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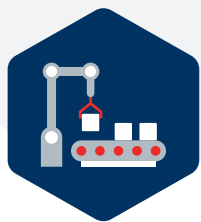
# RHI Magnesita

Performance of High -Purity  $\text{MgO}$  - $\text{Al}_2\text{O}_3$   
Spinel Refractories under Alkali -Rich  
and High -Humidity Conditions in  
Modern Glass Furnaces

Presenter: Daniela Messina

# The global leader in refractories

There for you, wherever you need us



**76 production sites**  
(incl. Recycling facilities)



**16 raw materials sites**



**5 R&D hubs and centres**

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**20,000**

Employees

---

**€ 3.4 bn**

2025 revenue

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**+ 1,700**

Active patents

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**+100**

Countries shipped to worldwide

# MgAl<sub>2</sub>O<sub>4</sub> (MA) spinel brick

## The Challenge in Modern Glass Furnace Technology

Technology shifts in the glass industry are placing new demands on refractory materials:



### Hybrid furnaces

Lower crown temperatures  
Higher risk of silica corrosion.



### Oxy-fuel and hydrogen firing

Higher humidity and alkali activity  
Higher chemical load



### High alkali concentrations

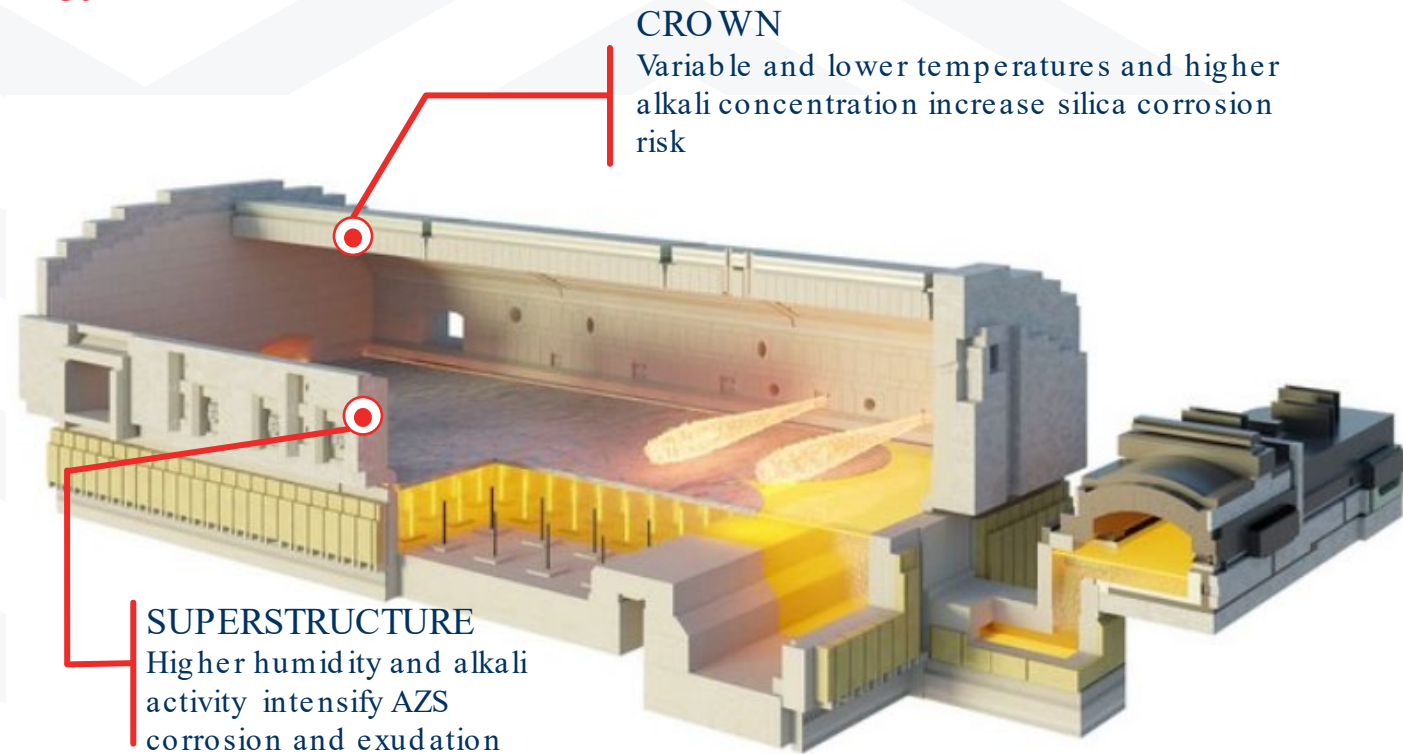
Accelerate the wear of standard silica  
and fused-cast AZS refractories.



