ancorro

Feuerfest- und Schmelztechnologie

Improvement of porous refractory material in contact with glass

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Why improvement of refractories?

- **reduction in energy consumption in the past**
- **corrosion of refractory reduces glass quality**

  → increasing of energy consumption per glass product
- **development of a treatment technology for all available porous refractories**

  → reduce the interaction with glass melt

  → independent from refractory producer

energy consumption of various glass furnaces

sector	energy consumption [GJ/t]
container glass	4.7
float glass	7.2
tableware	8.0
E-Glass fibers	13.0

Reference: Beerkens, 2006

Complexity of melt and refractory

factors:

furnace:
temperature/time/
atmosphere

refractory:
composition/grain distribution/
capillarity/porosity/
pore atmosphere

Reference: Mertens, 2014

Reference : HVG, 1996

Reference: RHI, 2014

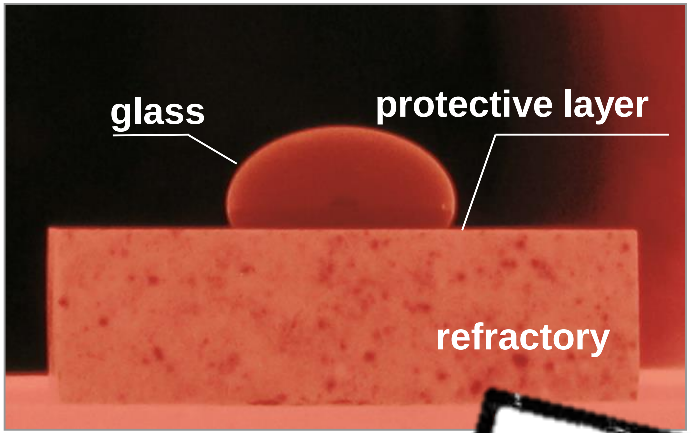
glass melt:
composition/viscosity/
surface tension

surface-volume-ratio:
glass melt-refractory

Principle - ancorro

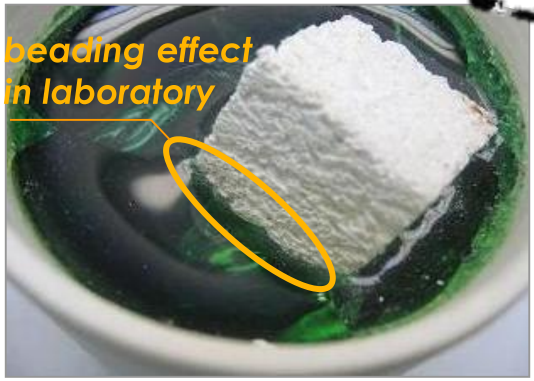
beading effect in nature

beading effect in the laboratory



patented process

strong infiltration/attack without ancorro-technology



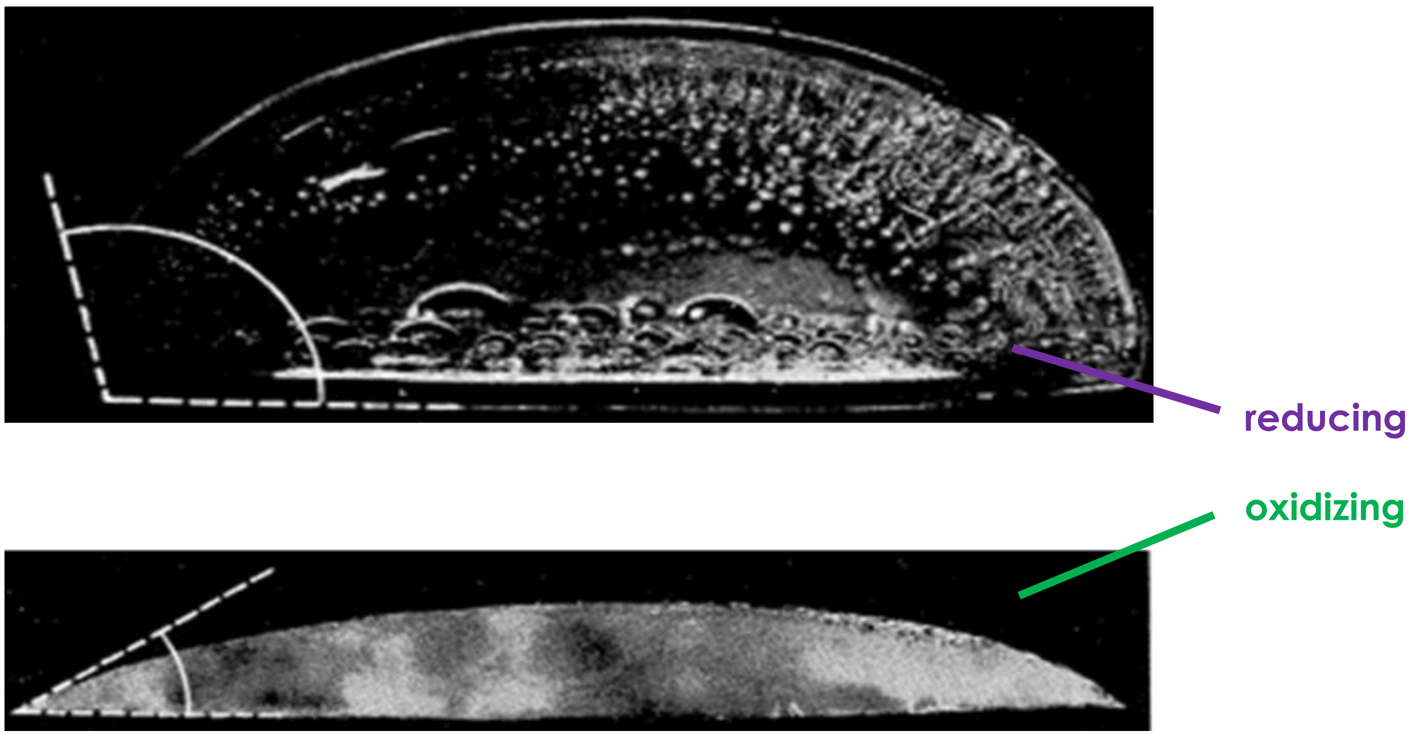
infiltration/attack reduced significantly with ancorro-technology

