RHI MAGNESITA

The 9th International Symposium on Refractories

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Low carbon refractory solutions for the glass industry

Hilmar Schulze-Bergkamen

Introduction_Technology trends in the glass industry

RHIM_General

H_2 compatible refractories

Glass furnace crown solutions

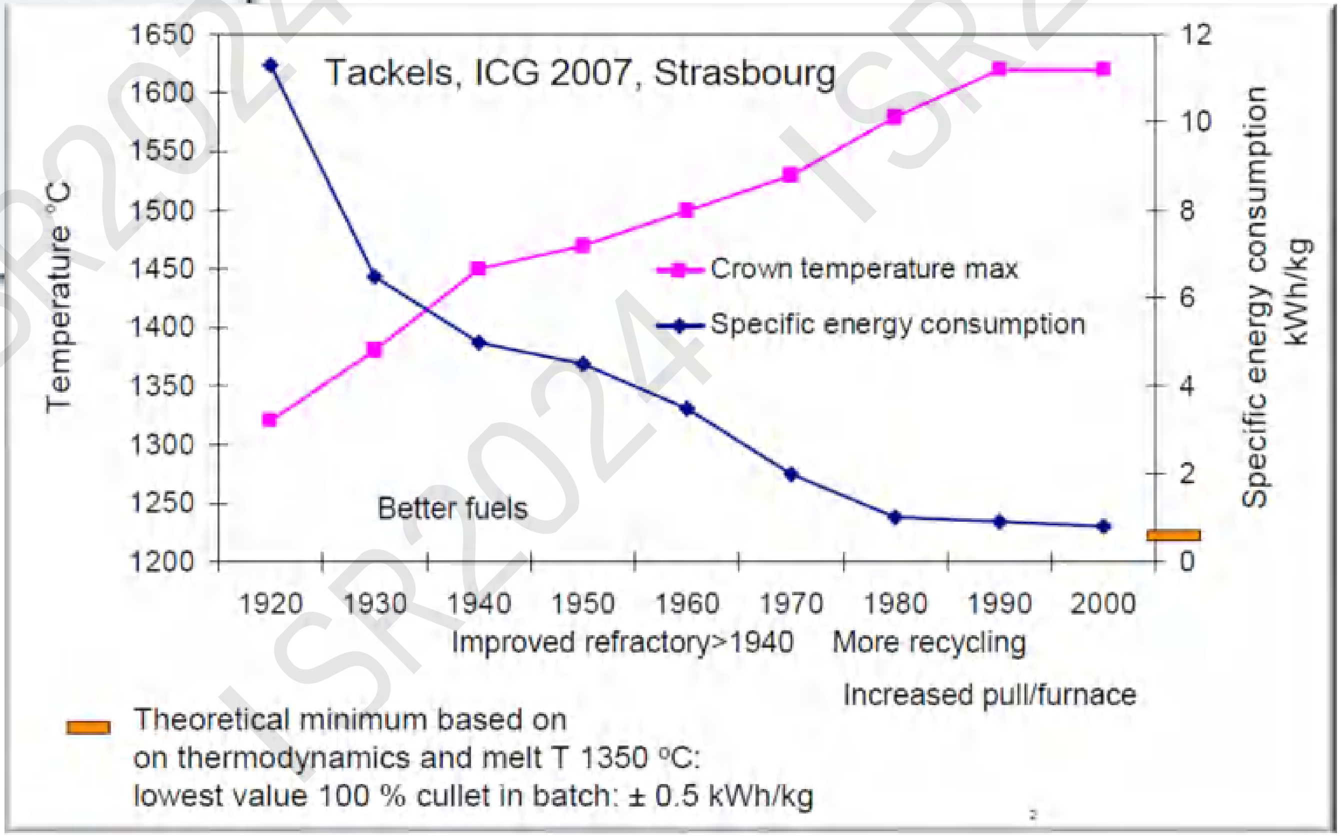
Glass tank regenerator solutions

Glass tank bottom solutions

Vibro and slip cast

Glass Industry_Current and Future Challenges

- Climate Change and Geopolitics
- Energy consumption
- Strict environmental obligations (net zero CO_2 by 2050)
- Emission trading and CO_2 costs
- Furnace lifetime
- New fuels
- Supply chain disruptions



Decarbonization of the glass industry

Renewable energy

Including transitioning to renewable energy sources, such as **solar**, **wind**, **hydropower**, **low carbon fuels (e. g. biofuels)** to power furnaces and other energy-intensive processes. This transition requires the development of advanced furnace designs.

Recycled glass

The glass industry is actively promoting the collection and recycling of **post-consumer glass**, which reduces the need for raw materials and lowers the energy required for production.

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Decarbonization of the glass industry

Carbon capture from glass furnaces

The implementation of CCS in the glass industry is still in its early stages, but several pilot projects and feasibility studies have demonstrated the potential of this technology.

Collaboration and industry initiatives

The glass industry is actively participating in **cross-sectoral partnerships** and **industry initiatives** to share best practices, develop common standards, and advocate for policies that support decarbonization efforts. Examples include the European Container Glass Federation's (FEVE) "**Close the Glass Loop**" program and the Glass Futures research and development project. For example, the **captured CO_2 can be used as raw material in the chemical industry**. Other waste can be used in **construction**, **agriculture** applications.

Development of low-carbon and low-melting glass formulations

Researchers are exploring **alternative glass compositions** that can be produced with lower carbon emissions, such as **pre-calcination of raw materials** or using alternative raw materials (wollastonite $CaSiO_3$ in place of $CaCO_3$)

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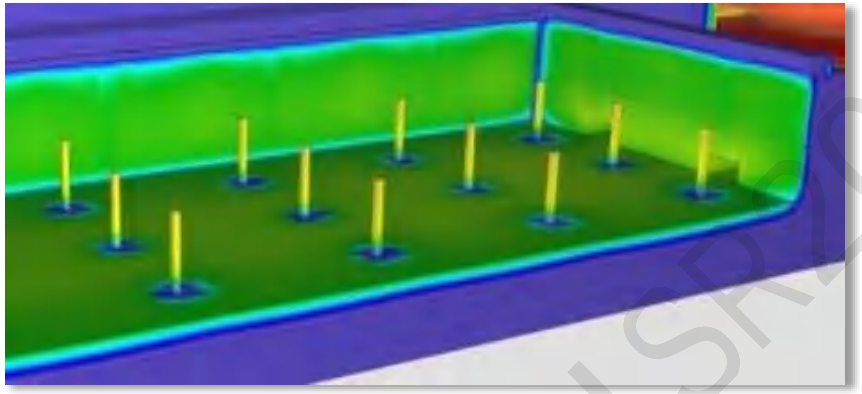
Decarbonization of the glass industry



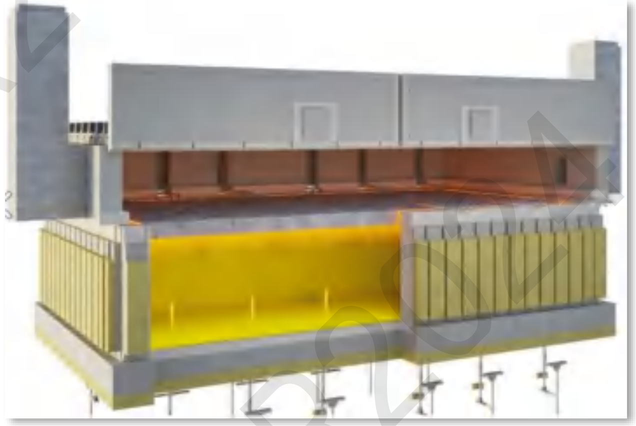
https://www.hornglass.com/

Oxy-fuel furnaces

The fuel (mostly natural gas) in oxy-fuel furnaces is combusted with pure oxygen, which reduces the amount of energy required (little nitrogen used for combustion) and lowers carbon emissions.

Full electric furnaces

This is a well-known technology, already adopted for high quality glasses and with low productivity (120 tpd has been a limit a few years ago). The source of electricity must be renewable; limitations include: no flexibility in furnace operation and production limited to flint glass.



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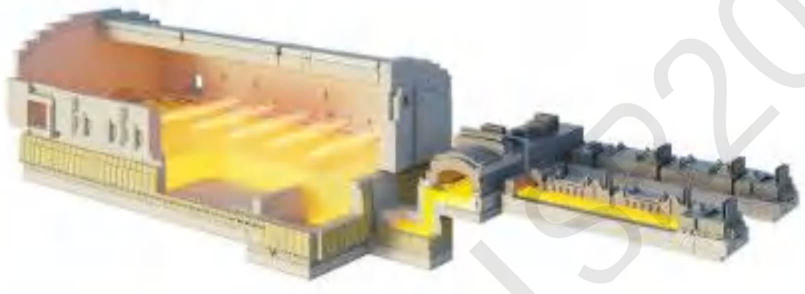
Decarbonization of the glass industry



https://www.hornglass.com/

Hydrogen fueled furnaces

Hydrogen is a carbon free fuel that can be used in intensive-energy processes; it does not produce CO2 as combustion product. However, the use of hydrogen is challenging:

1. **Hydrogen is not available in nature**, and it must be produced either with steam reforming (grey or blue hydrogen), or via electrolysis, providing that the electric energy is produced from renewable sources
2. **Amounts** necessary for firing a glass furnace are huge; for example, for a small glass furnace requiring approximately 1000 Nm3/h of natural gas, the quantity of equivalent hydrogen would be approximately 3.500 Nm3/h
3. **Infrastructure**-the combustion system must be suitable for hydrogen (larger pipe dimensions, suitable gaskets as the hydrogen molecule is smaller than the typical NG one, higher risks of leakages). Additionally, it must be produced or stocked on site since the network for NG is not yet suitable for 100% Hydrogen transport.