**Result:** faster degradation of the crown and superstructure.



Mg-Al spinel offers a solution to overcome the limitations of traditional refractory materials.



Horn –Hybrid Furnace - [www.hornglass.com/melting-conditioning/furnaces](http://www.hornglass.com/melting-conditioning/furnaces)

# MgAl<sub>2</sub>O<sub>4</sub> (MA) spinel brick

Spinel is a crystalline material with a typical form AB<sub>2</sub>O<sub>4</sub> where A and B are metal cations and O is oxygen. Oxygen ions form a nearly cubic close-packed framework

The metal ions occupy two types of interstitial sites:



- A cations occupy tetrahedral sites, coordinated by 4 oxygen ions.



- B cations occupy octahedral sites, coordinated by 6 oxygen ions.

The product we will discuss today is an equimolar magnesium aluminate spinel, MgAl<sub>2</sub>O<sub>4</sub>, where Mg<sup>2+</sup> usually occupies tetrahedral sites and Al<sup>3+</sup> occupies octahedral sites.

Important features of the spinel crystals:



High decomposition temperature

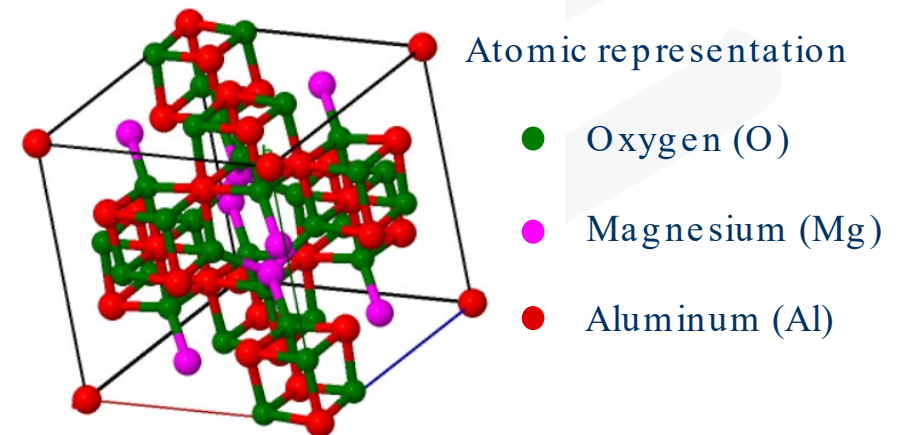
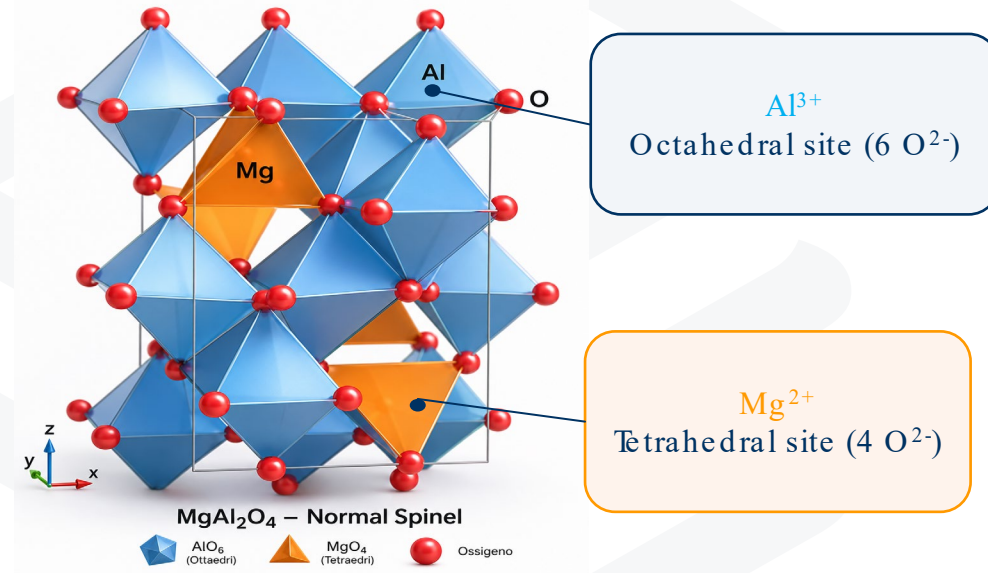