Principle - ancorro

- **surface-treatment-technology of ancorro creates reducing atmosphere in the pores**

  → reducing atmosphere increases in the boundary layer:

surface tension of the glass



Reference: Jebsen-Marwedel & Brückner, 2011

Principle - ancorro

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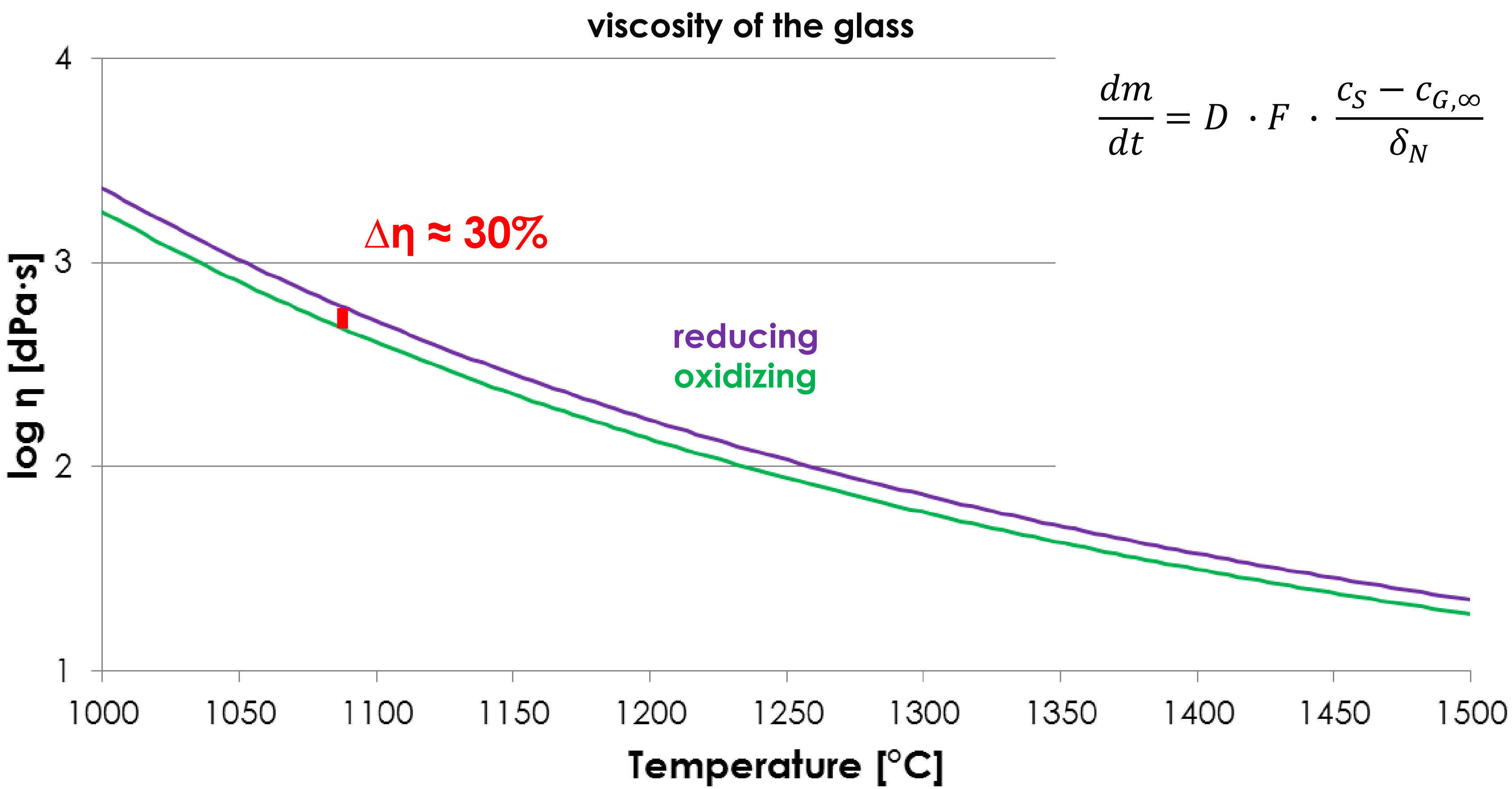


$$\frac{dm}{dt} = D \cdot F \cdot \frac{c_S - c_{G,\infty}}{\delta_N}$$

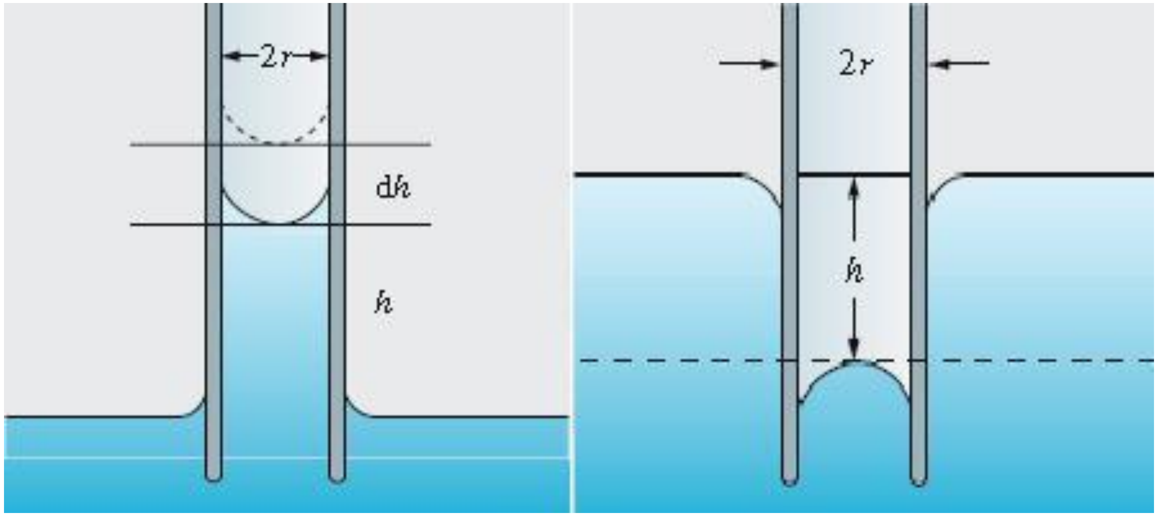
Principle - ancorro

- **surface-treatment-technology of ancorro creates reducing atmosphere in the pores**

