Developments in Refractories to Extend Glass Melting Furnace Life Time

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Introduction

RHI is the world's leading supplier of high-grade ceramic refractory products and services. The Group produces 1.8 million tons of raw material and refractory products per year.

RHI supplies high quality fused cast and bonded refractories and has an optimized worldwide network of production sites, sales and network. The Glass Industry is one of the key market segments for RHI.

The RHI brand comprises a larger number of successfully established trade marks:

Introduction

In early 2007 the takeover of the US refractory company,

Monofrax

was successfully completed. Monofrax is the sole manufacturer of fused cast refractory products in the USA. These products are mostly supplied to the glass industry.

The life time of a glass furnace depends on many factors. This presentation exclusively discusses the topic “Refractories for the Glass Industry” with the aim to cover different furnace areas.

We would like to arose your interests with this Technical Paper and would like to discuss individual cases later.

Float Tanks, Tin Bath Bottom Blocks

Float glass production needs a tin bath and a tin bath needs bottom blocks.

Peeling (also called flaking) in the hot bays of the tin baths has been the big problem of the float glass producers. Thin layers up to 10mm thick peel off the surface of the TBBB, float upwards and cause trouble in production.
Mineralogically these peels always contain Nepheline, a sodium-aluminium-silicate $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ which normally does not exist in a fireclay brick and is formed only as a result of enrichment with Na_2O.
The Na resp. Na_2O pass from the glass ribbon through the tin into the bottom blocks in an electrochemical process. In the contact area Sn/fireclay block, a reaction occurs between the crystal phase of the fireclay block and the Na_2O from the tin, which produce Nepheline.

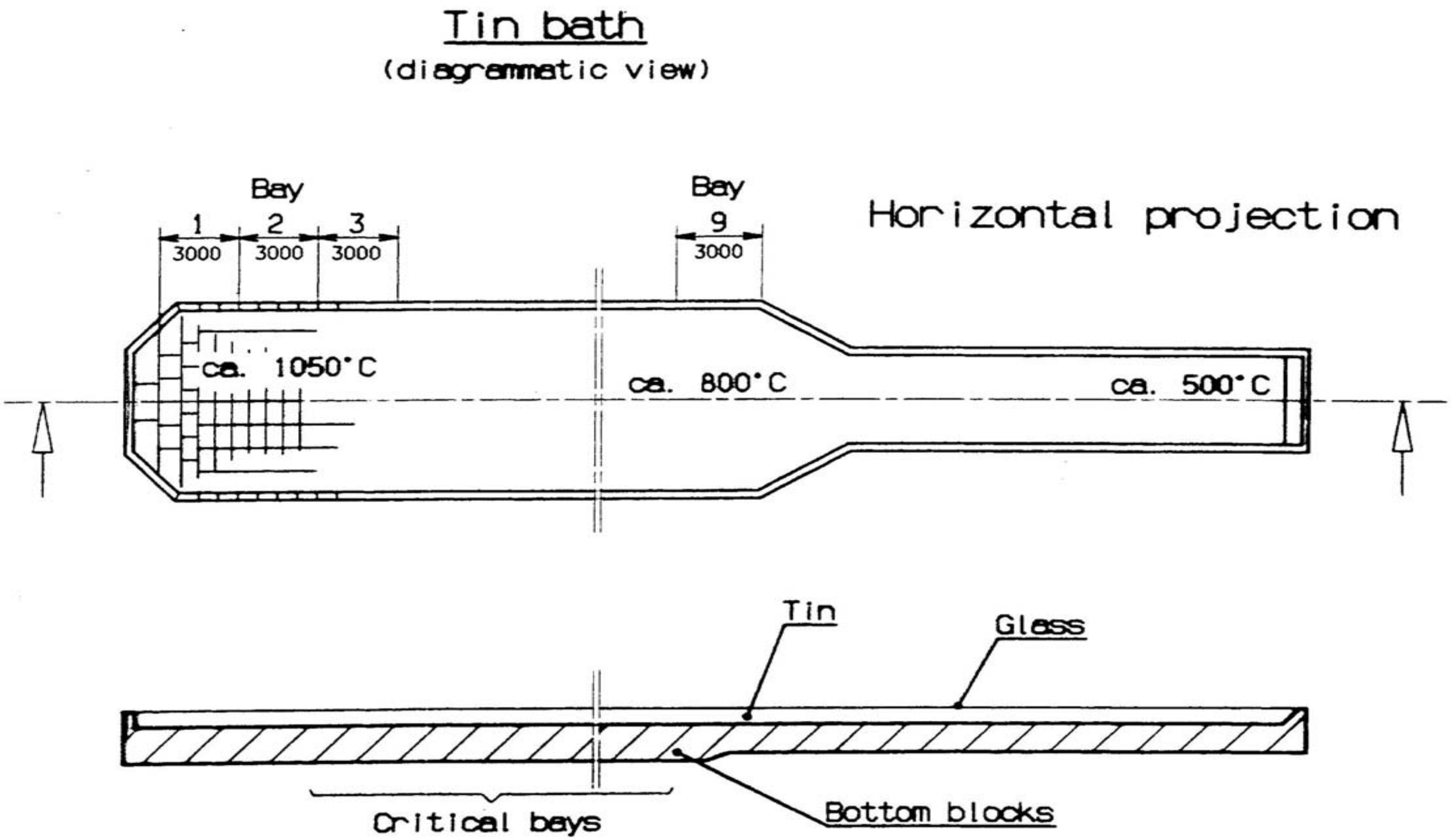
Float Tanks, Tin Bath Bottom Blocks

Critical aspect: Formation of Nepheline is accompanied by an increase in volume of about +20%. And the thermal expansion in the Nepheline-enriched areas is increased almost twice that of a normal fireclay block.

It is certain that changes in production that are accompanied by changes of temperature <u>increase</u> the frequency of the peels.

Nepheline Peeling
Approx. 40 cm diameter

Float Tanks, Tin Bath Bottom Blocks, Scheme



Float Tanks, Tin Bath Bottom Blocks

→ Reactions of alkalines with fireclay:

Original Main Mineral Phases in the block:

Al_2O_3 and SiO_2 ⇒ Mullite
SiO_2 ⇒ Cristobalite
Na_2O and SiO_2 ⇒ Glassy Phase

Transformations through Alkali Attack:

Na_2O + Al_2O_3 + $2SiO_2$ ⇒ Nepheline ⇒ volume growth

(from glass + brick component)

→ Nepheline is critical due to high thermal expansion

Float Tanks, Tin Bath Bottom Blocks

The solution for a long-term tin bath bottom lining = SUPRAL CA

SUPRAL CA is a brick based on **calcium aluminate** raw material. Being inert to alkali attack this compound is ideal for use in the tin bath bottom.