Chemical stability



Mechanical strength

## SPINEL CRYSTAL STRUCTURE (MgAl<sub>2</sub>O<sub>4</sub>)



# DURITAL SP70

## Physical and Chemical Properties



### CHEMICAL COMPOSITION \*

| Oxide                          | % weight |
|--------------------------------|----------|
| Na <sub>2</sub> O              | 0.03     |
| MgO                            | 28.1     |
| Al <sub>2</sub> O <sub>3</sub> | 70.9     |
| SiO <sub>2</sub>               | 0.27     |
| CaO                            | 0.35     |
| TiO <sub>2</sub>               | 0.04     |
| MnO                            | 0.02     |
| Fe <sub>2</sub> O <sub>3</sub> | 0.23     |
| ZrO <sub>2</sub>               | 0.08     |
| Loss of ignition               | 0.26     |

\*Typical values



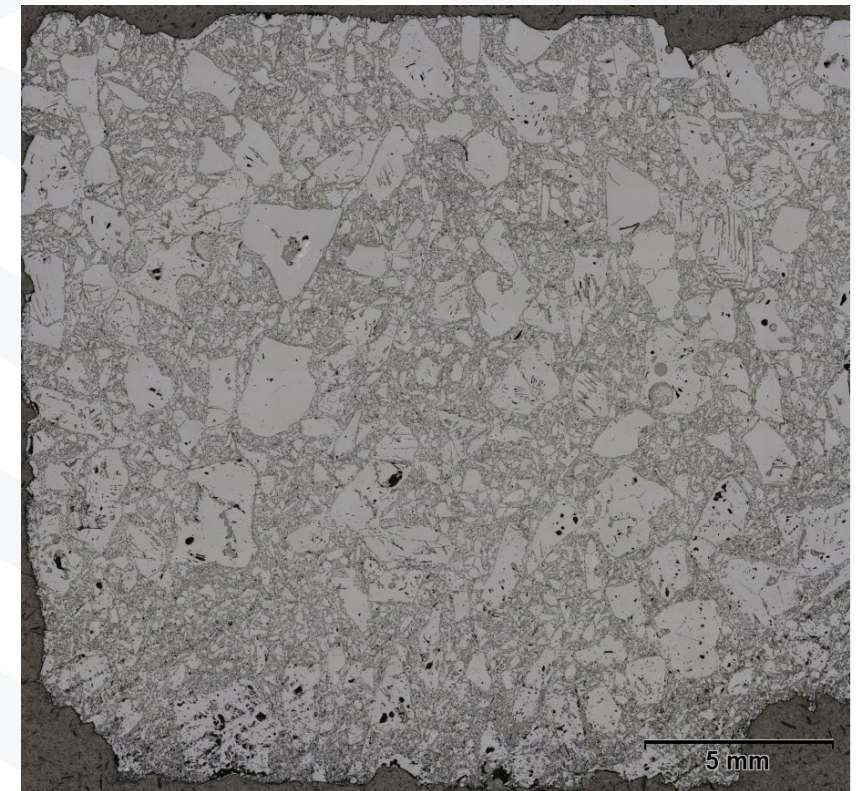
### PHYSICAL PROPERTIES \*

| Property            | Unit               | Value |
|---------------------|--------------------|-------|
| Density             | gr/cm <sup>3</sup> | 2.96  |
| Open porosity       | Vol %              | 17%   |
| CCS                 | MPa                | 85    |
| RULT <sub>0.5</sub> | °C                 | >1800 |
| TSR                 | Cycles             | >2    |

- ✓ Equimolar composition
- ✓ Fines composition is spinel slightly rich in MgO
- ✓ No free corundum, no  $\beta$ -alumina
- ✓ Low impurities content



### MICRO STRUCTURE



The micro texture of DURITAL SP 70 is well developed, with a homogeneous distribution of components