  → reducing atmosphere decreases:

capillarity

oxidizing



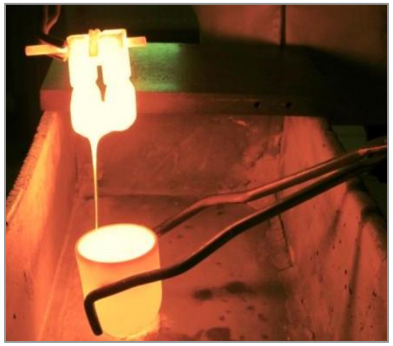
reducing

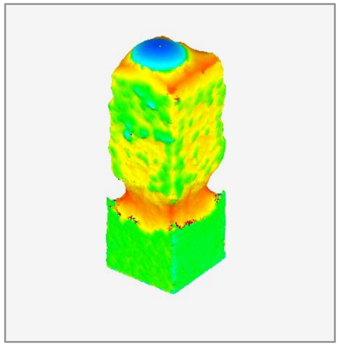
Reference: Gerthsen Physik, 2006

$$h = \sqrt{\frac{\sigma \cdot \cos\theta \cdot r \cdot t}{2\eta}}$$

Research

Since 2008 ancorro investigate materials to improve porous refractory.



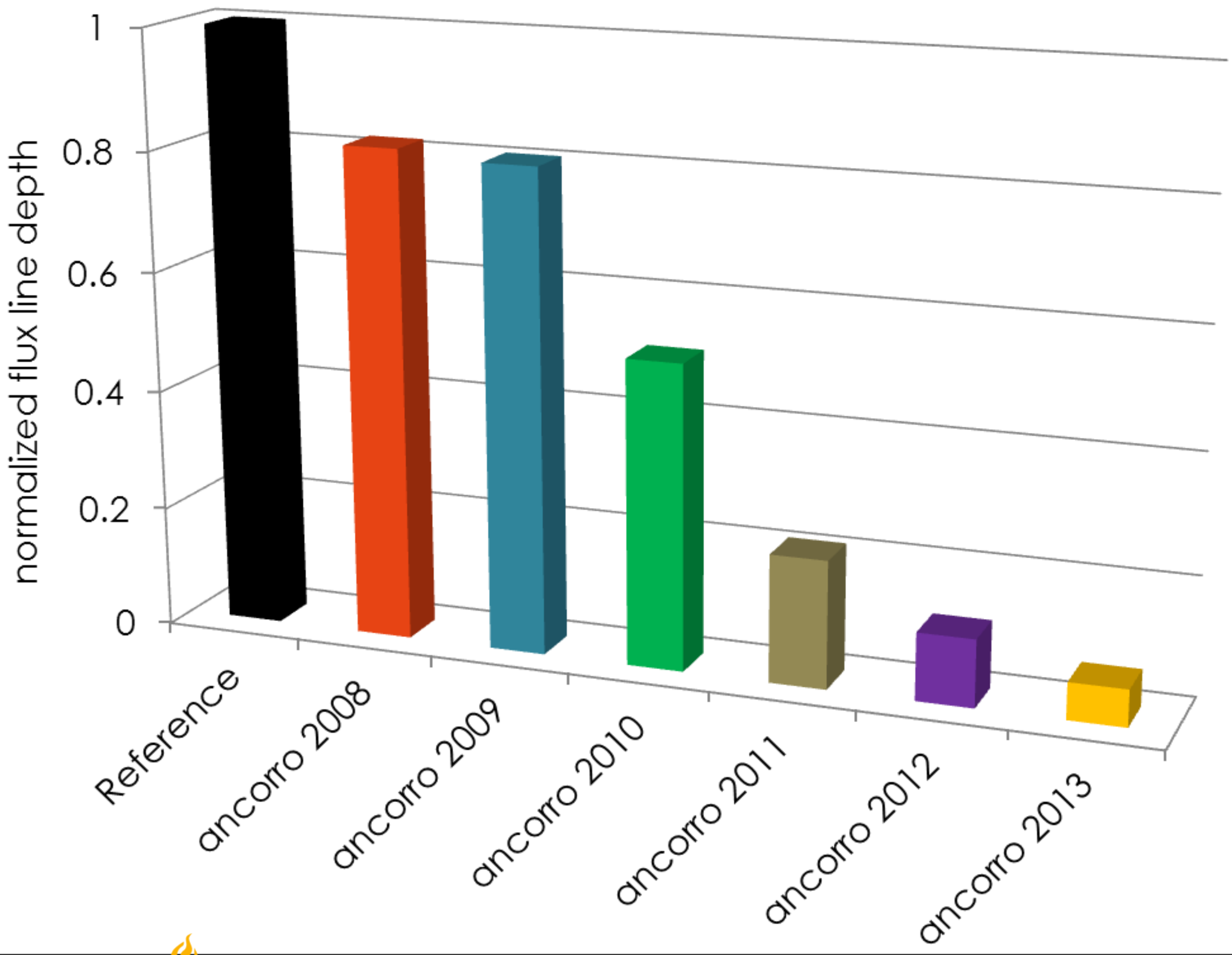


measurement and analysis:

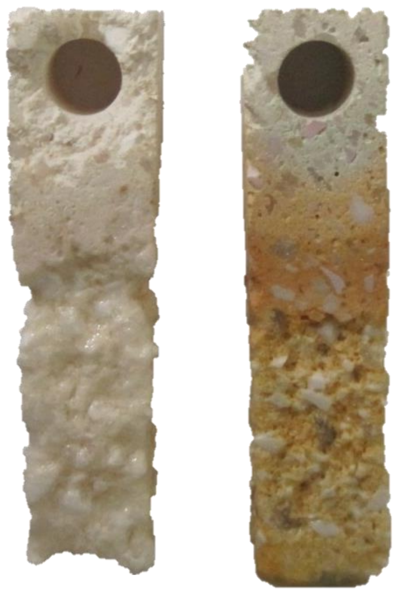
- **static finger test (corrosion measurement)**
- **dynamic finger test (corrosion measurement with flow simulation)**
- **evaluation and measurement (using a 3D-scanner)**
- **crucible test (measurement infiltration depth)**
- **blistering studies (measurement blistering formation)**
- **crystallization measurement (determine crystallization temperature)**
- **glass analysis (detailed analysis of glasses)**