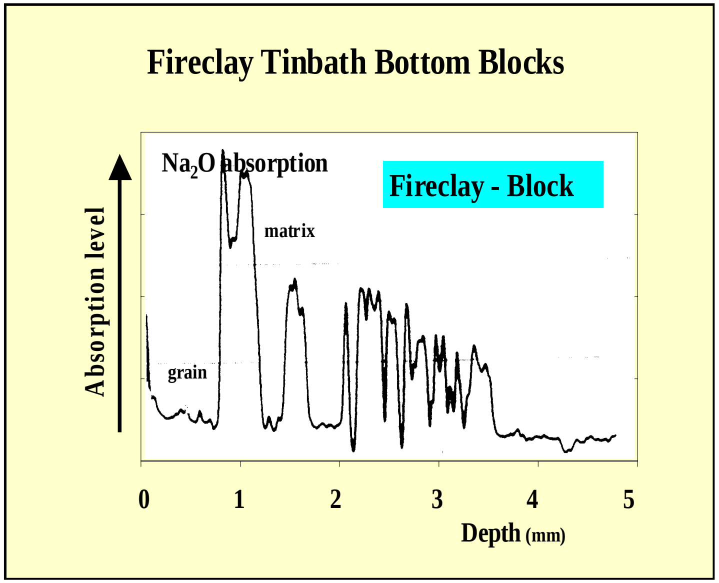
Thermal resistance is higher in comparison to fireclay blocks.

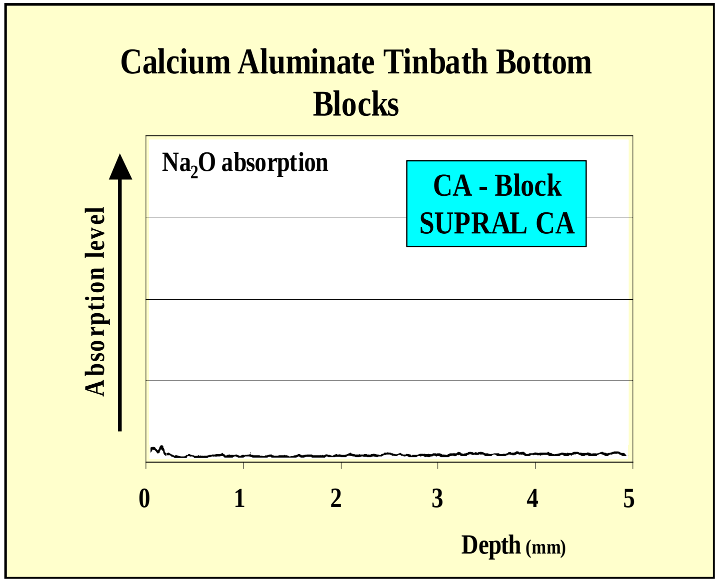
SUPRAL CA can work at a maximum temperature of 1,200°C, whereas fireclay starts to creep at 1,100°C $\Rightarrow$ solution where special glass are produced at high temperature (i.e. borosilicate and aluminate glasses).

Conventional fireclay shows clear signs of peeling, while SUPRAL CA remains impact. All its other properties are ideally gauged to use in the float process.

SUPRAL CA comparison to Fireclay

Alkali Penetration





Analysis of test crucibles (at 1,000°C, 100h, reducing atmosphere)

Float Tanks, Tin Bath Bottom Blocks

Chemical Composition of SUPRAL CA (wt%)

SiO_2 = 5.0 %; Al_2O_3 = 68.0 %; CaO = 24.0 %; MgO = 1.5 %

Physical characteristics

Bulk density	2.26 g/cm^3
Open porosity	23 %
Cold crushing strength	55 N/mm^2
Refractoriness under load t_{05}	1,350 °C
Young`s modulus	12,000 N/mm^2
Modulus of rupture	9 N/mm^2
H_2- diffusivity	10 mm WG
Gas permeability	7 nPm
Thermal expansion at 1,000 °C	0.65 %
Thermal conductivity at 1,000 °C	1.0 W/Km

Float Tanks, Tin Bath Bottom Blocks

Data of two Tin Bath Bottom blocks in comparison

Physical characteristics		SUPRAL 40FG fireclay block	SUPRAL CA CA block
Bulk Density	g/cm³	2.16	2.26
Open Porosity	vol%	19	23
Cold Crushing Strength	N/mm²	60	55
Refractoriness under Load t05	°C	-	1,350
Young's Modulus	N/mm²	13,500	12,000
Modulus of Rupture	N/mm²	9.5	9
H2-Diffusivity	mm WG	10	10
Gas Permeability	nPm	3	7
Thermal Expansion at 1,000 °C	%	0.6	0.65
Thermal Conductivity at 1,000 °C	W/mK	1.3	1.0
Chemical Composition			
$Si0_2$	%	56.0	5.0
Al_20_3	%	38.0	68.0
Ca0 + MgO	%	-	24.0 + 1.5
x-ray Amorpheous Phase	%	25 - 30	-

Fused Cast Refractories

The main application of fused cast AZS refractories are superstructure and glass contact.

High end fused cast refractories

- RHI supplies also α/β alumina, β alumina and has a family of high zirconia fused cast products which include standard Monofrax Z as well as two high resistivity Z grades for glass contact areas for specialty glasses.
- Because of the lower blistering potential, the traditional application of α/β alumina (Monofrax M) is the glass contact for lower temperature (working end, feeder and float tanks).
- Monofrax M is the most stable crown refractory in most glass melting applications.

Fused Cast Refractories

- **Monofrax H** is preferred for crown refractories exposed to high alkali glass melts (more than 26% Na_2O).
- **Monofrax Z**, with 94% ZrO_2 has excellent corrosion resistance against down drill. For this reason, it can be used as bottom pavers, for example, for the lead glass.
- Because of low blistering potential and low knots formation potential, high zirconia (**Monofrax Z and ZHR**) is used for tank sidewalls and paving for specialty glasses like TFT-LCD, aluminosilicate, hard borosilicate and halogen lighting.
- **REFEL 1334SC**, AZS with lower glassy phase content, high-creep resistant and high corrosion resistance against the sand carryover can be used for oxy-furnace crowns and superstructure.

Fused Cast Refractory Linings for Specialty Glasses
Monofrax M (α/β-Alumina) Crown, pre-assembly

Overview of Fused Cast Refractories

RHI

	REFEL REFRATTARI ELETTROFUSI	Monofrax
Plant	Italy	USA
AZS 32	REFEL 1532	Monofrax CS-3
AZS 36	REFEL 1334S	Monofrax CS-4
AZS 36 with low glassy phase	REFEL 1334SC	
AZS 40	REFEL 1240	Monofrax CS-5
α/β alumina		Monofrax M
β alumina		Monofrax H
High zirconia		Monofrax Z
High zirconia with higher electrical resistivity		Monofrax ZHR Monofrax ZHR
Throat blocks with high corrosion resistance	REFEL 1240 FVMo	Monofrax CS-4 EPIC-3 Mo Monofrax K-3 Monofrax E