Hybrid furnaces

Advanced technology; developed for mostly using electrical energy from green sources, e. g. from nuclear power, as melting media. The electrical power can sum up to 80% of the total energy required to melt the glass. The remaining 20% is supplied via gas, eventually hydrogen.

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Decarbonization of the glass industry

Lightweight glass production

Some glass manufacturers have developed technologies to produce lighter-weight glass products, which require less energy to melt and transport. This can include the use of thinner glass walls or the incorporation of lightweight fillers in the glass composition.

Predictive maintenance (partially developed by Paneratech and SEFPRO)

Glass manufacturers are using predictive maintenance technologies to monitor the condition of their furnaces and other critical equipment. By analyzing sensor data and historical performance patterns, they can identify potential issues before they occur and schedule proactive maintenance to prevent unplanned downtime and ensure optimal energy efficiency.

Decarbonization of the glass industry

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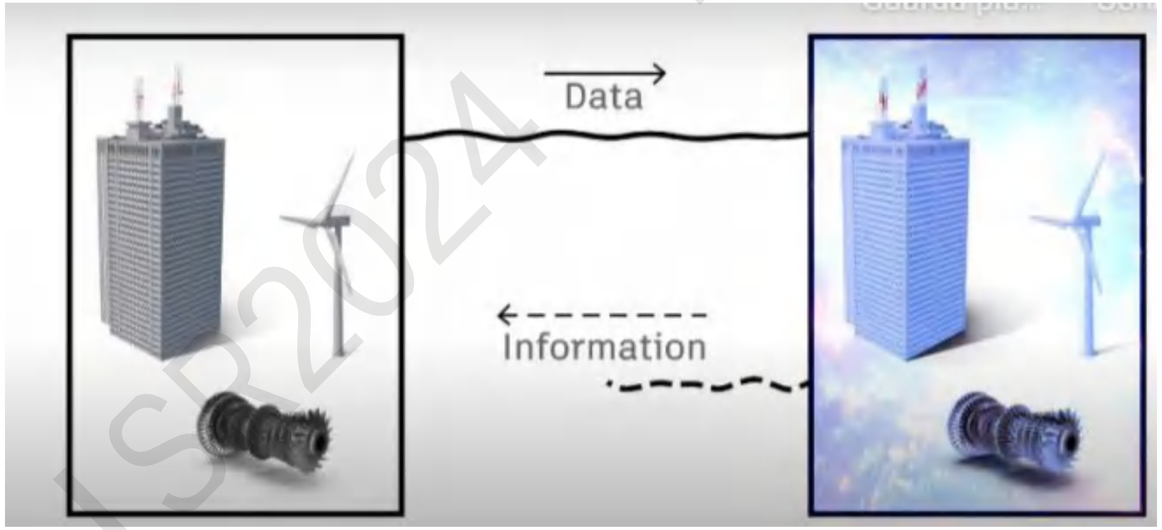
Digital twins

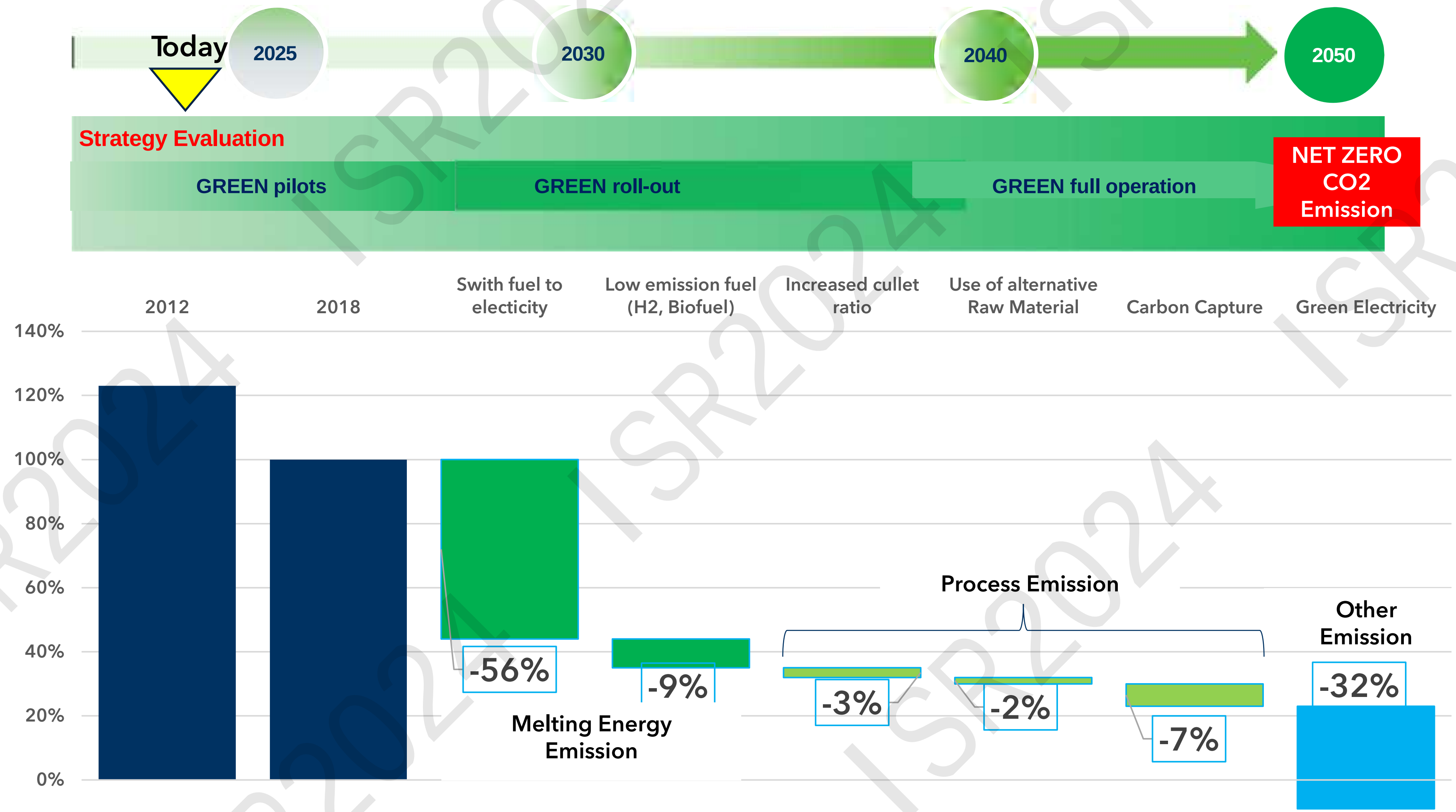
Some glass manufacturers are creating digital twins of their production facilities, which are virtual replicas of the physical system. They can be used to **simulate and test different process optimization scenarios**, allowing manufacturers to identify the most energy-efficient configurations before implementing them in the real world.



Artificial intelligence and machine learning

Glass manufacturers leverage AI and machine learning algorithms to analyze vast amounts of data from their production processes and identify patterns and insights that can be used to optimize energy efficiency.

Reducing the CO_2 footprint: The roadmap



Source British Glass

Low carbon refractory solutions for the glass industry

RHIM_General

The global leader in refractories

There for you, wherever you need us

47 production sites
(incl. raw material sites)

8 recycling facilities (e. g. MIRECO, Austria)

+100 countries shipped to worldwide

5 R&D hubs and centres

> 21,000
Employees

€ 3.6bn
2023 revenue

+ 1,700
Active patents

€ 83m
Investment in R&D and Technical Marketing

Status of RHIM's glass business

Integration of recently acquired companies

P-D Group, Dalmia/OCL, Seven Refractories

Creation of silica hub in Europe

Czech Republic

Evolution of silica crown bricks

Combination of different technologies

Development of new unfired glass tank bottom blocks

Significant reduction of carbon footprint

Strong focus on reducing product carbon footprint

Developing circular economy

Overview of former PD Group

4 **production sites** in Germany and Czech Republic

2 **raw material sites** in Czech Republic (fireclay mine and processing plant + **quartzite mine** in Slovenia

Rebranding: RHIM-Si96 (new)

>**10 tunnel kilns** with a total nominal capacity of >120kt/a

Product portfolio
Silica, **fireclay**, **andalusite**, **mullite**, **insulation** (perlite), **bottom blocks** (pre-assembly, fired and unfired)

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Low carbon refractory solutions for the glass industry

H_2 compatible refractories

H_2 compatible refractories

H_2 as process gas and fuel

Steel, petrochem..