Results corrosion minimization

- **90% lower corrosion after 21 hour static finger test on zirconium-corundum brick at 1450 °C in green glass**



samples after the finger test



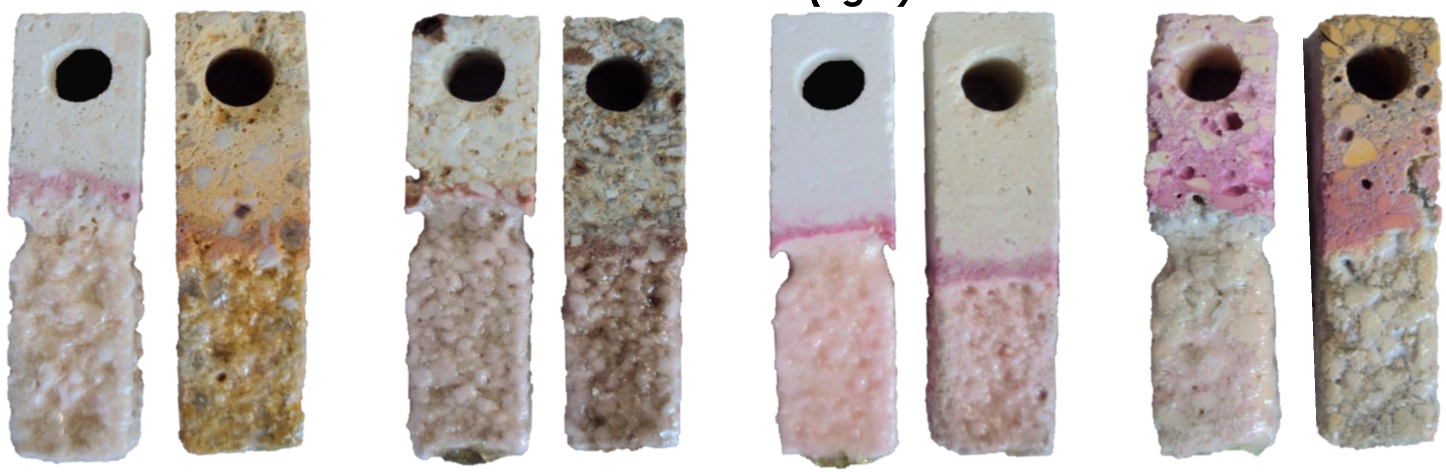
Reference ***ancorro***

Implementation of the ancorro - technology on

…refractories of the type:
- → fireclay
- → bricks containing chrome
- → bricks containing zircon
- → sillimanite
- → corundum
- → mullite

…melts of the type:
- → soda lime glass
- → lead glass
- → soluble glass
- → different enamels

effect of the ancorro technology on different refractories, reference (left) and ancorro treated (right):



zirconium-corundum *sillimanite* *mullite* *AZS-joint compound*

Examples

AZS - soda-lime glass

sillimanite - enamel

Crystallization

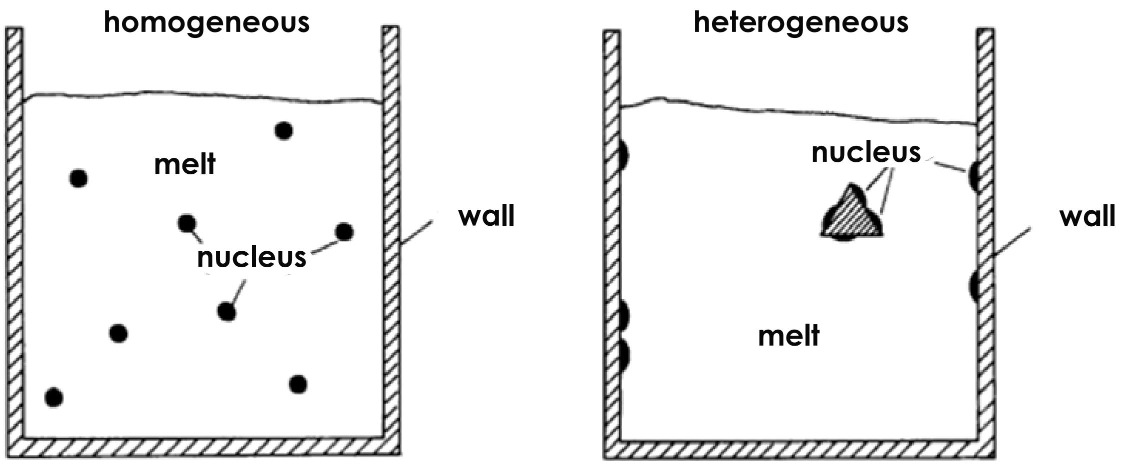
- **homogeneous nucleation:** **– temperature gradient**
  – no interface present

  ≠ industrial glass production

- **heterogeneous nucleation:** **– temperature and/or saturation gradient**
  – interface present
  → wetting