Container Tanks, Throat Area
Refel 1240 FVMo & Monofrax CS-4 EPIC-3 Mo

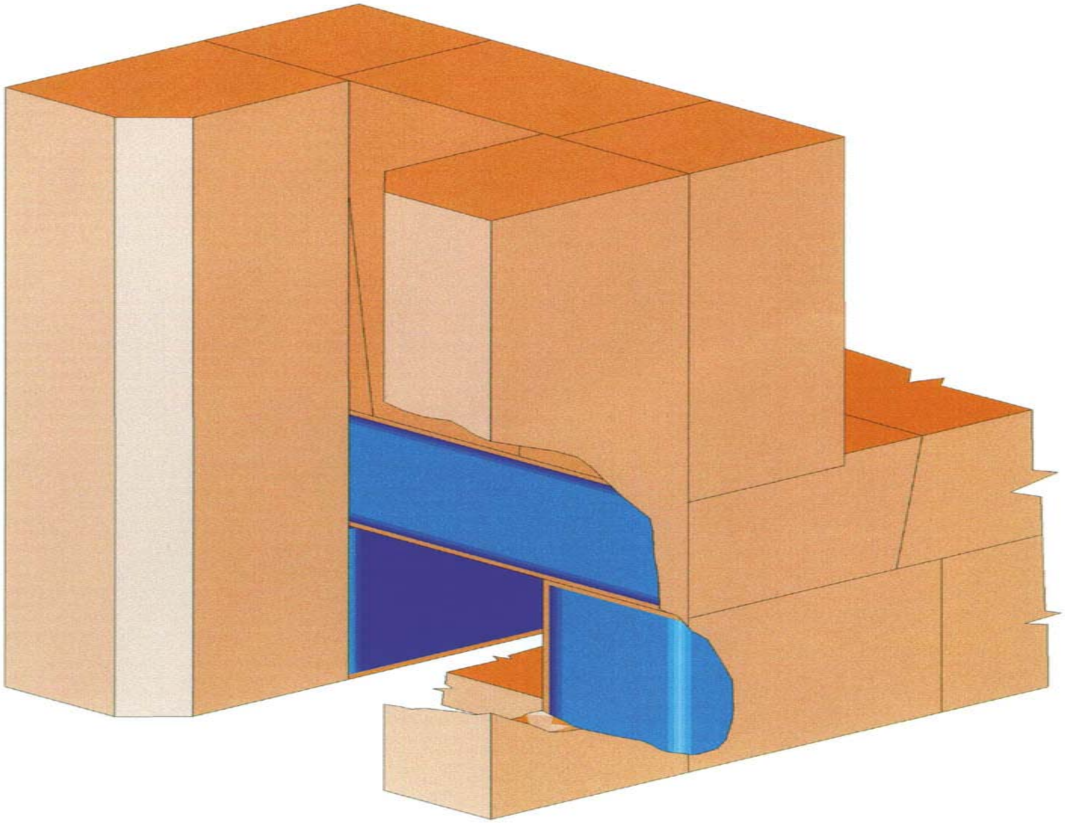
Refel 1240 FVMo is a special product, patented by REFEL, composed of fused cast 41% ZrO_2 material, reinforced with a molybdenum insert, and is particularly suitable for those areas of the glass tank that are submerged and subjected to strong attack like throat and submerged weir blocks

REFEL 1240 FVMo block provides:

- Improved performance and longer service life
- Superior glass quality without coloring effects
- Environmental friendly material

Throat Area, Refel 1240 FVMo

Throat construction example

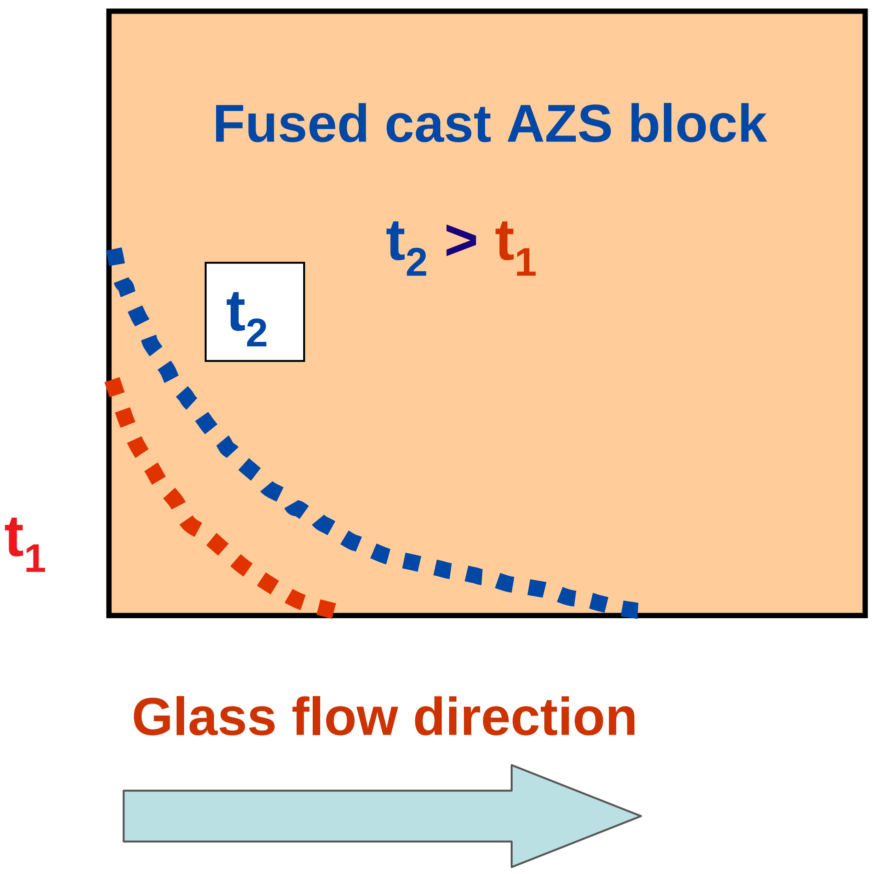


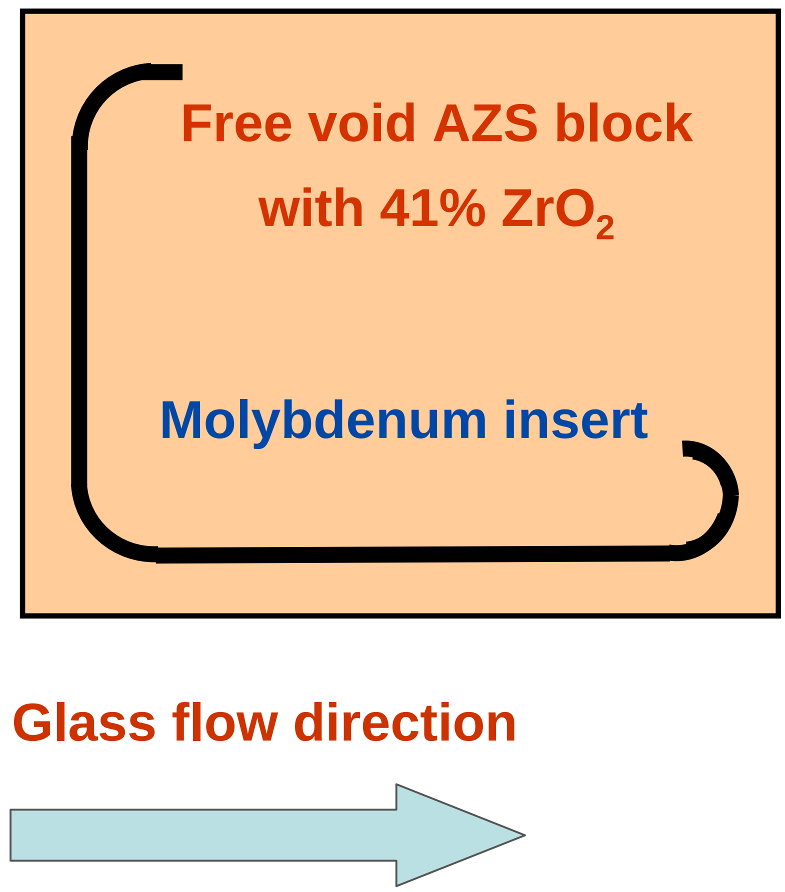
Throat Area
REFEL 1240 FVMo, sample

Construction sample with 3 REFEL 1240 FVMo throat cover blocks

Throat Area

Schematic progress of the corrosion profile of the throat cover block





Throat Area
Results of REFEL 1240 FVMo, special product

Soda lime glass
Throat after 5 years with
AZS 40, but without Moly

Soda lime glass
Throat after 5 years with
Refel 1240 FVMo, no
corrosion of molybdenum