Non-ferrous, glass, cement and lime …

The injection of hydrogen in the blast furnace

Injection of hydrogen in the blast furnace to partially replace coke

DRI (direct reduced iron)

Use of hydrogen as reducing agent in the solid-state reduction of iron

HPSR (hydrogen plasma smelting reduction)

Reduction of iron by hydrogen plasma; technology with a low TRL

The use of hydrogen as fuel

Partial or full replacement of fossil fuels to provide energy for industrial furnaces

- Global plant footprint for alumina silica products
- References for different technologies
- Decades of track-record with refractories under hydrogen atmospheres
- R&D program and in-house test equipment

- Pilot & industrial scale trials with customers, OEMs and suppliers in steel, aluminum and cement
- Invest in-house: hydrogen fired industrial kiln Germany to be started in Q3/2024
- R&D program and post-mortem analysis

Technological leadership

What changes?	To be considered
Little amounts of hydrogen left after combustion	No issues
Depending on the chosen gas mix (pure H_2, mixed with CH_4, etc..) the **flame temperature** and **shape** can be different compared to using natural gas	Lining (and burner) **concept should be re-evaluated** and eventually adapted according to temperature profile values
Firing of H_2 potentially results in higher percentages of **water** (up to 100%).	Most **pure refractory oxides are not affected**. Magnesia will not react with water.
	Alkali attack increased and must be considered using refractories with low glassy phase
	Insulation most likely affected as water condensation can occur at colder spots
	Water of fumes and possible interaction in the lower part of regenerators with SO_2
Different combustion atmospheres, especially with high water content result in different **heat transfer**	A slight impact on **insulation values** of the refractory lining and change in temperature gradient throughout lining is to be expected.

Low carbon refractory solutions for the glass industry

Glass furnace crown solutions

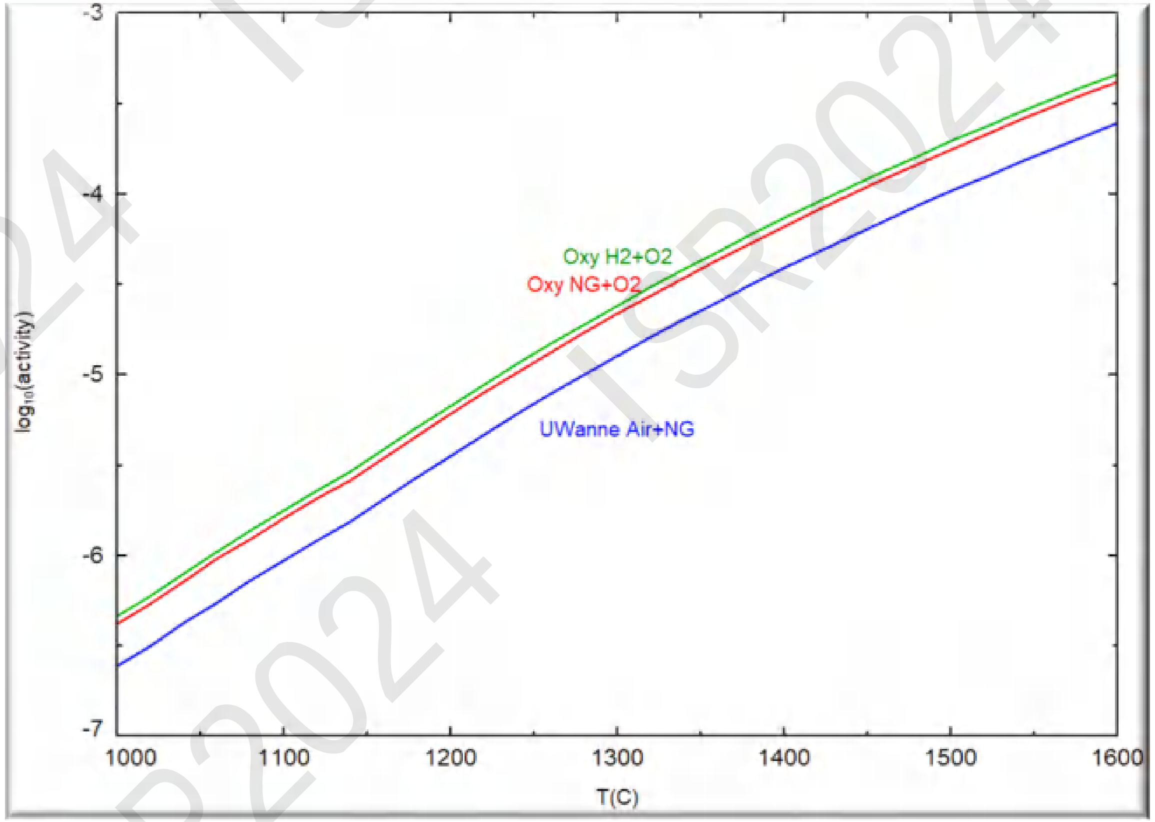
Silica bricks

Variants

Standard	RHIM-Si96 ≙ STELLA GGS
Low lime	RHIM-Si97ll (based on quartzite)
Low flux	RHIM-Si97lf (based on quartzite)
No lime	RHIM-Si100nl (based on fused silica)
ε-technology	RHIM-□ε
Hand-rammed	
Insulation	

Main requirements for glass furnace crowns

- Withstand high thermomechanical load
- No source of glass defects
- Corrosion resistant against batch carry-over in doghouse area and evaporation products



$\log_{10}$ pNaOH between 1000 and 1600°C under different atmospheres

Typical Properties

Material Selection

Characteristic	STELLA GGS	STELLA GNL
SiO_2	~ 96%	~98,5%
CaO	2,5%	<0,05%
Al_2O_3	~0,4%	~0,1%
Fe_2O_3	0,5%	~0,1%
Residual Quartz	<0,5%	~0,0%
Bulk Density	1,84 gr/cm^3	1,9 gr/cm^3
Apparent Porosity	<20% Vol.	<16% Vol.
CCS N/mm^2	40	45
RuL	1660°C	1690°C
Creep Z5-25 (typical)	-0,1%@1550°C	0,01%@1650°C
TE	1,3% (700°C)	0,85% (600°C)

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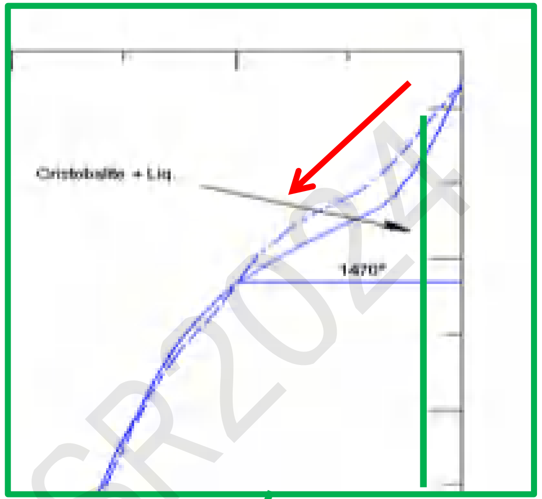
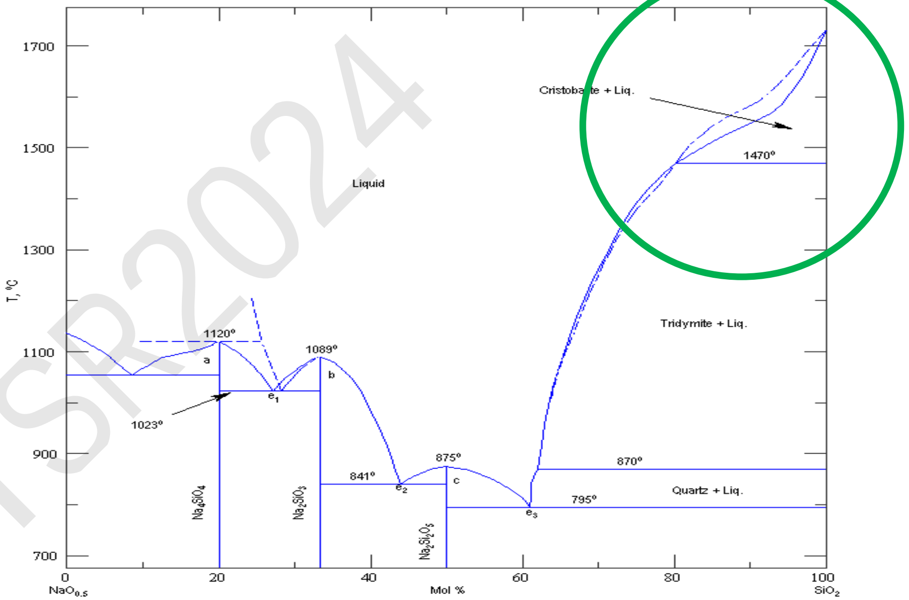
Influence of Alkalis and CaO on Glass Phase and on Refractoriness