  = comparable with industrial glass production

homogeneous and heterogeneous nucleation



Reference: Leibniz Institut Dresden, 2012

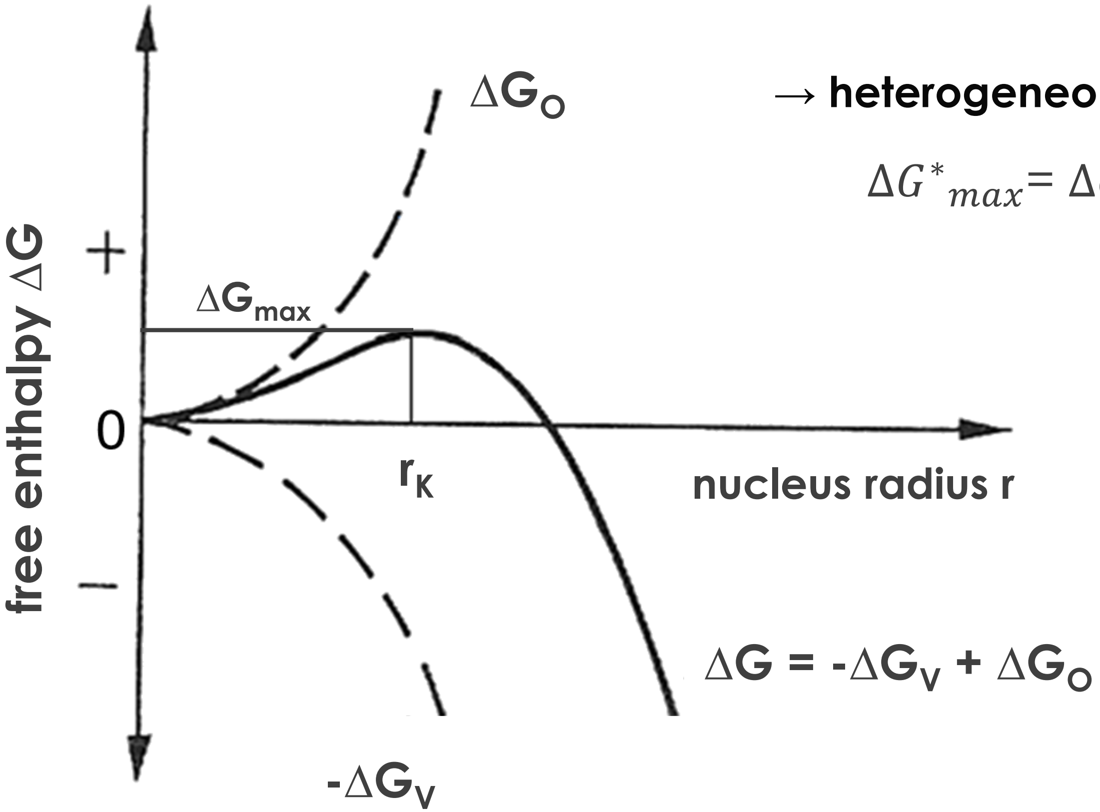
Crystallization

- **nucleation in the glass melt:** → **homogeneous nucleation**

$$\Delta G_{max} = \frac{16\pi \cdot \sigma^3}{3\,(\Delta g_V)^2}$$

→ **heterogeneous nucleation**

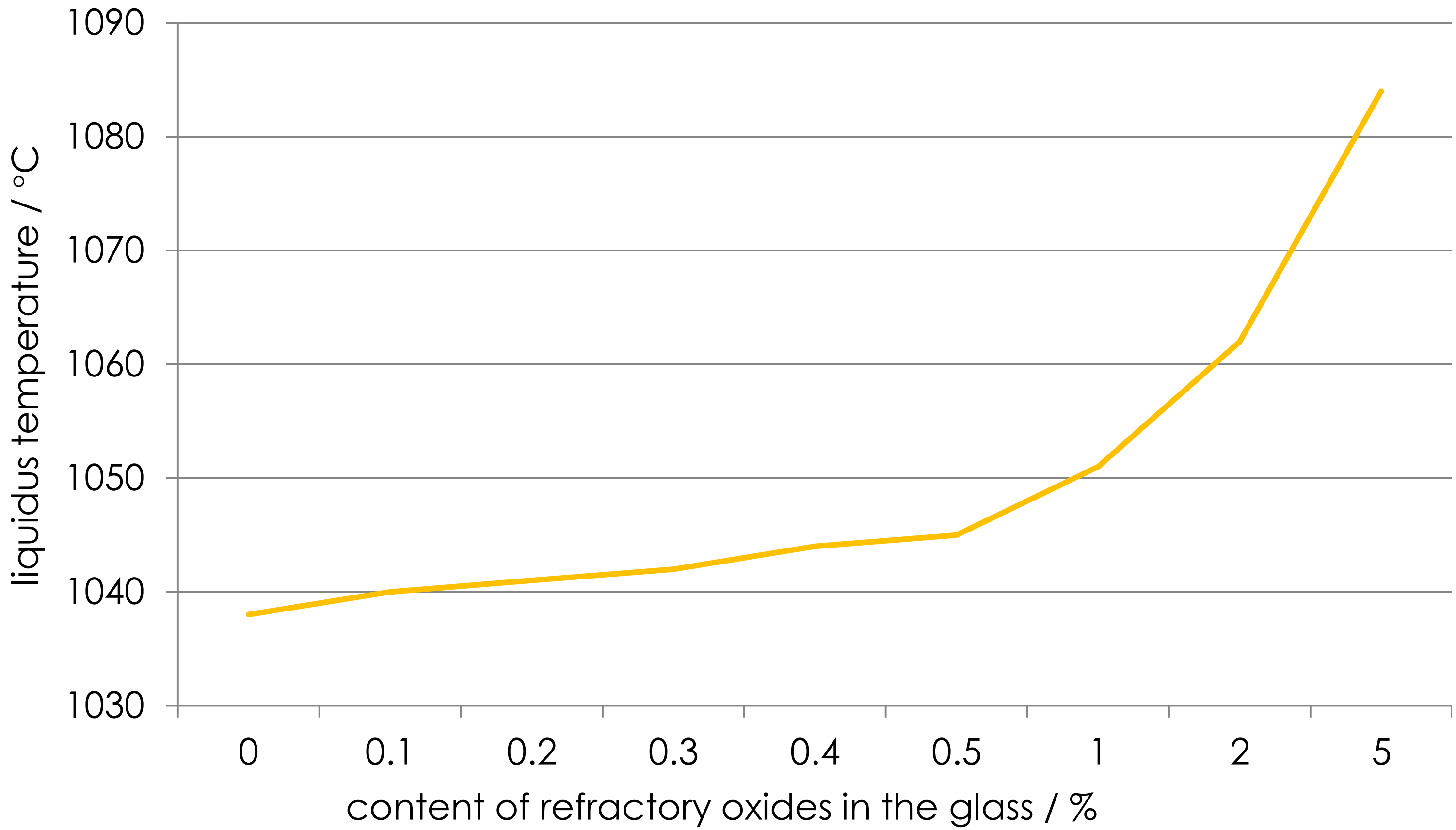
$$\Delta G^*_{max} = \Delta G_{max} \cdot \left[(1 - \cos\varphi)^2 \cdot \frac{(2 + \cos\varphi)}{4}\right]$$