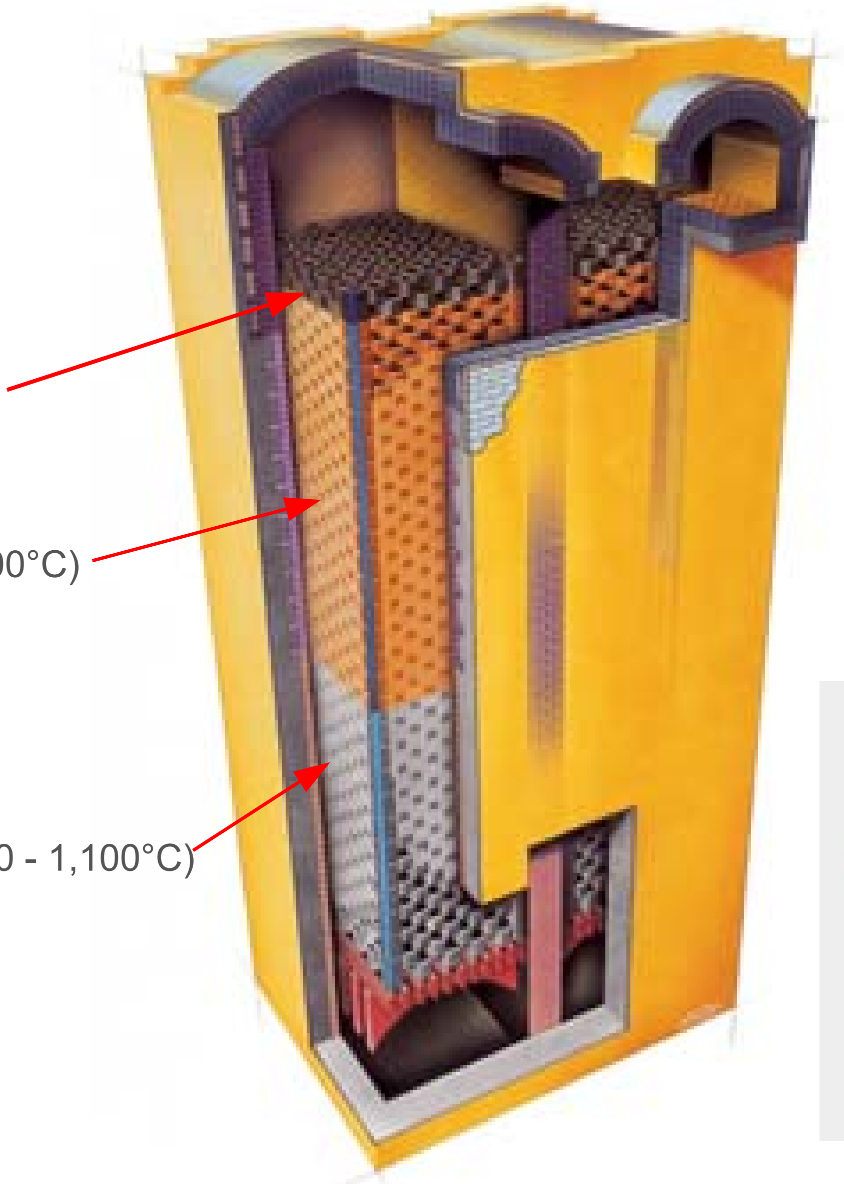
Regenerators, checkers

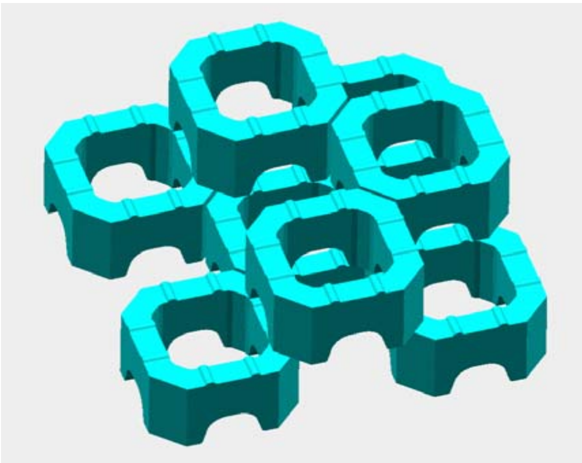
The service life of glass tanks depends also on the regenerators. During the last years there are increasing numbers of demands on the refractory materials for the checkers of soda lime glass furnaces. The mandatory need to fulfill the new environmental regulations, coupled with demand for energy savings have changed present day requirements. The chimney blocks developed by RHI ensure the efficiency of the checker-systems and are notable for the following properties:

- Maximum efficiency
- High stability
- Outstanding corrosion resistance

Nowadays there is **no standard concept**, each lining needs a tailor made solution.

Construction of a regenerator and its checker pack





Oxidizing conditions, reactions in checkerwork:

- **Top and middle courses (> 1,100°C)**

1. SiO_2 attack:
   $MgO + SiO_2$ → $2\ MgO•SiO_2$
   $2\ CaO•SiO_2 + SiO_2 + MgO$ → $CaO•MgO•SiO_2$, $3\ CaO•MgO•2\ SiO_2$, $2\ MgO•SiO_2$
2. CaO attack:
   $2\ MgO•SiO_2 + CaO$ → $CaO•MgO•SiO_2$, $3\ CaO•MgO•2\ SiO_2$
3. V_2O_5 attack:
   C_2S, CMS, $C_3MS_2 + V_2O_5$ → Ca-Vanadate and Ca-Vanadite

- **Condensation zone (700 – 1,100°C)**

1. Sulfate formation:
   $2\ SO_2 + O_2$ → $2\ SO_3$
   $SO_3 + 2\ NaOH$ → $Na_2SO_4 + H_2O$
2. Direct attack of SO_3:
   $MgO + SO_3$ → $MgSO_4$ (< 900°C)
   $CaO + SO_3$ → $CaSO_4$
3. Attack of Na_2SO4:
   $MgO + Na_2SO4$ → Na-Mg-Sulfates
   no attack on M_2S

Mineral	Formula	Abbreviation	Meltingtemp. °C
Periclase	MgO	M	2,800
Forsterite	$2\ MgO•SiO_2$	M_2S	1,890
Monticellite	$CaO•MgO•SiO_2$	CMS	1,495
Merwinite	$3\ CaO•MgO•2\ SiO_2$	C_3MS_2	1,575
Dicalcium silicate	$2\ CaO•SiO_2$	C_2S	2,130

Reducing conditions, reactions in checkerwork:

- **Top and middle courses (> 1,100°C)**

1. SiO_2 attack:
   $MgO + SiO_2$ → $2\ MgO\bullet SiO_2$
   $2\ CaO\bullet SiO_2 + SiO_2 + MgO$ → $CaO\bullet MgO\bullet SiO_2$, $3\ CaO\bullet MgO\bullet 2\ SiO_2$, $2\ MgO\bullet SiO_2$
2. CaO attack:
   $2\ MgO\bullet SiO_2 + CaO$ → $CaO\bullet MgO\bullet SiO_2$, $3\ CaO\bullet MgO\bullet 2\ SiO_2$
3. V_2O_5 attack:
   C_2S, CMS, $C_3MS_2 + V_2O_5$ → Ca-Vanadate and Ca-Vanadite

- **Condensation zone (700 – 1,100°C)**

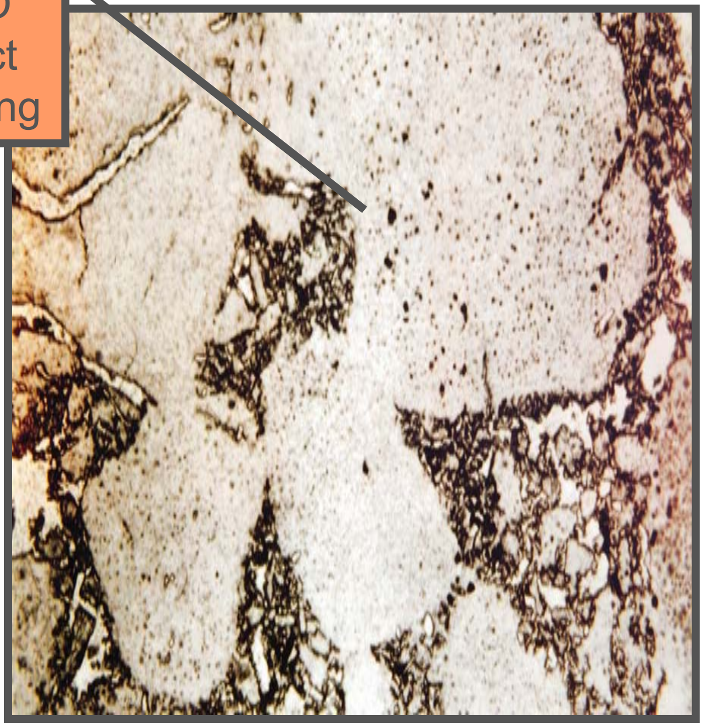
1. Only strongly reduced Sulfate formation, therefore no attack of Sulfates
2. Attack of NaOH on Forsterite:
   M_2S + NaOH → Na-Mg-Silicates + H_2O
3. Attack of NaOH on Sillimanite, Fireclay, Mullite, AZS:
   A_xS_x + NaOH → Nepheline + Al_2O_3 (ΔV = 6 - 36%)
4. Attack of NaOH on Alumina:
   Al_2O_3 (α-Alumina) + NaOH → β-Alumina (ΔV = 28%)

Mineral	Formula	Abbreviation	Meltingtemp. °C
Periclase	MgO	M	2,800
Forsterite	$2\ MgO\bullet SiO_2$	M_2S	1,890
Monticellite	$CaO\bullet MgO\bullet SiO_2$	CMS	1,495
Merwinite	$3\ CaO\bullet MgO\bullet 2\ SiO_2$	C_3MS_2	1,575
Dicalcium silicate	$2\ CaO\bullet SiO_2$	C_2S	2,130

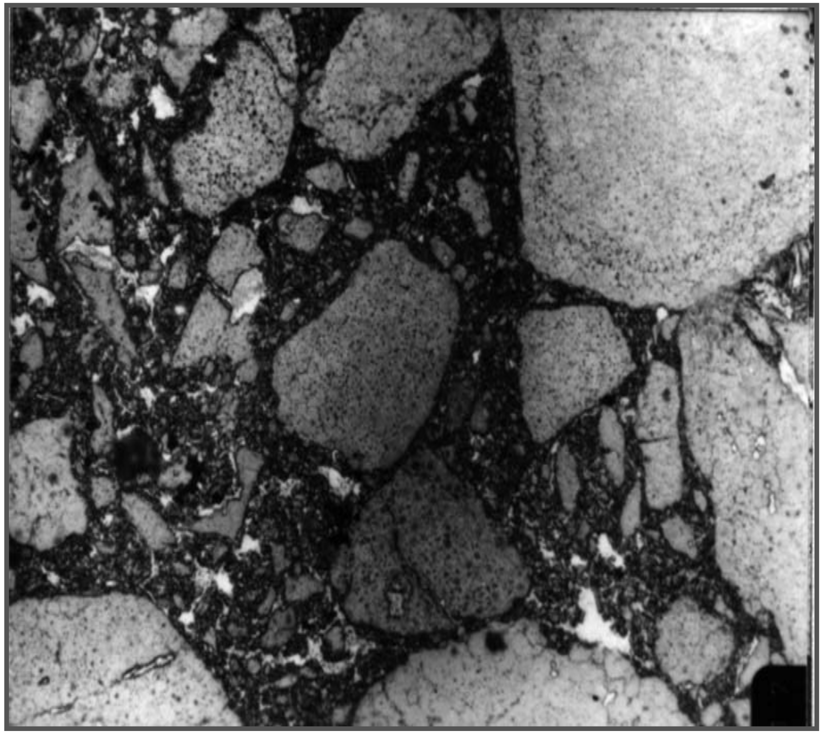
Regenerators, checkers,

Difference high fired vs. low fired

MgO direct bonding



High fired – direct bonding



low fired – no direct bonding

Lining Recommendations for the Checkerwork

	Oxidizing Conditions	**Reducing Conditions**
Top courses > 1,450°C	Magnesia-Zircon: **RUBINAL VZ** Ceramically bonded fused Alumina: **DURITAL K99 EXTRA**	Magnesia-Zircon: **RUBINAL VZ** Ceramically bonded fused Alumina: **DURITAL K99 EXTRA**
Middle courses, ***gas*** 1,100 – 1,450°C	C_2S-bonded Magnesia (partly direct bonded): **ANKER DG1**, **RUBINAL VS**	C_2S-bonded Magnesia (partly direct bonded): **ANKER DG1**, **RUBINAL VS**
Middle courses, ***oil*** 1,100 – 1,450°C	Magnesia-Zircon: **RUBINAL VZ**	Magnesia-Zircon: **RUBINAL VZ**
Lower courses < 1,100°C	Magnesia-Zircon: **RUBINAL EZ**	C_2S-bonded Magnesia (partly direct bonded): **ANKER DG1**, **RUBINAL VS**
Rider arches < 1,000°C > 1,000°C	 **RESISTAL S 65G** **DURITAL E 75 EXTRA**	 **RESISTAL S 65G** **DURITAL E 75 EXTRA**

STELLA GNL, a New Fused Silica Brick

Practical experience showed the outstanding performance of fused silica bricks installed during the hot repair in crowns. The disadvantage of this grade is the shrinkage at t > 1,100°C which reduces dramatically the range of application.

STELLA GNL is a brick based on fused silica without lime.

In standard silica, CaO content is normally 2.5-3.0 wt%;

$CaO-SiO_2$ bonding phase can react with $Na_2O \Rightarrow Na_2O-CaO-SiO_2$-phase with low melting point $\Rightarrow$ gradual corrosion of the SiO_2-coarse grain in the $Na_2O-CaO-SiO_2$-melting phase.