# DURITAL SP70

## Microstructure



The coarse and medium grains are mostly well embedded, with clear sintering



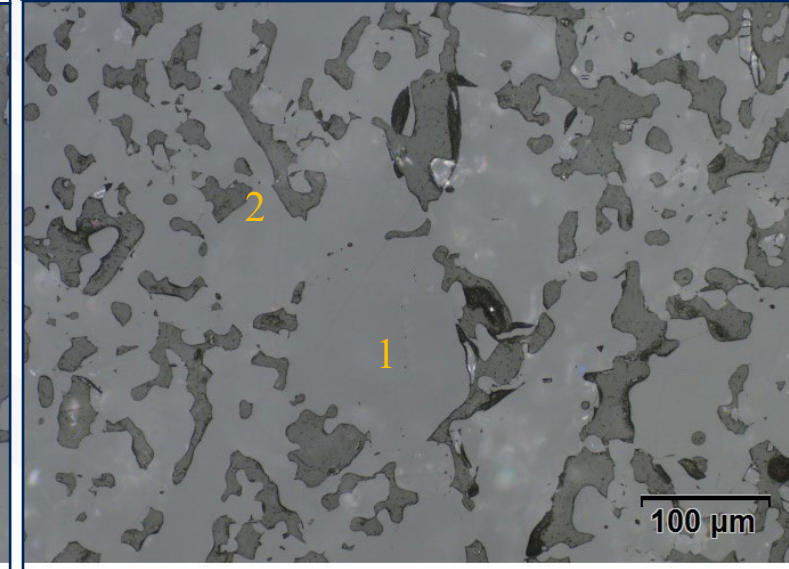
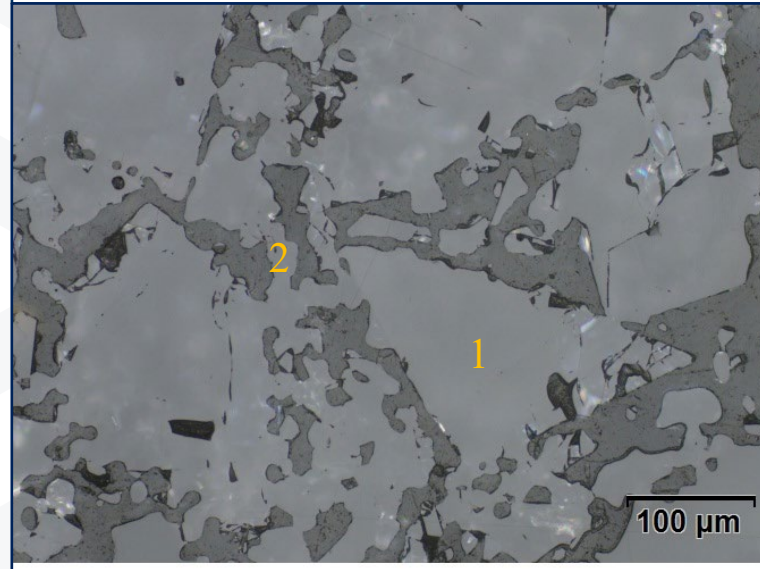
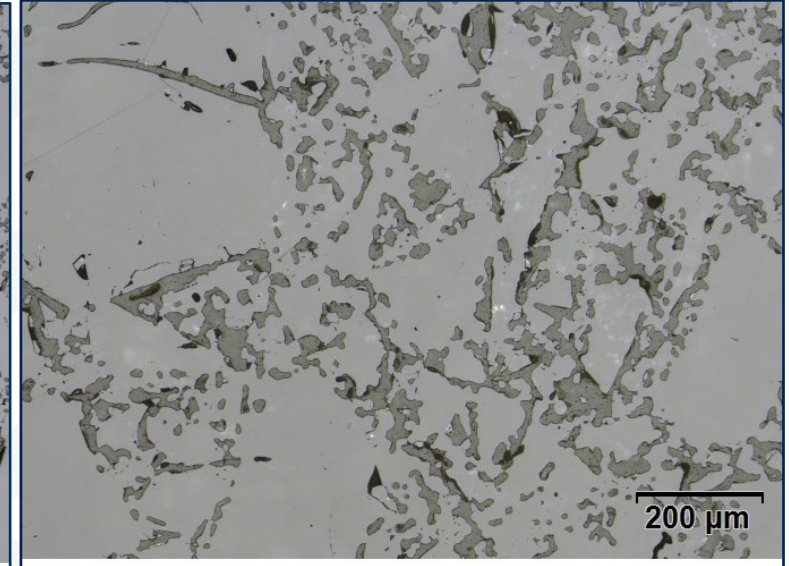
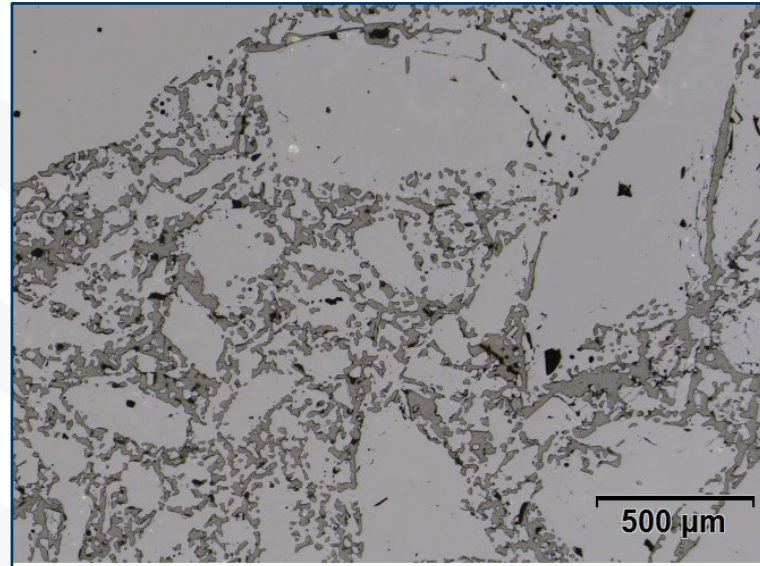
No impurities or components foreign to the formulation can be found.