Material Selection

Refractory	SiO_2 (wt%)	Na_2O (wt%)	Al_2O_3 (wt%)	CaO (wt%)	Total melt content at 1500°C (wt%)
STELLA GNL	98.6	1.0	0.3	0.1	0,0074
Standard Silica #1	95.9	1.0	0.6	2.5	4,32
Standard Silica #2	95.4	2.0	0.6	2.0	6,66



- The higher the number of alkalis, the higher the amount of molten glass phase
- The alkalis preferably react with CaO-rich phases, therefore No Lime Silica is less sensitive to high alkali concentration
- 2-Phase System Na_2O-SiO_2: Increased Alkali content quickly lowers the refractoriness



STELLA GNL – Corrosion resistance

High in water content atmospheres → alkali attack

No lime silica in Oxy-fuel furnace
after 11 years in operation

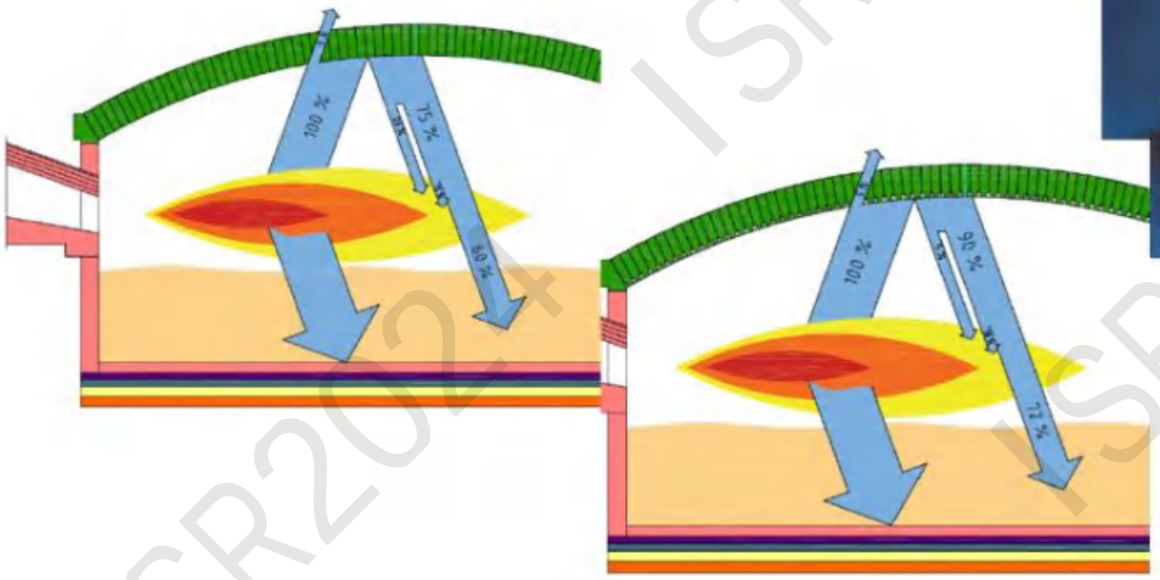
Standard silica in Oxy-fuel furnace
after more than 10 years in operation

Brick´s Hot Face
- Very low infiltration of Na_2O (<1%), low porosity (14%), main mineral cristobalite, low glass phase content

Brick´s Cold Face
- Nearly no infiltration from furnace atmosphere, original structure of brick intact

Honeycomb Crown – Increased Heat Transfer

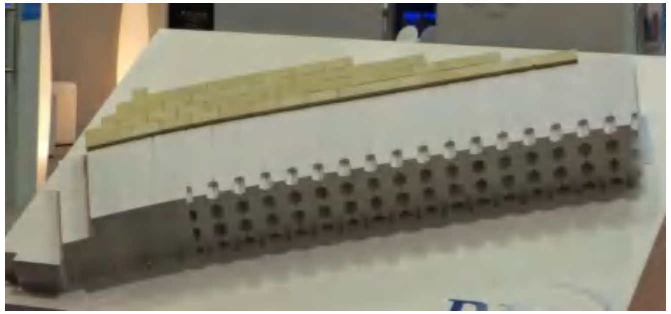
Flat Standard Crown versus Honeycomb Crown



$$Q_{G,W} = A_w \cdot C_S \cdot \varepsilon_W (T^4_W - T^4_G)$$

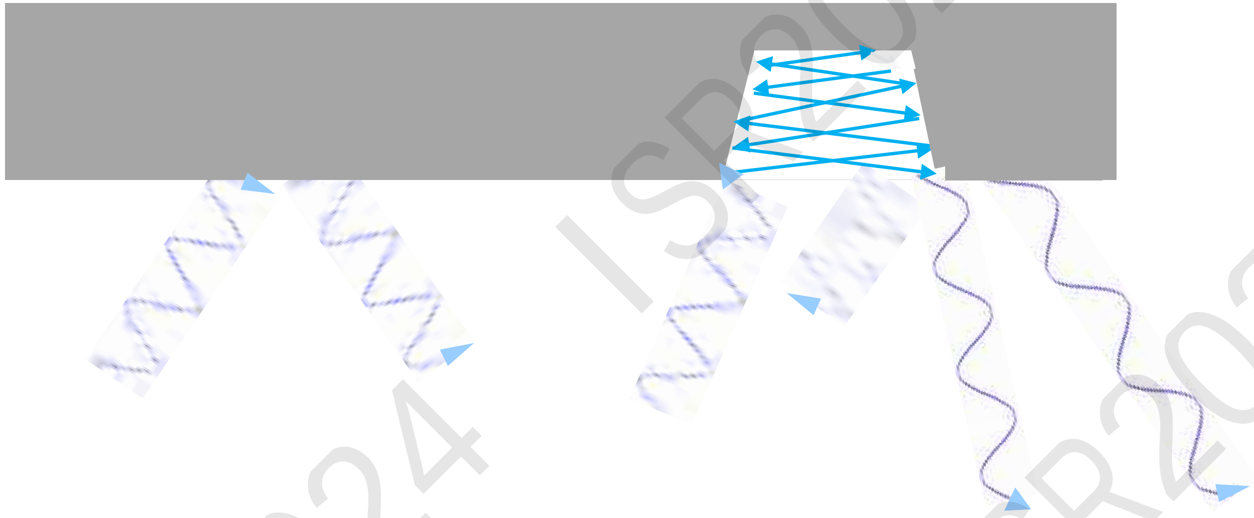
Increase of heat exchange from the Crown to the Glass

- More crown surface area A_w
- Increased emission coefficient ε_W of the crown



Reflection becomes useful

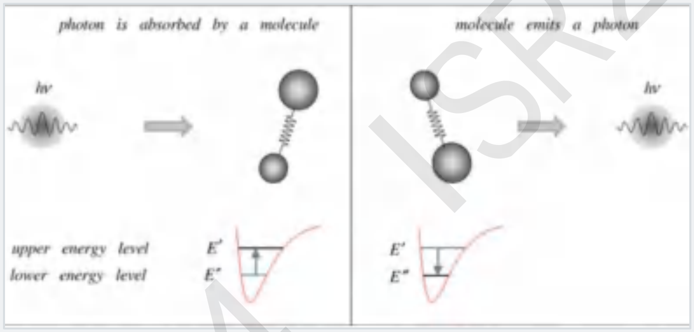
Change in Wavelength avoids waste gas losses



Flat surface
Energy is reflected with the same wavelength at point of arrival

Honeycomb
The structured surface changes the reflected wavelength.

Emission and absorption of radiation for a determined gas molecule happens in the same energy wavelength.



With Honeycomb surfaces the incoming wavelength ν is transformed into various different reflected wavelengths.

Therefore, the waste gas only absorbs a portion of the remaining radiation with original wavelength.