Reference: Jebsen-Marwedel & Brückner, 2011; Varshneya, 2006

Crystallization

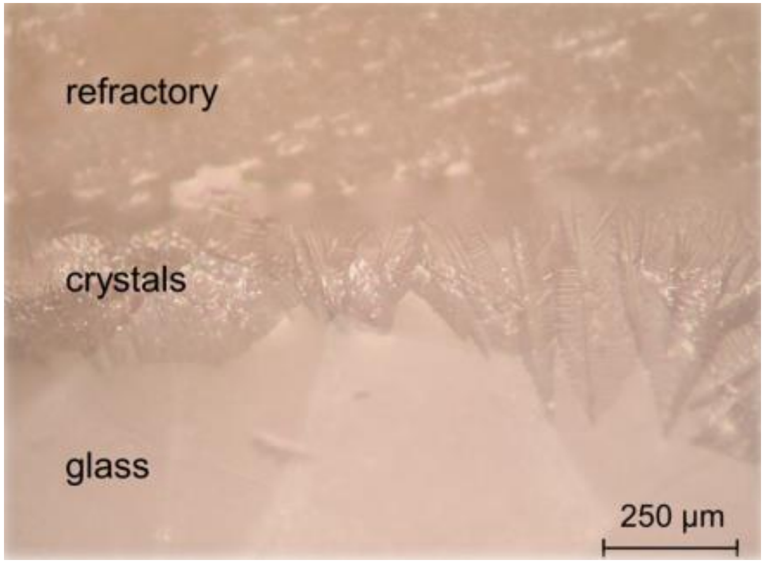
- **influence of the refractory corrosion to the liquidus / crystallization temperature of the glass:**

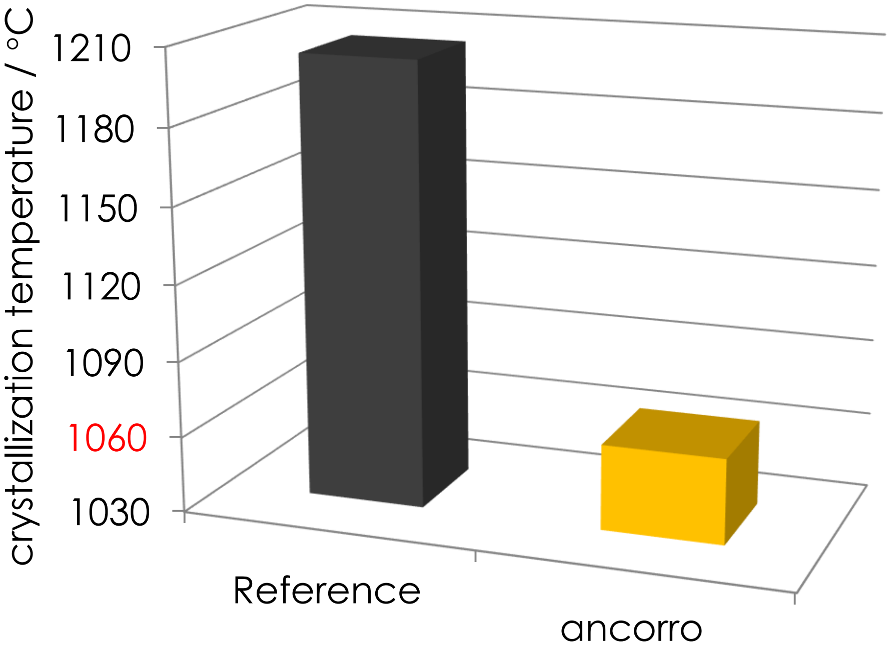


Crystallization

- **detecting crystallization via gradient furnace**
- **refinement of the refractory samples to minimize crystallization**
- **reduction of the crystallization temperature about 140K - inhibition of the heterogeneous nucleation**

crystal formation in the contact zone glass melt - refractory





Industry

Since 2010 tests have been carried out continuously in collaboration with industrial partners.

results:

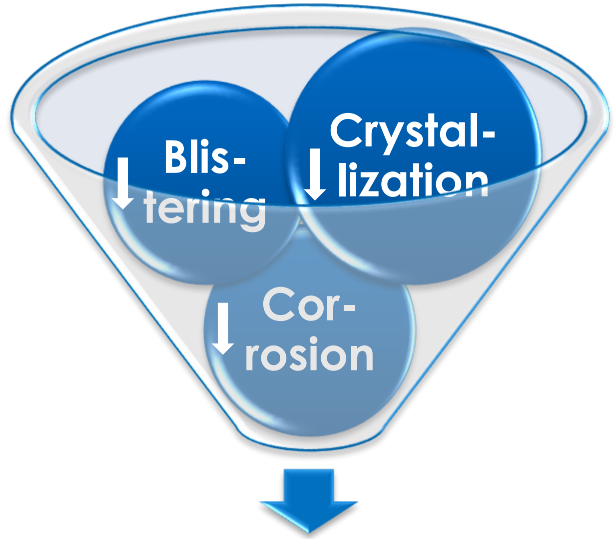
- **fireclay pots - life extension by 50%**
- **plungers - reduction of blistering after change up to 95%**
- **orifice rings - reduction of crystal formation in the glass by factor 6**
- **orifice rings - life extension from 3 to 5 weeks**

Further tests are conducted with the following components:

tank block, stirrer, lip stone, superstructure of the feeder, regenerator bricks, plunger, torque, fireclay pots

Value for industry

reduction of the interactions between glass melt and refractory



- porous bricks show the same properties as expensive, fused cast refractory
- increasing service life and reduction of production downtimes
- reduction of rejects
- energy savings through lower heat losses / minimized CO_2 emissions
- flexibility - applicable to all refractories
- enormous savings through batch conversion (container glass)