sinter bridges with thicknesses of up to 20  $\mu\text{m}$  are generally present

### LEGEND

- 1. Spinel crystal
- 2. Sinter bridge

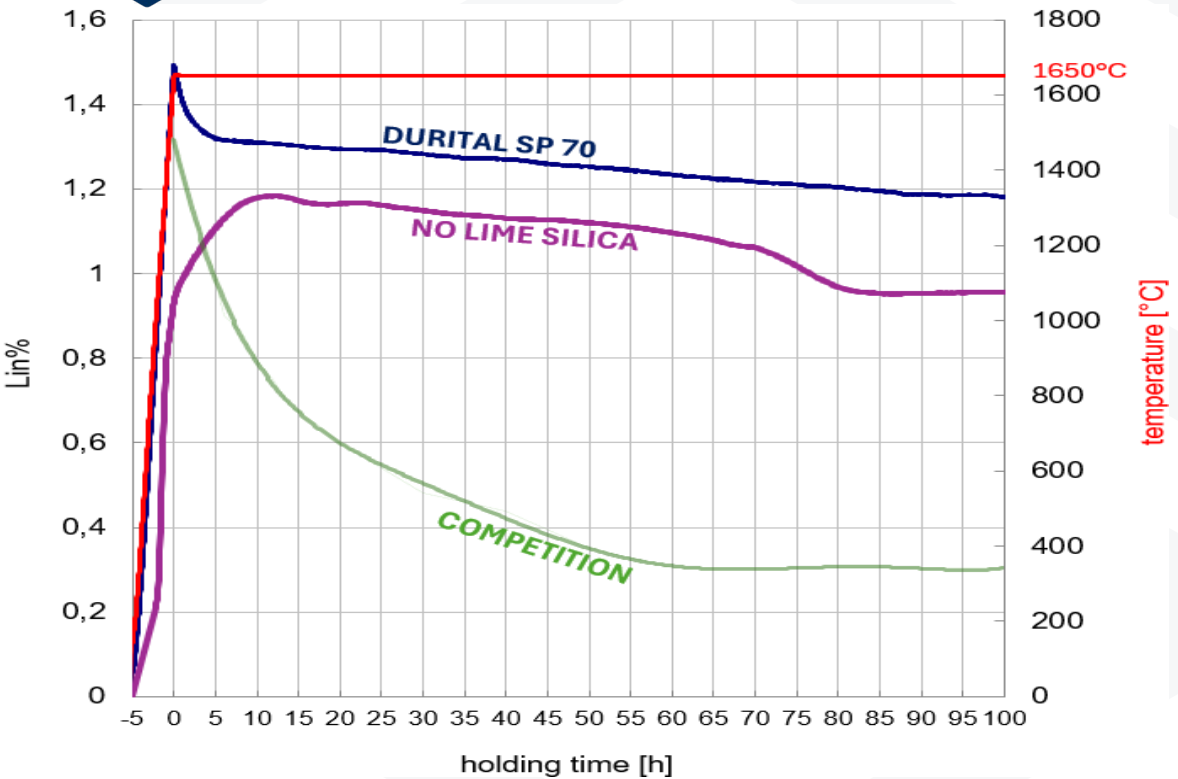


High creep resistance

# DURITAL SP70

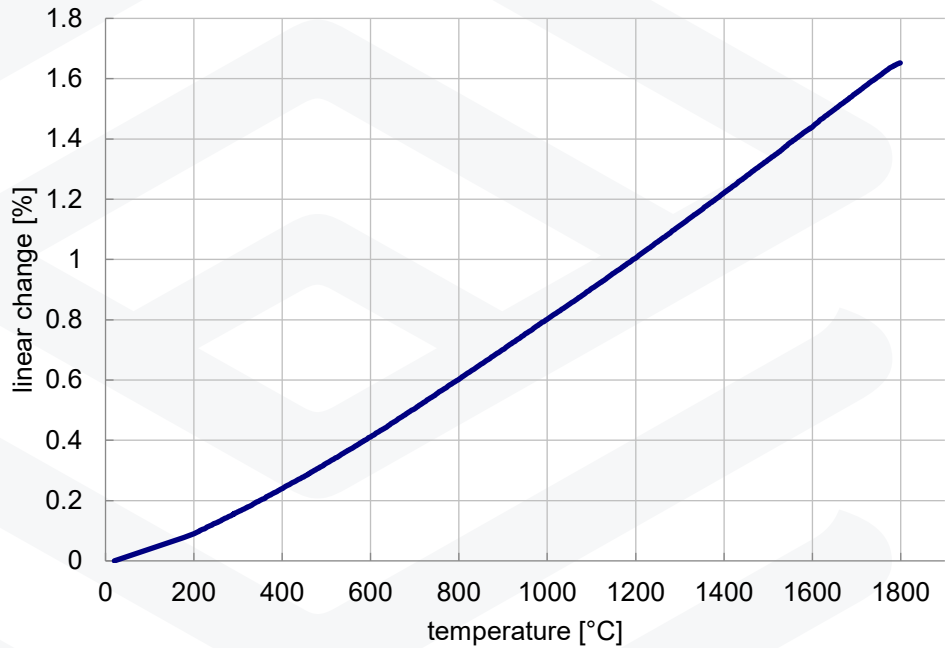
## Thermo -mechanical properties

 CREEP @1650°C of different materials



- ✓ Durital SP70 shows superior creep resistance at 1650°C maintaining lower deformation over extended holding time
- ✓ Durital SP70 delivers the best thermo-mechanical performance, with the lowest deformation and the highest reliability at high temperature

 RUL-DURITAL SP 70



|  | DURITAL SP 70 | NO LIME SILICA | COMPETITION |
|--------------------------------------------------------------------------------------|---------------|----------------|-------------|
| Z <sub>5-25</sub> Lin%:                                                              | -0,024        | -0,0207        | -0,345      |