Honeycomb Shapes

Melter Crown Design

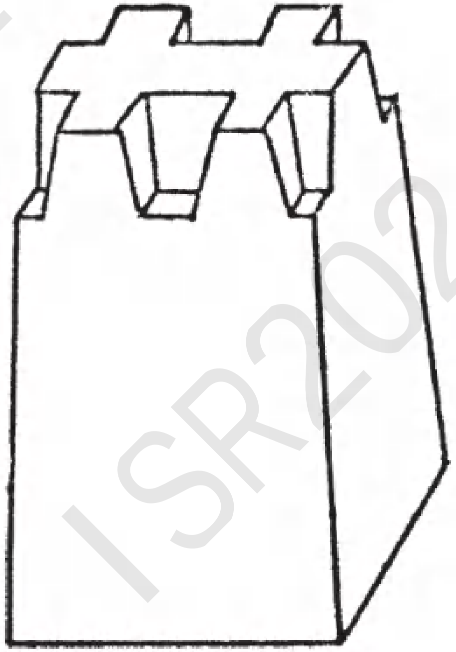
Energy savings in range of **5 to 8%**

Lower superstructure temperature of **up to 40°C**

Glass melts faster **(up to 15%)**

More space for **refining**

Improvement of **glass homogeneity**

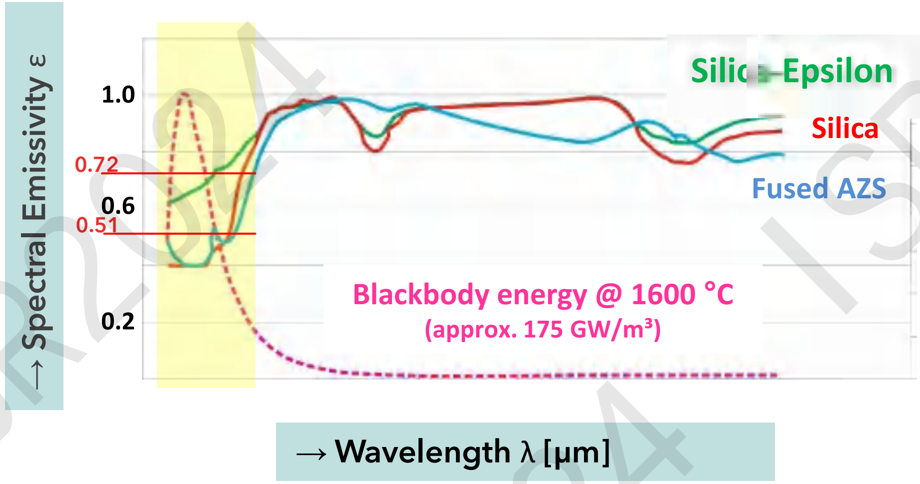


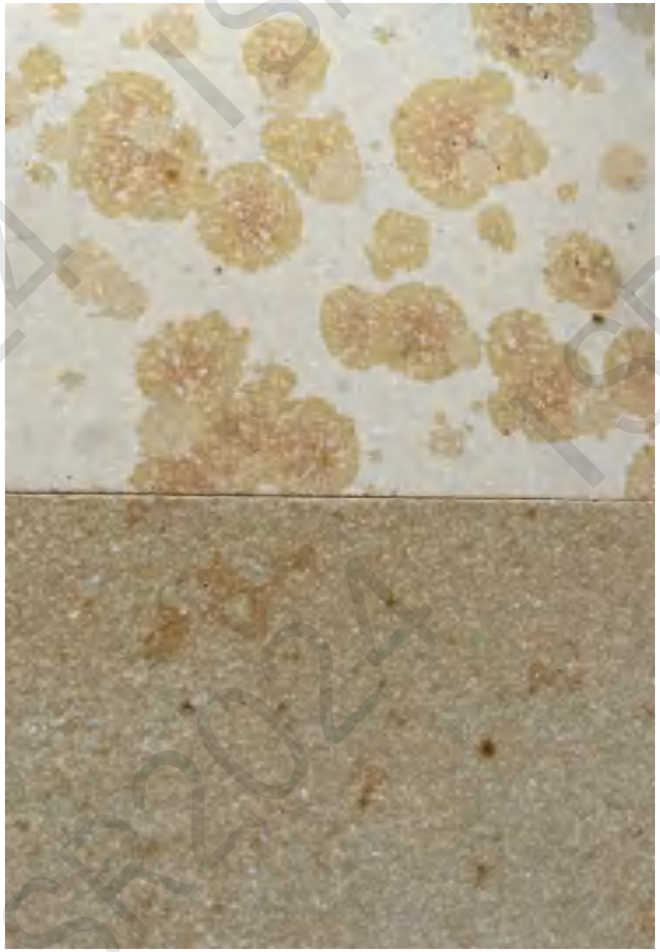
Silica with ε-technology

Emissivity increase by introducing additives

Emissivity ε = f (λ, ϑ, material)

(Total) Emissivity @ 1600 °C:
0.51 for conventional silica types
0.72 for silica-ε (example)





Standard Silica

ε-Silica

Benefits of increasing crown efficiency

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Reference case
- 450 tpd
- 128.8 m2
- Fuel Consumption 1365 Nm3/h

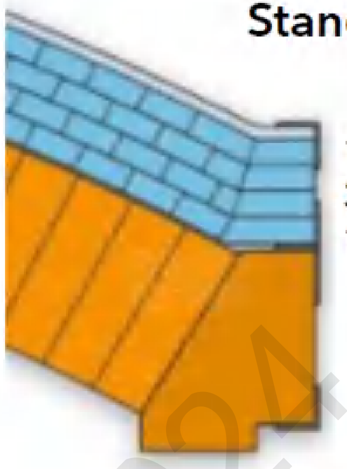
	Estimated Energy Savings	Δ Fuel	ΔCO_2	Savings €*
Honeycomb Shape	4 %	-54,6 Nm3/hr -478.296 Nm3/Y	-939 T/y	243.337 €
Epsilon Technology	2 %	-27,3 Nm3/hr -239.148 Nm3/Y	-469.5 T/y	121.669 €

*Cost of CO2 EU= 70 €/t Cost of NG EU= 0,352€/stcm (June 2024)

High Performing furnace crown insulation

Standard Bricks vs Monolithic Insulation

Less manpower
Better sealing of furnace crowns
Ratholing likelihood reduced



Standard Bricks

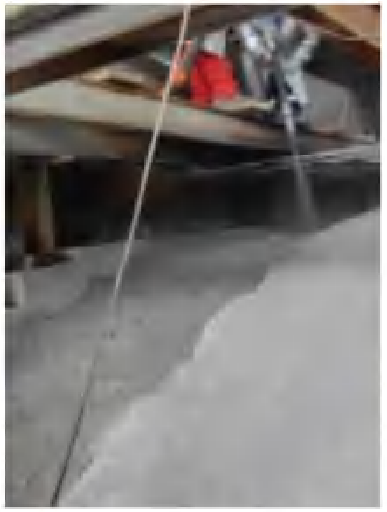
1 Layer (30mm) STELLIT GH 0-1-DE
3 Layer (64mm/L) RHIM-LiSi-06
1 Layer (64mm/L) RHIM-LiSi-08

Monolithic

LEGRIT 105-0,5E 0-2 (150mm)
LEGRIT 135-1,0G 0-6-DE (135mm)
COMPAC SOL FS99G-3-DE (100mm)

Applied by Dry-Gunning after heat-up

Option	Description	Heat Loss	Delta CO2	Delta Energy
Market STD	450mm-Stella GGS 64 mm 160 1-L 3x64mm 150 0.6-L 30 mm STELLIT GH 0-1-DE	1567 Wh/m2	0	0
RHIM-High Efficiency Concept	450mm-Stella GGS 64 mm RHIM-LiSi-08 (155 0,85/L) 3x64mm RHIM-LiSi-06 (150 0.65-L) 30 mm STELLIT GH 0-1-DE	1323 Wh/m2	- 42 t/y	- 213 MW/y
RHIM-Monolithic High Efficiency	450mm-Stella GGS 150 mm Compac Sol FS99G-3-DE 135 mm Legrit 135-1,0G 0-6-DE 150 mm Legrit 105-0,5E 0-2AT	1066 Wh/m2	- 87 t/y	- 438 MW/y



Compac Sol FS99G-3

Melter Crown Insulation Design

- The new lining solution has been developed for *dry gunning* process application
- The installation method is much faster and requires less manpower
- New material is based on *fused silica* with addition of *silica sol* (Divasil, Divasil FP)
- Compac Sol FS99G is completely in line with the crown brick material concept
- Hot repairs

Physical properties	Unit	
Bulk density 110 °C	[g/cm³]	1.73
Bulk density 1000 °C	[g/cm³]	1.73
CCS 110 °C	[MPa]	12
CCS 1000 °C	[MPa]	18
Thermal conductivity (1000°C)	[W/mK]	1.18
Thermal expansion (1000 °C)	[%]	0.0

Chemical analysis	Unit	
SiO_2	[%]	99.1
Al_2O_3	[%]	0.5
Fe_2O_3	[%]	0.1
CaO	[%]	0.1

Sample out of a crown
Compac Sol FS99G-3/Legrit 135-1,0G 0-6

Installation of Compac Sol FS99G-3

Energy saving and low CO_2 technologies

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Silica insulation bricks

Material Choice Stella GNL is able to work efficiently in the range of temperatures 1.100°C - 1.650°C

Crown Design Honeycomb design is able to reduce the energy consumptions up to 5-8%; the Ɛ-technology enables further reduction

Crown Insulation Design The concept of a monolithic crown insulation is able to reduce the energy consumption and the risk of ratholing

Long lifetime in a wide range of furnace temperatures and atmospheres
Less maintenance due to lower risk of ratholing
Significant improvement of energy efficiency
Fast Installation

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Low carbon refractory solutions for the glass industry