Potential batch conversion

- crystallization at the orifice ring
  → gob temperature ca. 1150°C
- increasing the lime content
- elimination of the crystallization due to ancorro-technology

composition [in wt. %]	Glass I	Glass II
SiO_2	72.6	71.2
Al_2O_3	1.5	1.5
Na_2O	12.5	11.9
K_2O	0.6	0.6
MgO	2.5	2.5
CaO	10	12
Fe_2O_3	0.04	0.04
SO_3	0.3	0.3
fining temperature [°C]	1465	1445
liquidus temperature [°C]	1038	1093

Glass I: untreated orifice ring

Glass II: orifice ring treated by ancorro

Potential batch conversion

- lowering the batch free time about 33% by increasing of CaO-content
- minimization of the residue quartz dissolution
- same thermal stress of the furnace

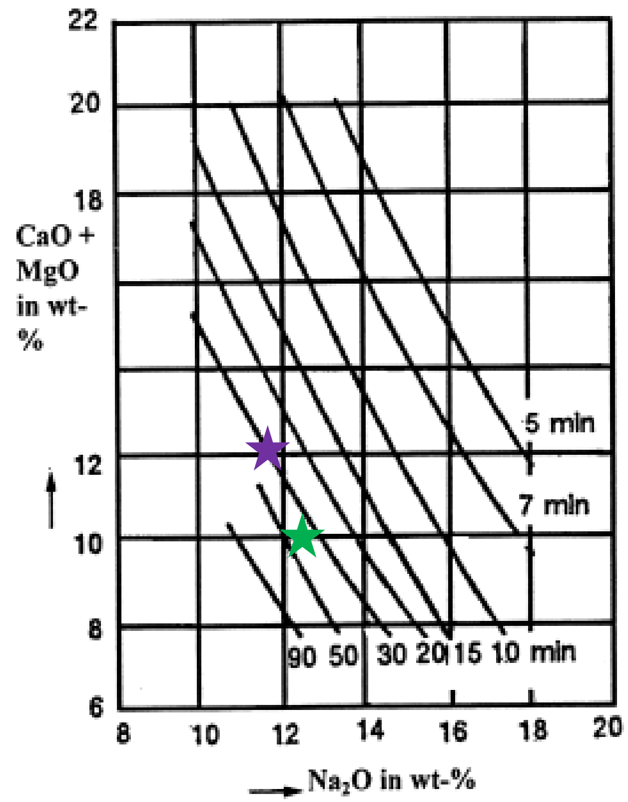
  = increasing of the tonnage

  → rise of capacity

  → depending on forming machines

  → realizable often only for new construction

- increase of turnover about 5.5 million EUR/a possible



Reference: TNO; 1997

Glass I untreated orifice ring

Glass II orifice ring treated by ancorro

Non-glass contact refractory materials:

Silica crown material: Two aspects

a.) Improvement of the heat transfer by radiation

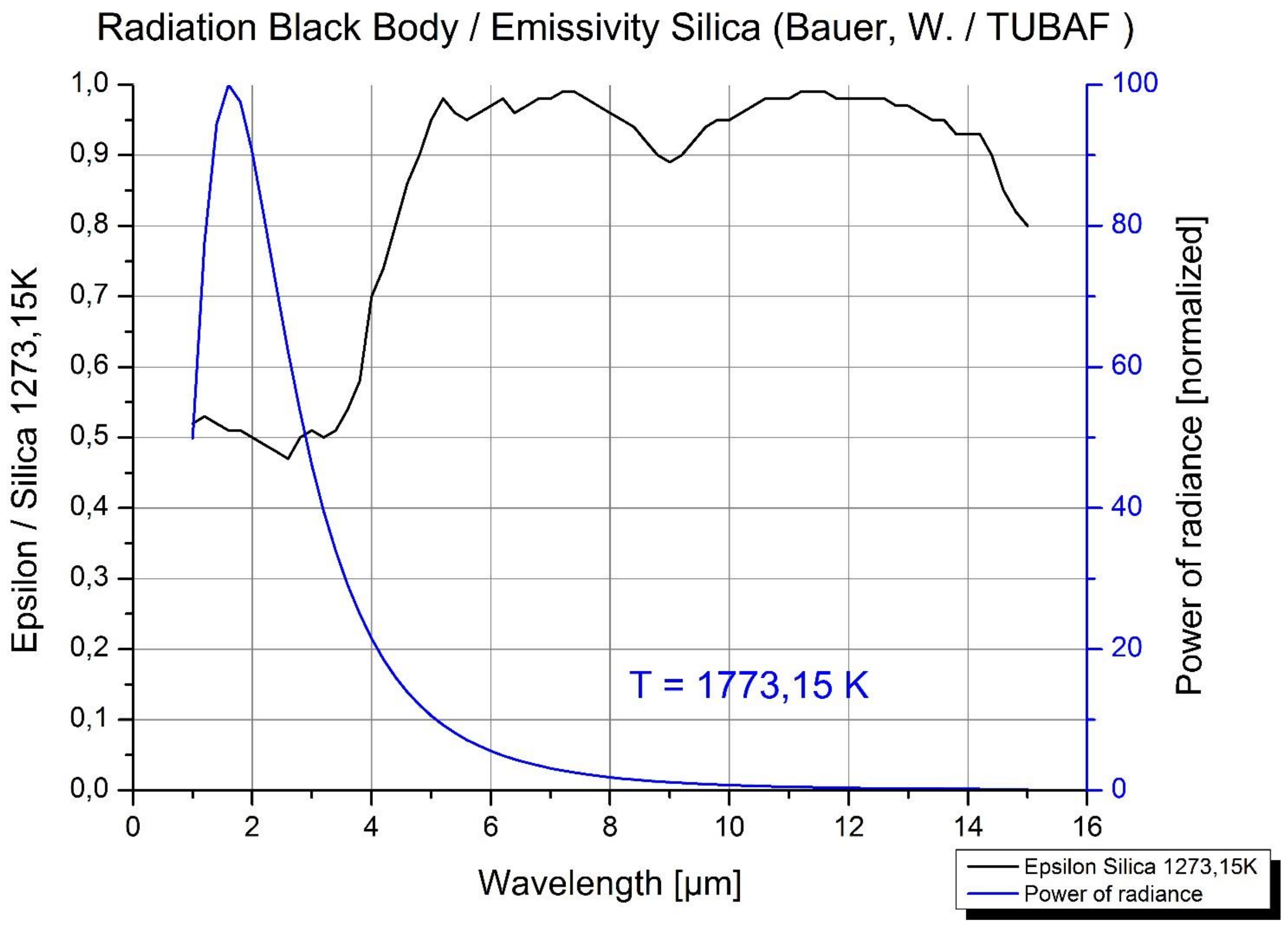
b.) Corrosion improvement especially against NaOH attack