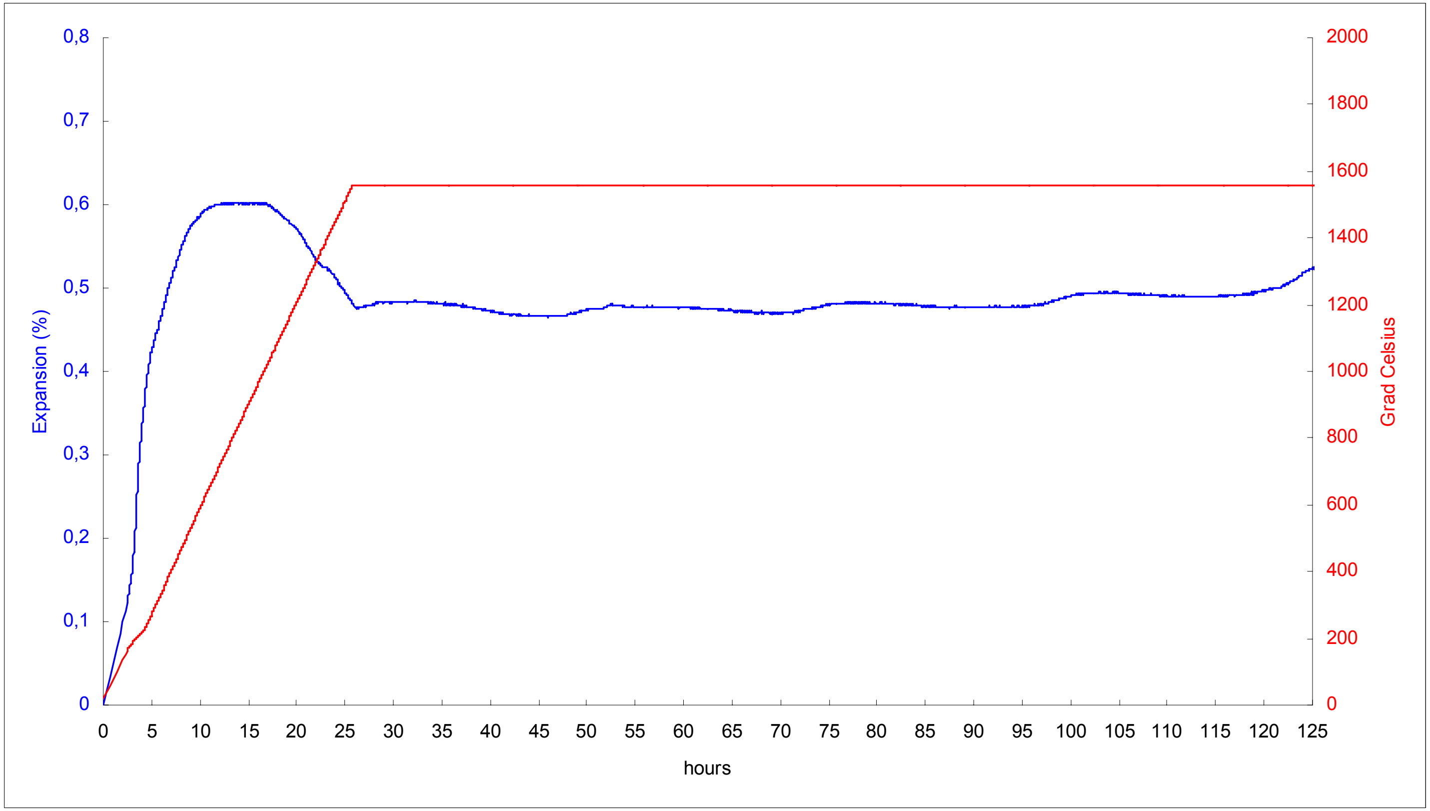
STELLA GNL, a New Fused Silica Brick, comparison

	Super Duty Silica Stella GGS	No Lime Silica Stella GNL
Bulk Density	1.86 kg/dm³	1.83 kg/dm³
Open Porosity	19.5 %	19.5 %
Cold Crushing Strength	40 N/mm²	35 N/mm²
Creep, 0.2N/mm²	- 0.6 % (1,600°C)	0.0 % (1,650°C)
Refractoriness under Load $T_{0,5}$	1,650°C	1,690°C
Thermal Expansion	1.3 % (700°C)	0.65 % (600°C)
Chemical composition in %		
SiO_2	96.5	99.1
Al_2O_3	0.4	0.1
Fe_2O_3	0.5	0.1
CaO	2.5	0.1
Alkalis	0.1	0.1

STELLA GNL, a New Fused Silica Brick

Creep test at 1,550°C

Thermal Expansion under Load (Creep); at 1,550°C, 100h; given load = 0.2 N/mm²; 20°C – 1,550°C = 60K/h,