Glass tank regenerator solutions

Expectations on regenerators

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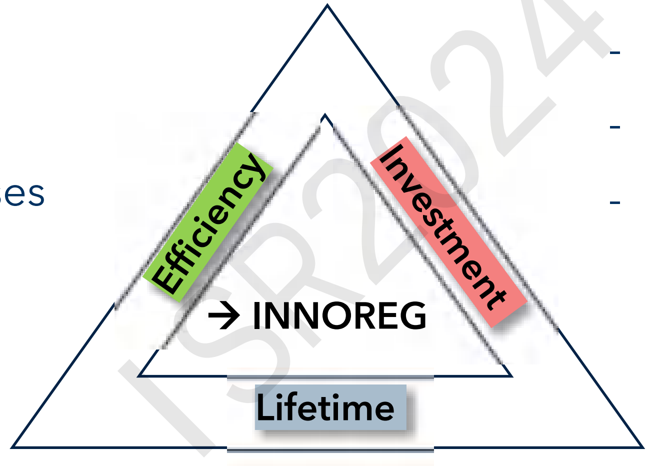
- **As high as possible**
- Design of the regenerators
  - Section (Flue gases speed 0,30-0,35 m/s)
  - Height (specific checker volume /air pre-heated)
- Checker Shape
  - Specific heat exchange area
  - Turbulence
  - Clogging potential
  - Homogeneous distribution of gases
- Stable during the complete campaign
- Air infiltration
- Clean checkers
  - Operation & maintenance



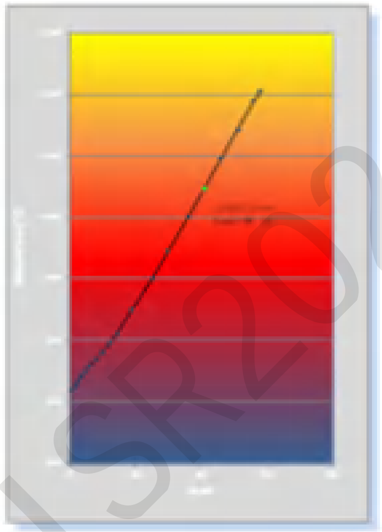
As low as possible

- checker work design (flue size → total weight)
- size of regenerator
- material selection (quality and kind of product)

- **As long as possible**
- Checkerwork shape (flue size & checker shape)
- Corrosion resistance for a long campaign (quality and grade)
- -Operation & maintenance (clean checkers – no clogging due to condensation or collapse)

What is INNOREG?

INNOREG is a Toolbox aimed to design a tailor made regenerator, optimized for each customer



R21 Thermal Model

Is RHI Magnesita´s tool that allows easy determination of the thermal performance of a regenerator layout, therefore being a reliable design tool.

- Temperature profile
- Condensation zone estimation
- Thermal efficiency
- Comparison & evaluation

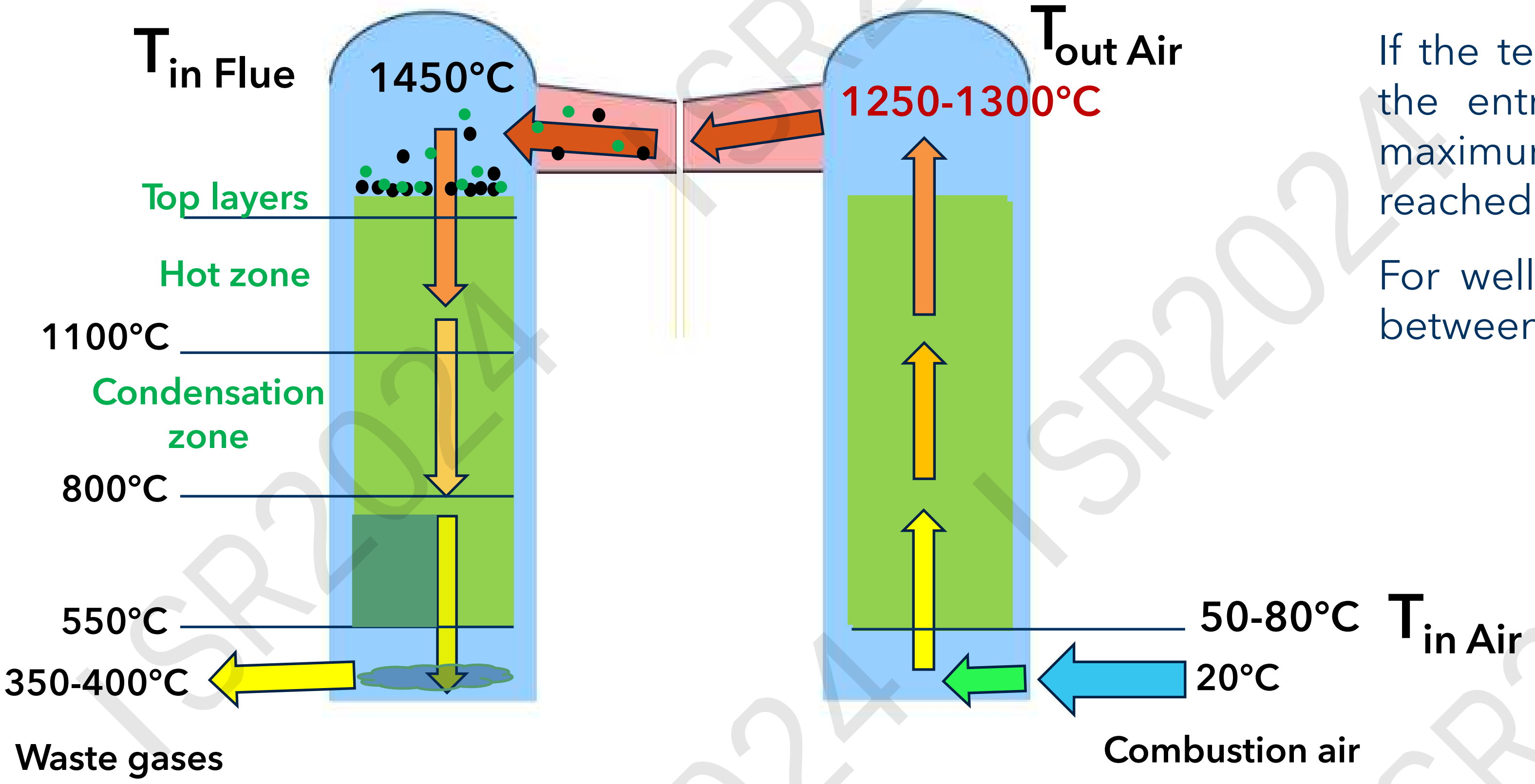
STEP 1 Customer Input

- Dimensions
- Expected operating conditions
- Furnace experiences
  - Previous lining performance
  - Observed corrosion or clogging
  - Maintenance requirements
- Future expectations

STEP 2 RHIM Analysis

- General assessment; fuel, Combustion, main corrosive components
- Clogging potential evaluation
- **R21 Thermal Model**

Thermal Efficiency



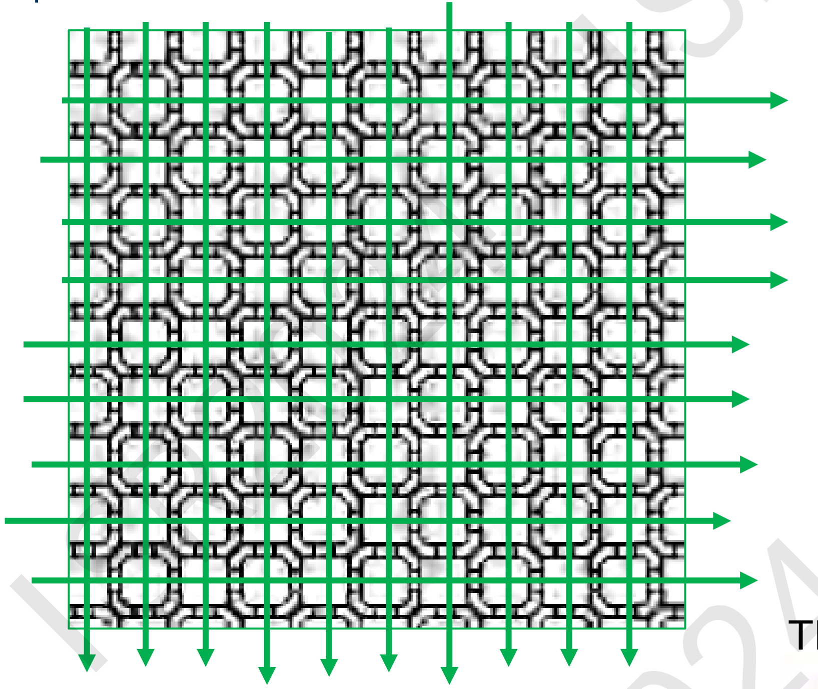
If the temperature of the preheated air is equal to the entrance temperature of the waste gas the maximum specific efficiency of a regenerator is reached.