| Z <sub>25-50</sub> Lin%:                                                             | -0,040        | -0,0124        | -0,215      |
| Z <sub>50-100</sub> Lin%:                                                            | -0,071        | -0,187         | -0,05       |

Creep resistance is the most critical property for spinel bricks especially for melter crown constructions; excellent production parameters are essential to ensure the crown's mechanical stability at high temperatures, preventing the risk of sagging

# Durital SP70

## Chemical Stability



In Hybrid and Oxy-fuel furnaces the alkali vapor concentration is enhanced



In case Hydrogen is used as a fuel, the alkali concentration is even higher

**Corrosion reaction of Silica in presence of Alkalies :**



Corrosion products : Na-Silicates

- Viscosity depending on temperature
- Kinetic of reaction is depending on crown temperature

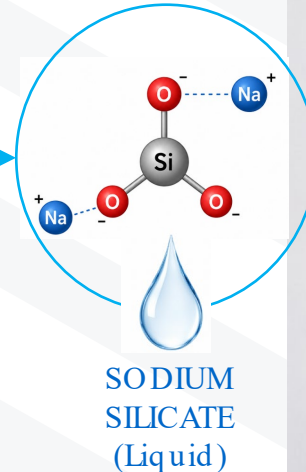
**Corrosion reaction of Spinel in presence of Alkalies :**