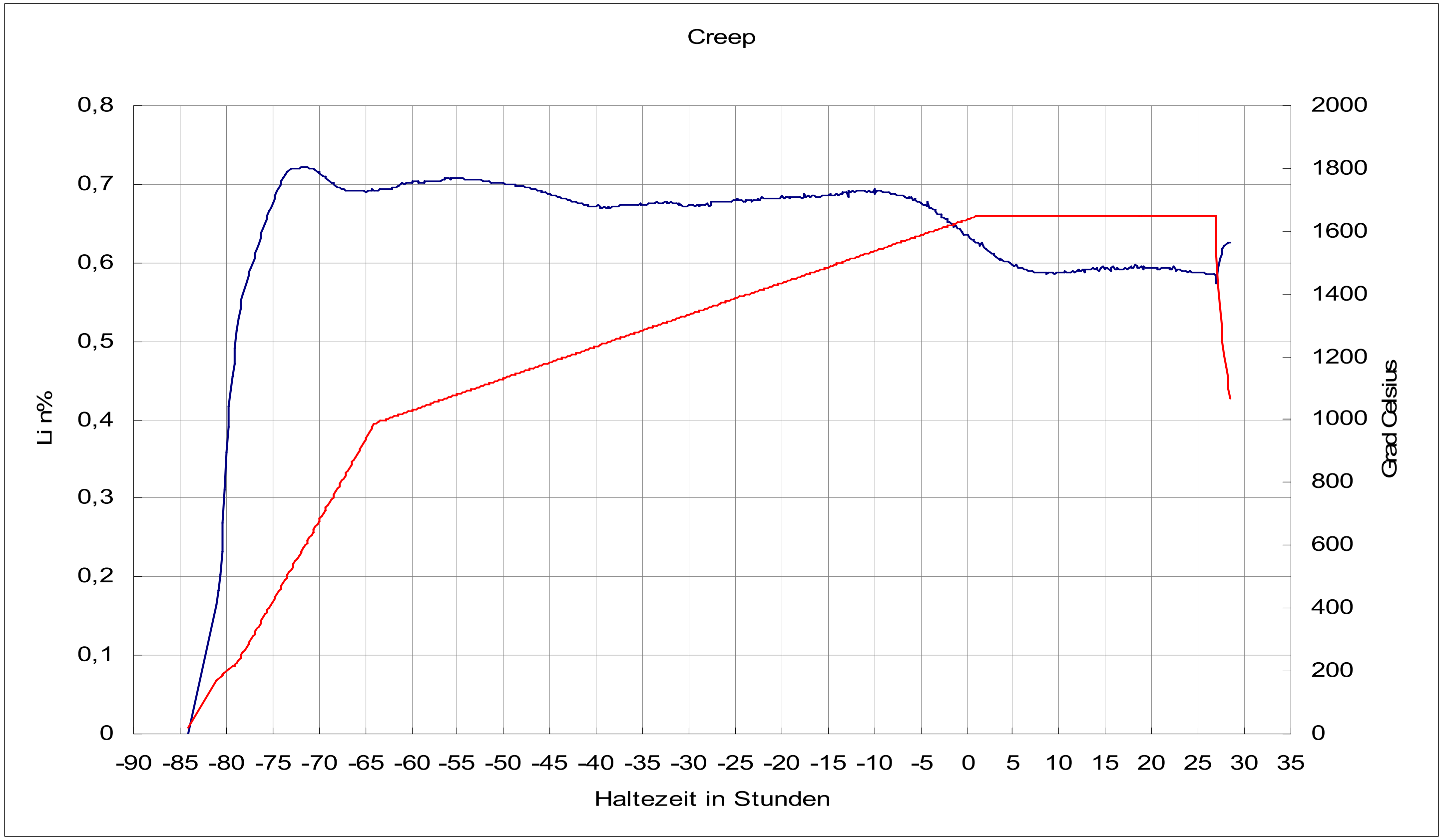


STELLA GNL, a New Fused Silica Brick

Creep test at 1,650°C

Thermal Expansion under Load (Creep); at 1,650°C, 25h, given load 0.2 N/mm²

20°C – 1,000°C = 50K/h and 1,000°C – 1,650°C = 10K/h, given load = 0.2 N/mm²



STELLA GNL, a New Fused Silica Brick

Applications:

- **Superstructure of refiners in the float process**
- **Crown of oxy-fuel fired soda-lime furnaces (reason: NaOH concentration in the atmosphere 2 - 6x higher, less waste gas volume)**
- **Inexpensive alternative to fused cast α/β alumina and fused cast AZS**
- **GNL can be used for higher temperature than standard silica**

- **Maximum dimension: 820x620x168 mm^3**

New Dense and Microporous Refractory Materials

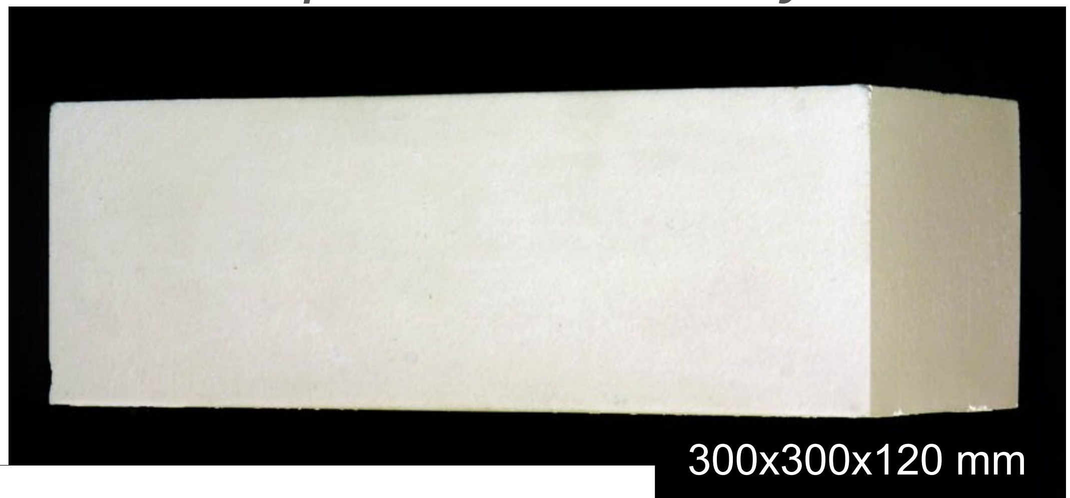
- The requirements on the refractory materials in glass furnaces are increasing permanently. The demand on the lifetime and the low glass defect potential are only two examples for it.

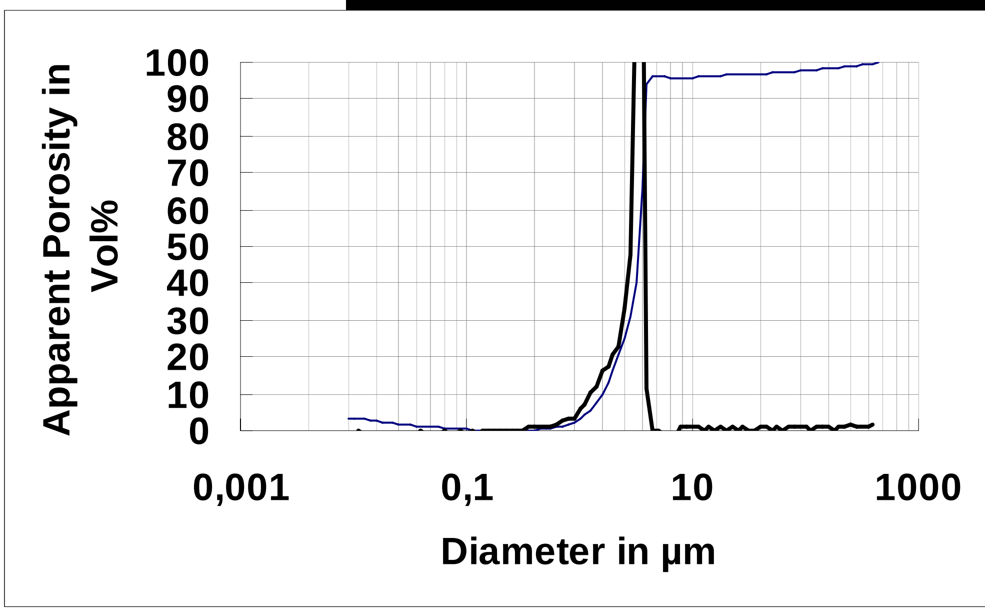
- On the other hand, the development potential of the traditional fused cast and bonded materials is limited.

- RHI developed a new class of sintered, dense and microporous refractory products: <u>Dense Alumina</u>, Dense Zircon (and Dense Alumina-Zirconia).

