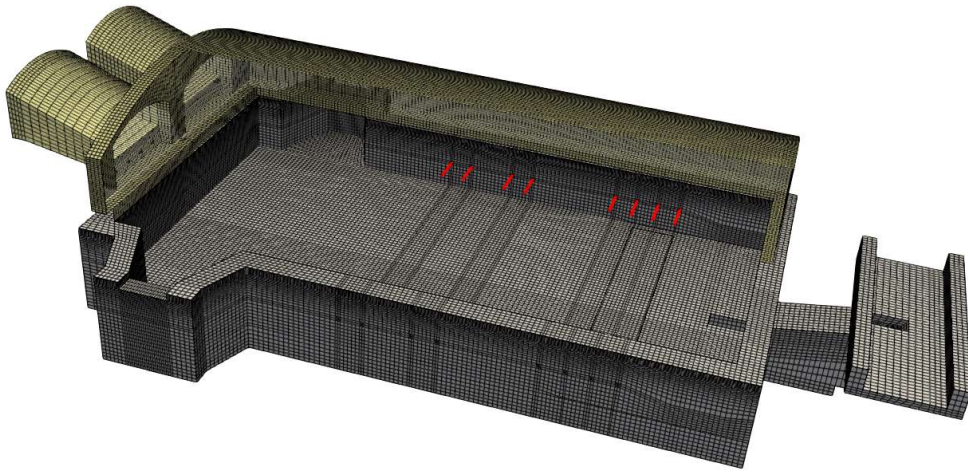
Saving energy BUT keeping quality
Thermodynamics + flow



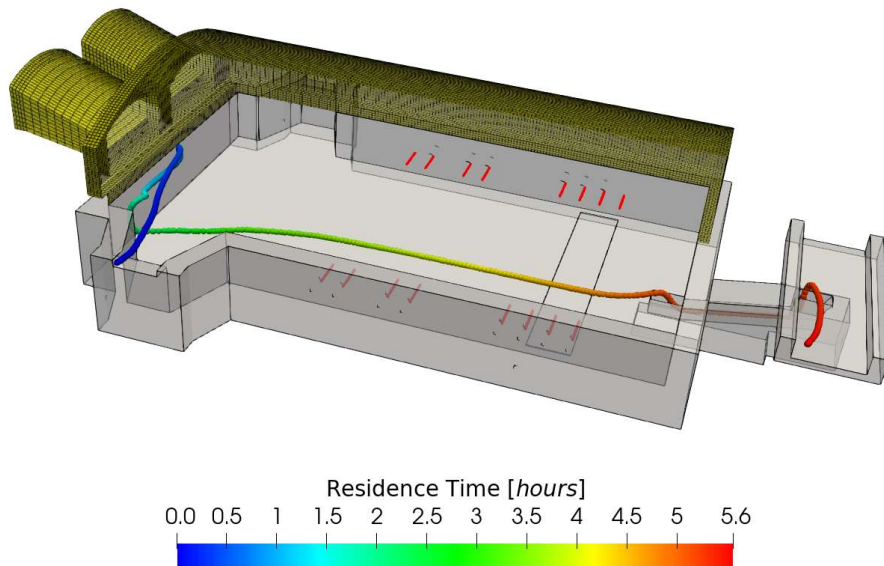
Computational Fluid Dynamics



CFD simulation – domain discretization



Classic sources of bubbles : shortcut flow and reboil



2020-10-27 13:06 - 1399°C



Temperature: 600



Conclusion

- Elegant and efficient approach to accurately describe the energy exchanges taking place in furnaces.
- Powerful to quantify potential energy savings and optimize furnaces.
- For quality issues, the additional understanding of flows is a necessity.
- Excellent educational tool.

DO IT !





Thank you for your kind
attention!