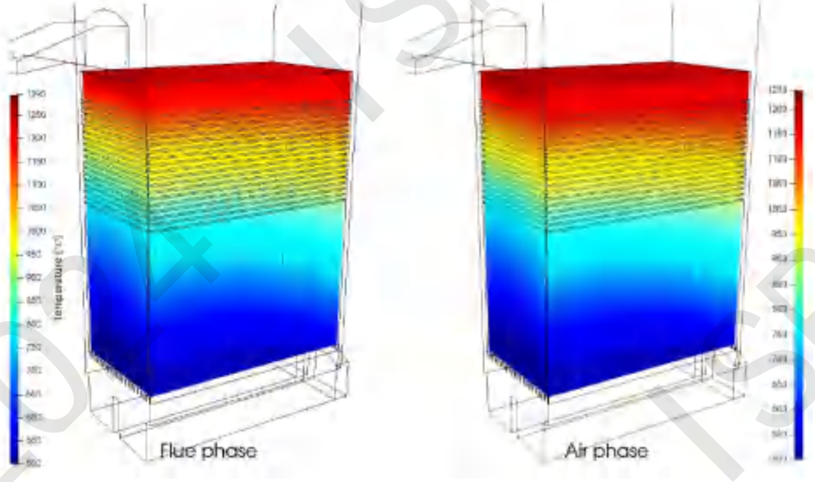
For well-designed regenerators ε is >88%, usually between 90 and 92%

$$\varepsilon = \frac{T_{out\ AIR} - T_{in\ AIR}}{T_{in\ FLUE\ GAS} - T_{in\ AIR}}$$

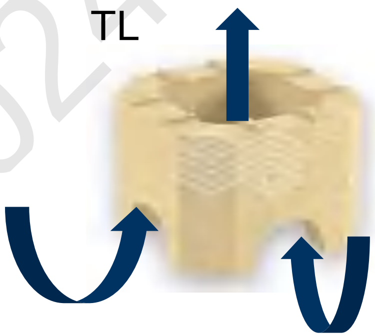
Homogeneous Heat Distribution in the Regenerators

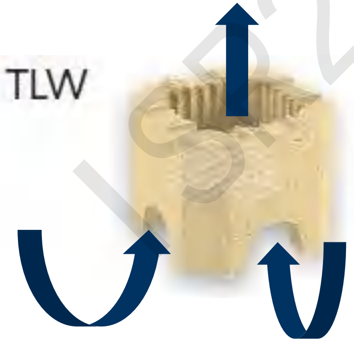
The "mouse" holes of TL and TLW chimney blocks enable a proper gas circulation across the regenerator´s cross section leading to a homogeneous temperature distribution and a complete checker work utilization.





CFD modeling based on data collected at customer site, shows the waste gases and combustion air flow temperatures, and a homogeneous distribution of the flows across the regenerator section.





What is INNOREG?

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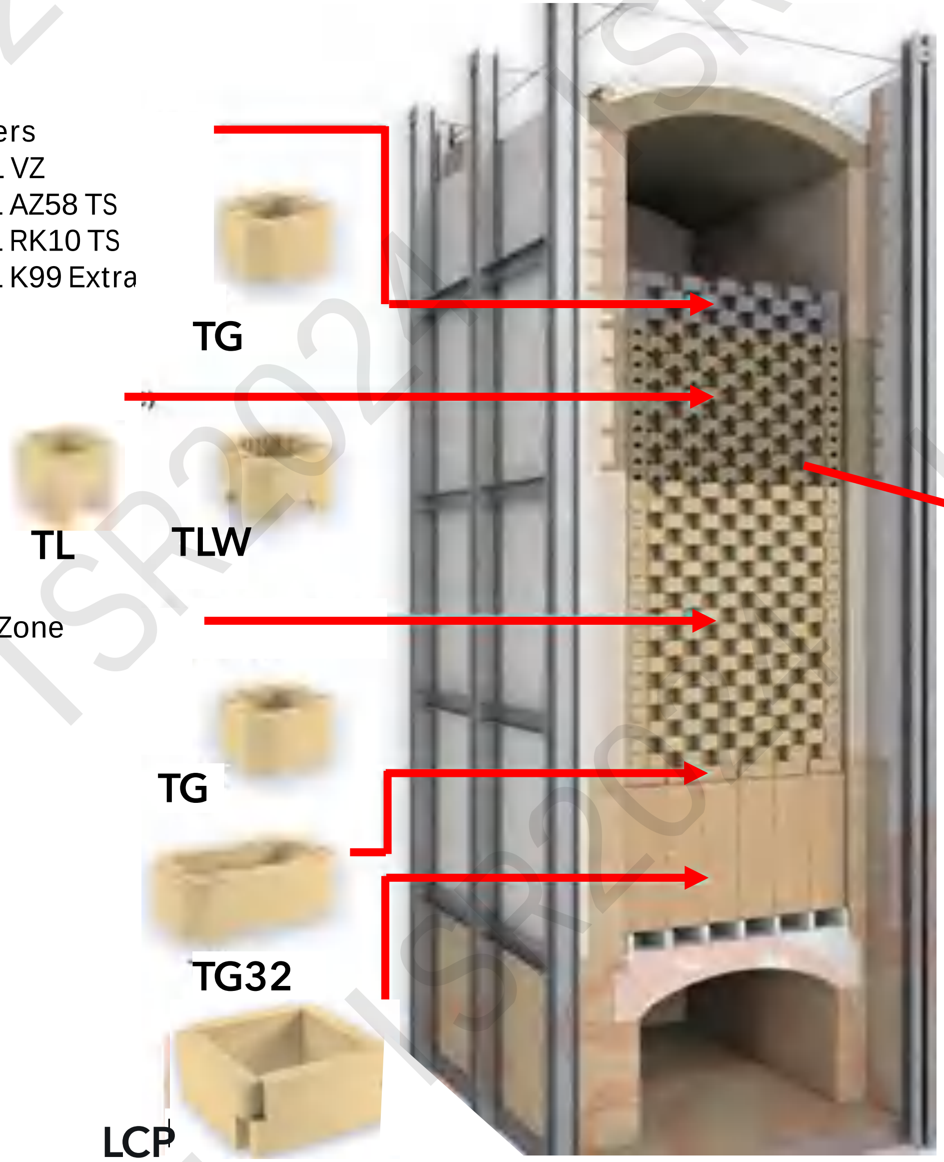
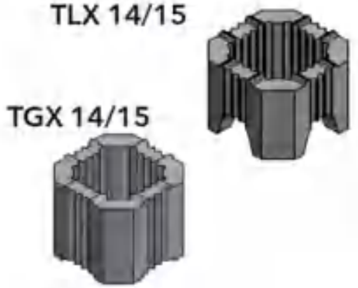
STEP 3 Recommendations
- Zone layer definition
- Grade & shape selection
- Clogging risk reduction
- Simplify cleaning
- Casing grade configuration

Top Layers
RUBINAL VZ
DURITAL AZ58 TS
DURITAL RK10 TS
DURITAL K99 Extra

Hot Zone
RUBINAL VZ
ANKER DG1

Condensation Zone
<1100 ° C
RUBINAL EZ
RUBINAL ESP





LCP offers a larger flue cross section area to reduce the risk of clogging due to sodium sulfate

Benefits of Increasing the Regenerator´s Efficiency

Energy saving solutions for glass furnaces

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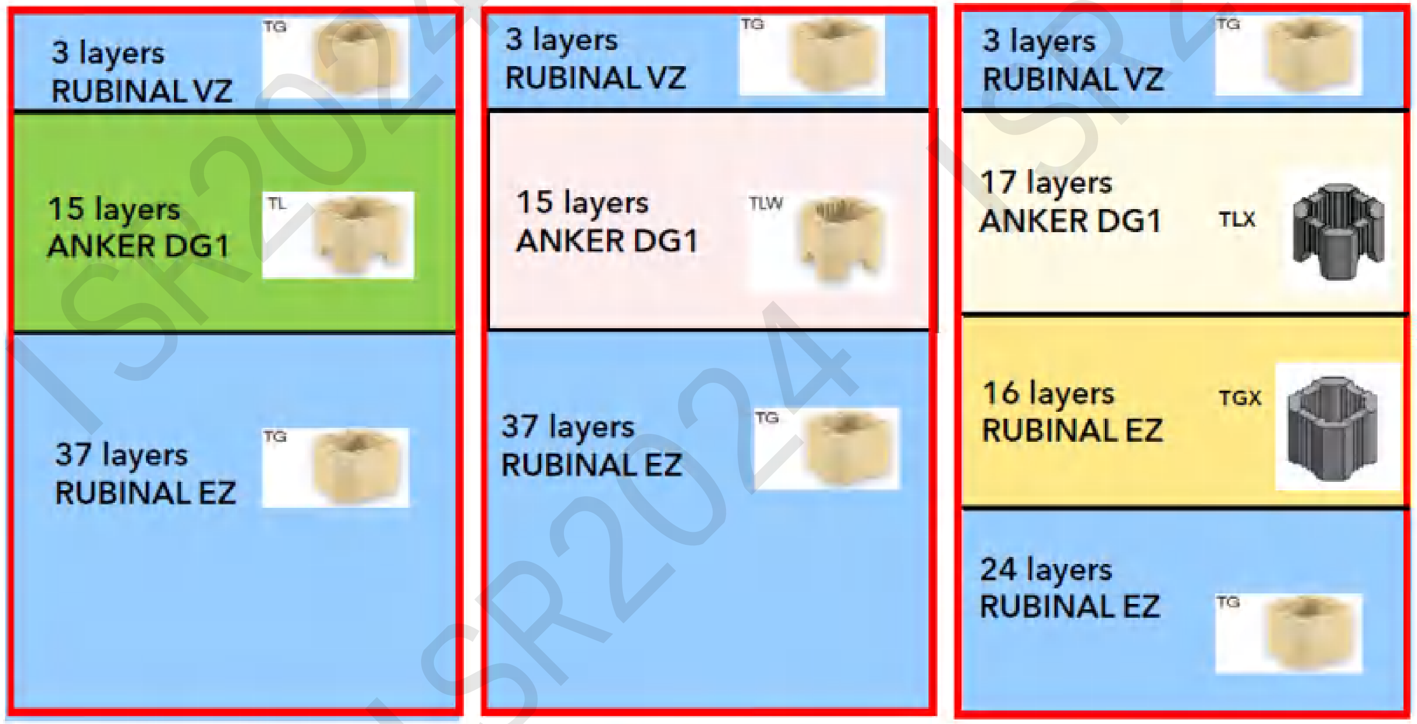
The figures given below are a real case example.