- Tests indicate on better properties in comparison to conventional refractories:
    - Higher thermal shock resistance
    - Better corrosion resistance

New Dense and Microporous Refractory Materials





Typical Properties:

Al_2O_3 (w.%): > 99

Bulk Density (g/cm^3): 3.4 – 3.5

Apparent porosity (vol.%): 10 – 12

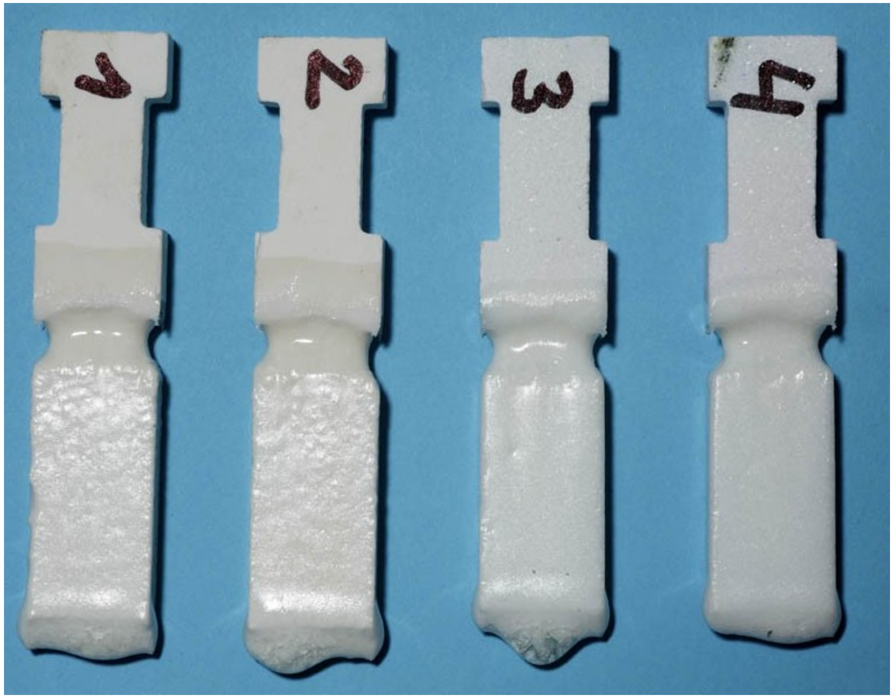
Cold crushing strength (MPa): > 280

Thermal shock (cycles) measured by water method: 10 - 13

New Dense and Microporous Refractory Materials

Dense Alumina Refractory Material – Corrosion resistance

Dense Alumina (left) and Fused cast α/β Alumina (right)



Static Plate corrosion test:

Soda-Lime-Silica Glass

Temperature: 1,400°C

Hold Time: 72 hours

	Wear at Glass line	Wear below Glass line
Microporous Alumina	**2,9**	**0,3**
Alpha-beta Alumina	**3,2**	**0,4**

→ **Better corrosion resistance compared to alpha-beta Alumina**

Recommended application:

→ **bottom pavings of refining area of float furnaces**

Hot Repairs/Overcoating

DURITAL RK30NP and DURITAL RK 50P

The metal line is one of the most corroded areas. To reduce corrosion speed, intensive air-cooling is applied; but in spite of the cooling it has to be repaired during a normal furnace campaign. The repair consists normally in overcoating the corroded part with tiles, in most cases fused cast AZS tiles.

DURITAL RK 30NP is based on chrome alumina with 30% Cr_2O_3 with following advantages:

- **High corrosion resistance**
- **Very high thermal shock resistance**
- **Installation without preheating**

Hot Repairs/Overcoating

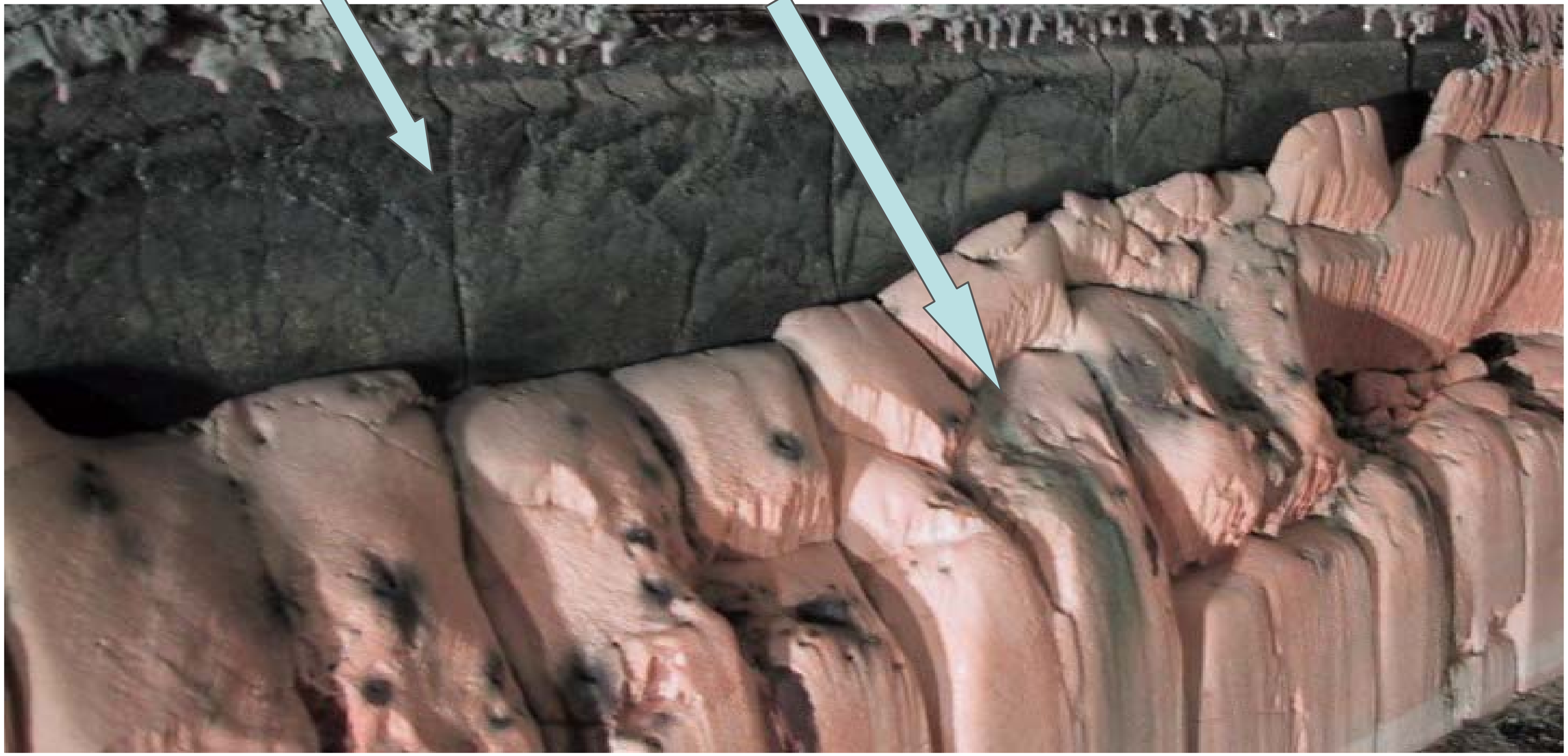
DURITAL RK 30NP, overcoating tiles based on chrome alumina

Installation as overcoating in a green glass container tank:

Over coated area

New overcoating

Hot Repairs/Overcoating
DURITAL RK 30NP   Fused Cast AZS



Overcoating in a green glass container tank after three years

Summary

In this presentation a lot of different topics were discussed how you extend the life time of glass melting furnaces.

These mentioned examples are partly latest developments of the RHI Group and certainly further “old and new” recommendations and solutions are available.

RHI is the world`s leading supplier of high-grade ceramics refractory products and services. As a reliable and competent partner for the **Glass Industry** (we supply the complete range of bonded and fused cast refractories) RHI has the constant objective to offer refractory systems solutions with the best price/performance ratio.

Thank you very much for your attention!!

Vielen Dank!!

For further information please contact:

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