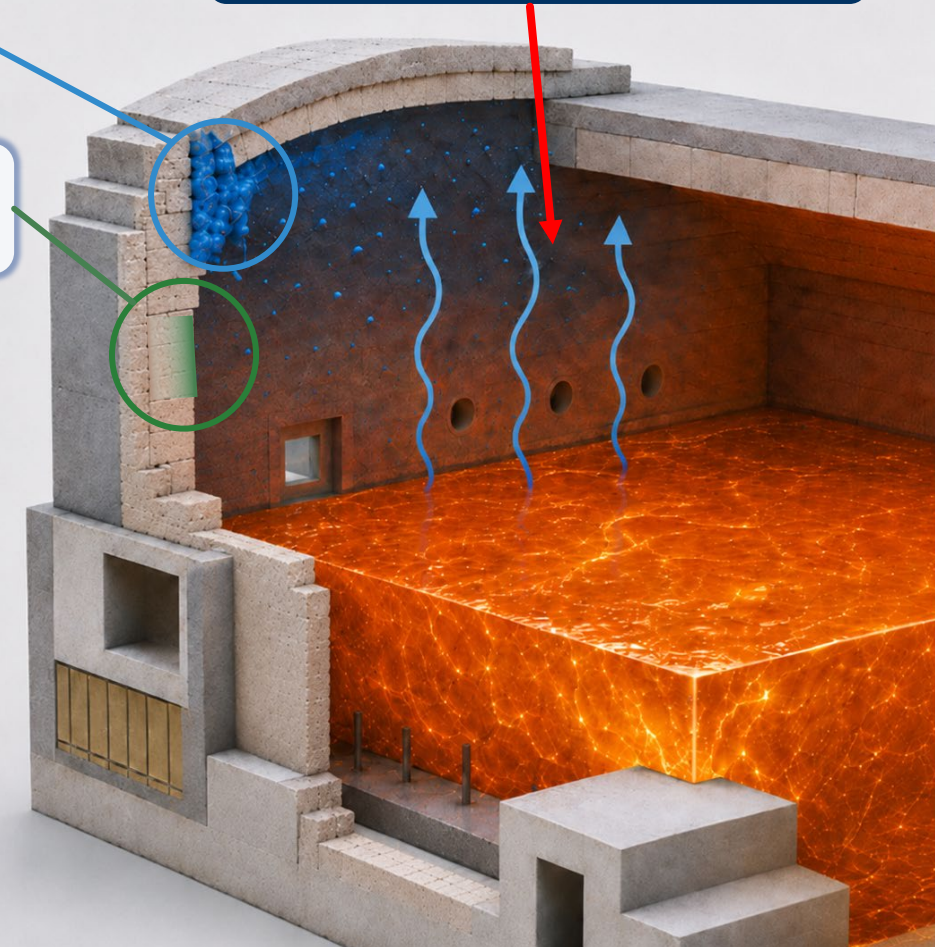
Corrosion products : MgO and alkaline aluminates

Silica ( $\text{SiO}_2$ ) corrosion (sodium silicate is formed as liquid and it continues to melt the material)

Spinel ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ) attacked ; MgO remains more stable while aluminates are formed



ALKALI-RICH ATMOSPHERE



MA Spinel is attacked only when the NaOH levels are much higher. NaOH transforms the aluminos components, while MgO remains more stable. This is why MA spinel is thermodynamically and microstructurally much more resistant

# Durital SP70

## Alkali Vapor test

\* WHITE GLASS CHEMICAL COMPOSITION

| Oxide                          | % weight |
|--------------------------------|----------|
| Na <sub>2</sub> O              | 11.0     |
| MgO                            | 0.46     |
| Al <sub>2</sub> O <sub>3</sub> | 2.08     |
| SiO <sub>2</sub>               | 74.1     |
| CaO                            | 11.0     |
| K <sub>2</sub> O               | 1.35     |
| Fe <sub>2</sub> O <sub>3</sub> | 0.10     |
| Loss of ignition               | 0.19     |



Test equipment set up



### Test Conditions



T= 1500°C



Charging mix: white glass \*including 20% Na<sub>2</sub>O



Holding time : 170h (7 days)



Samples :  
MA spinel brick  
Standard Silica  
No Lime Silica



The different samples reflect the traditional materials used for glass furnace crowns