Customer data (furnace conditions)

Furnace area	128,8 sqm
Regenerator depth	6590 mm
Regenerator width	4790 mm
Checker Height	9625 mm
Air Temp below rider arches	150°C
Temp Flue gases top checkers	1450°C
Reversal time	20 min
Fuel consumption (NG)	1365 Nm³/hr
Furnace melting rate	450 tpd
Cullet ratio	70%
Batch Humidity	5%
Batch preheating	NO
O_2 excess in the waste gases	2%
Electric boosting	3600 KW



Base Case | CASE 1 - TLW | CASE 2 - TLX + TGX

Benefits of Increasing the Regenerator´s Efficiency

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CHECKER CONFIG	EFF	PREHEAT AIR TEMP	FUEL CONS	ΔCO_2	Savings €*
BASE CASE TG 14/175 TL14/175 TG 14/175	88.5%	1301°C	1365 Nm3/hr	23.473 T/Y	-
CASE 1 TG14/175 TLW14/175 TG 14/175	89.3%	1310°C	1358 Nm3/hr -61.320Nm3/Y	-120 T/y	31.200 € /Y 250.900CNY/Y
CASE 2 TG14/175 TLW14/150 TLW14/150 TG14/175	91,0%	1333°C	1339 Nm3/hr -227.760 Nm3/Y	-447 T/y	115.900 € 931.800CNY/Y

*Cost of CO2 EU= 70 €/t Cost of NG EU= 0,352€/stcm (June 2024)
*Cost of CO2 CN = 93 CNY/t Cost of NG CN= 5475 CNY /ton (September 2024)

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Low carbon refractory solutions for the glass industry

Glass tank bottom solutions

Upper & Lower Layers

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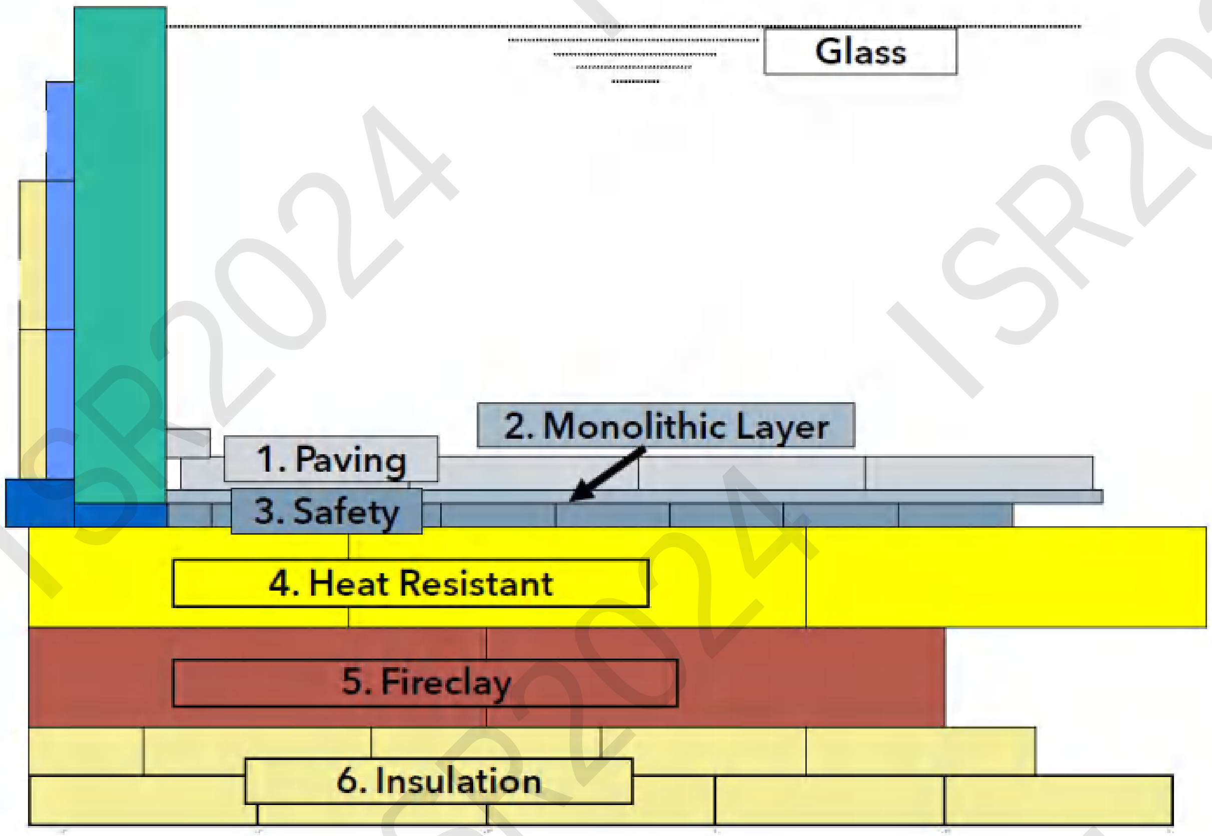
Due to specific requirements, RHIM divides the bottom in two parts



Upper Layers

1. Paving
2. Monolithic Layer
3. Safety Layer

Requirements

- ***Corrosion resistance*** against glass
- Resistance against ***metal drop drilling*** (two approaches: **metal encapsulation** and **metal corrosion resistance**)
- ***Upward Drilling*** *prevention*
- High refractoriness

Lower Layers

4. Heat Resistant
5. Fireclay Layer
6. Insulation

Requirements

- **Refractoriness** according to the expected temperature profile
- **Mechanical** Properties; Cold Crushing Strength
- Optimum **compromise between insulation and bottom lifetime**

Upper Layers

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Monolithic layer

- Avoids glass penetration through the joints under the paving, prolonging the furnace lifetime
- Requires good glass corrosion resistance.
- Low shrinkage during heat-up to obtain a sealed layer with no gaps.
- Resistance against metal penetration is also needed

New developments : Self flowing mix for a faster and easier installation
DIDOFLO ZM 30-3-DE based on zircon mullite
DIDOFLO A89CR-3-DE based on Chrome alumina , metal drilling resistant, for coloured glasses

TWO APPROACHES

Metal corrosion resistant grades

Based on Zircon Mullite or Chrome Alumina

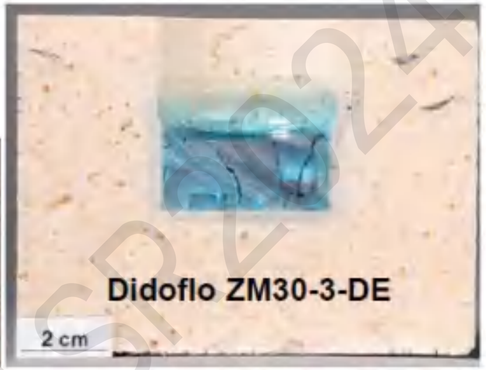
DIDURIT ZM 465 0-3
DIDOFLO ZM 30-3
DIDOFLO A89CR-3
RESISTIT ZM 260

Metal encapsulating grades

Based on Zircon Silicate

RESISTIT ZS748

Cup Tests; Soda Lime Glass with cupper droplet 120h @1370°C



Bottom blocks (incl. tin bath)

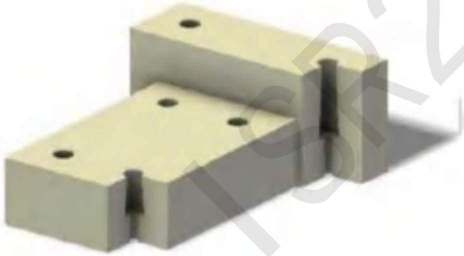
Unfired products show excellent dimensional accuracy

No grinding neccessary

Thickness of tin bath bottom blocks up to 400mm

Low CO_2 footprint product

	Formats available (in mm)
RHIM-LiF13bh	1000x500x200
RHIM-F40bh	1000x500x350
RHIM-S60bh	1000x498x300
RHIM-ZC20bh	1000x500x200



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Low carbon refractory solutions for the glass industry

Vibro and slip cast

Vibro and slip cast products

Forehearth components incl. feeder channels, substructures, superstructures, and a full range of feeder expendables (specialities **Danner pipes** and **lip blocks**).

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Thank you for your attention

Get in Touch

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