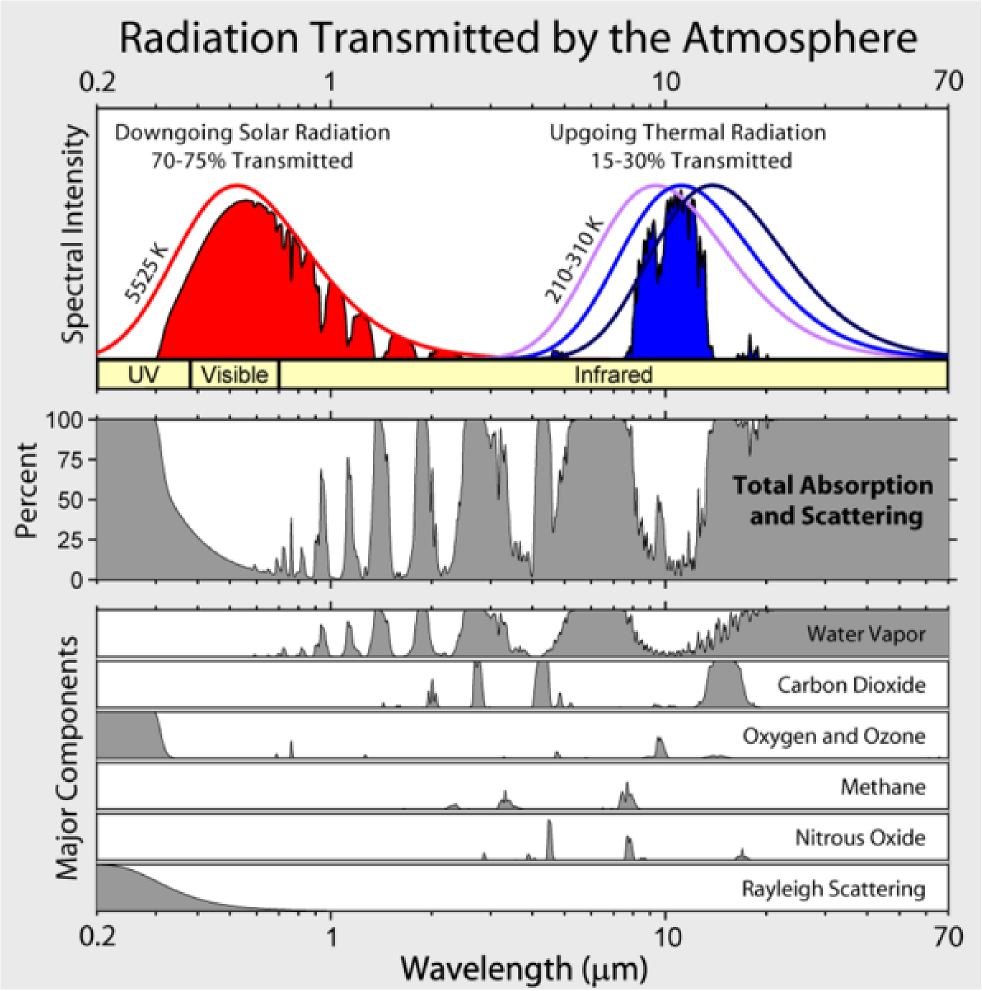
Higher crown temperature below 1700 °C could be an answer to a.)

Limited due to corrosion problems

Coatings could be a possible answer

New cheap and effective coatings for the problems of a.) and b.)


Radiation Black Body / Emissivity Silica (Bauer, W. / TUBAF)
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
Epsilon / Silica 1273,15K
100
80
60
40
20
0
Power of radiance [normalized]
T = 1773,15 K
0
2
4
6
8
10
12
14
16
Wavelength [µm]
Epsilon Silica 1273,15K
Power of radiance


Radiation Transmitted by the Atmosphere
0.2
1
10
70
Spectral Intensity
Downgoing Solar Radiation
70-75% Transmitted
Upgoing Thermal Radiation
15-30% Transmitted
5525 K
210-310 K
UV
Visible
Infrared
Percent
100
75
50
25
0
Total Absorption
and Scattering
Major Components
Water Vapor
Carbon Dioxide
Oxygen and Ozone
Methane
Nitrous Oxide
Rayleigh Scattering
Wavelength (µm)

Examples

silika brick– NaOH-atmosphere
(1500°C – 3 hours)

ancorro after the treatment

ancorro after the test

Reference after the test

Potential batch adjustment

- container glass furnace with a tonnage of 250 $^{t}/_{d}$ and campaign of 10 years
- refinement of the orifice ring to prevent crystallization

  → increasing of CaO-content possible
- lowering of the fining temperature by ≈20K

  → > 3 % energy savings/ minimization of CO_2-Emission

  → reduction of the thermal stress of the furnace

  = decreasing of cat scratches

  = ≈10% service life increasement
- reduction of costs by soda ash
- total savings > 500,000 EUR/year and glass furnace possible
- payback time < 3 months

cat scratches in the glass

Reference: Martinek, Zwiesel 2007

6 Conclusion

- reduction of the refractory corrosion // blistering // crystallization of the glass

  → porous refractories show properties of fused cast refractories

- scale-up of the ancorro-technology from laboratory into industry realized

  → 50% increasing service life fireclay pots

  → 95% lower blistering after plunger change

  → prevent of crystallization at orifice ring by factor 6

  → >65% increasing service life orifice ring

- saving potential container glass > 500,000 EUR/ year and furnace

Further fields of application

metallurgy, cement industry, special glasses, waste incineration, dust and condensation zones in high temperature processes

Reference: Schweizer Fleisch, online 2011

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We are looking for further industrial partners to implement and improve our process.

Reference: http://www.cfoworld.de, online 2013