# Durital SP70

## Alkali Vapor test –Results

### 1 DURITAL SP70

#### No mass loss

The sample remained dimensionally stable after alkali vapor exposure

### 2 STANDARD SILICA

#### ~5.9% mass loss

Visible discoloration and measurable degradation of the cut section

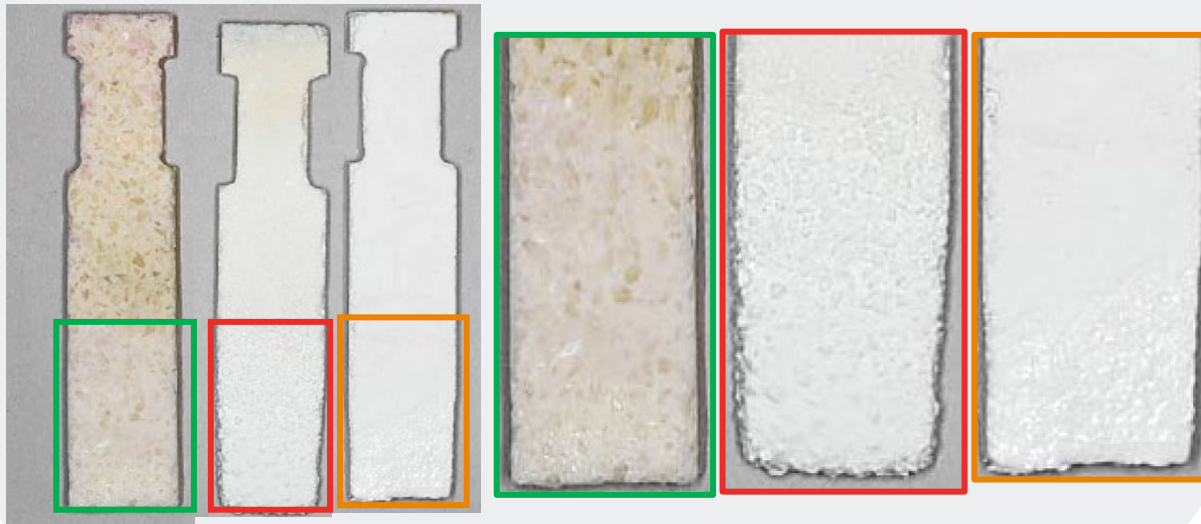
### 3 NO LIME SILICA

#### ~3.7% mass loss

Lower mass loss than standard silica, but still affected by exposure

Finger test samples

1 2 3



Cut sections of the samples

1 2 3

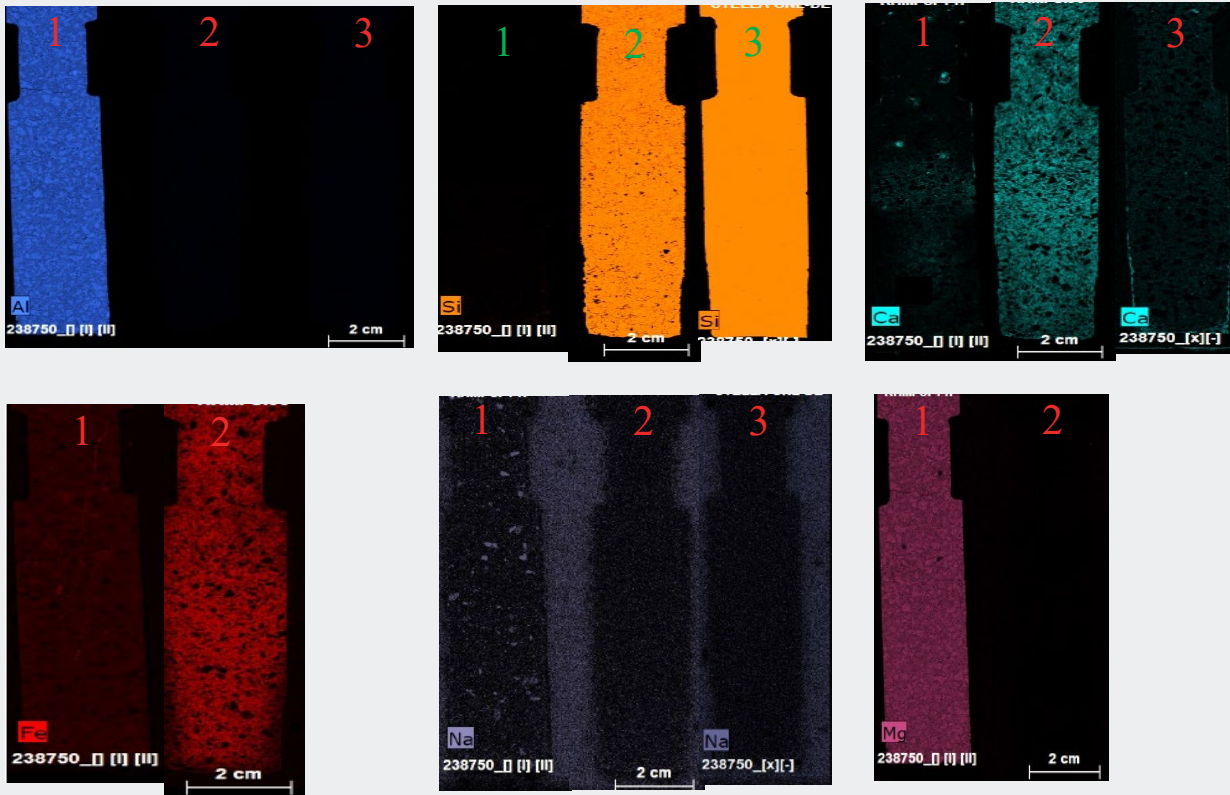


DURITAL SP 70 shows the strongest resistance in the alkali vapor test with no measured mass loss

# Durital SP70

## Alkali Vapor test – Infiltration

Elemental mapping/ Na up-take



1 Durital SP70

2 Standard Silica

3 No lime silica

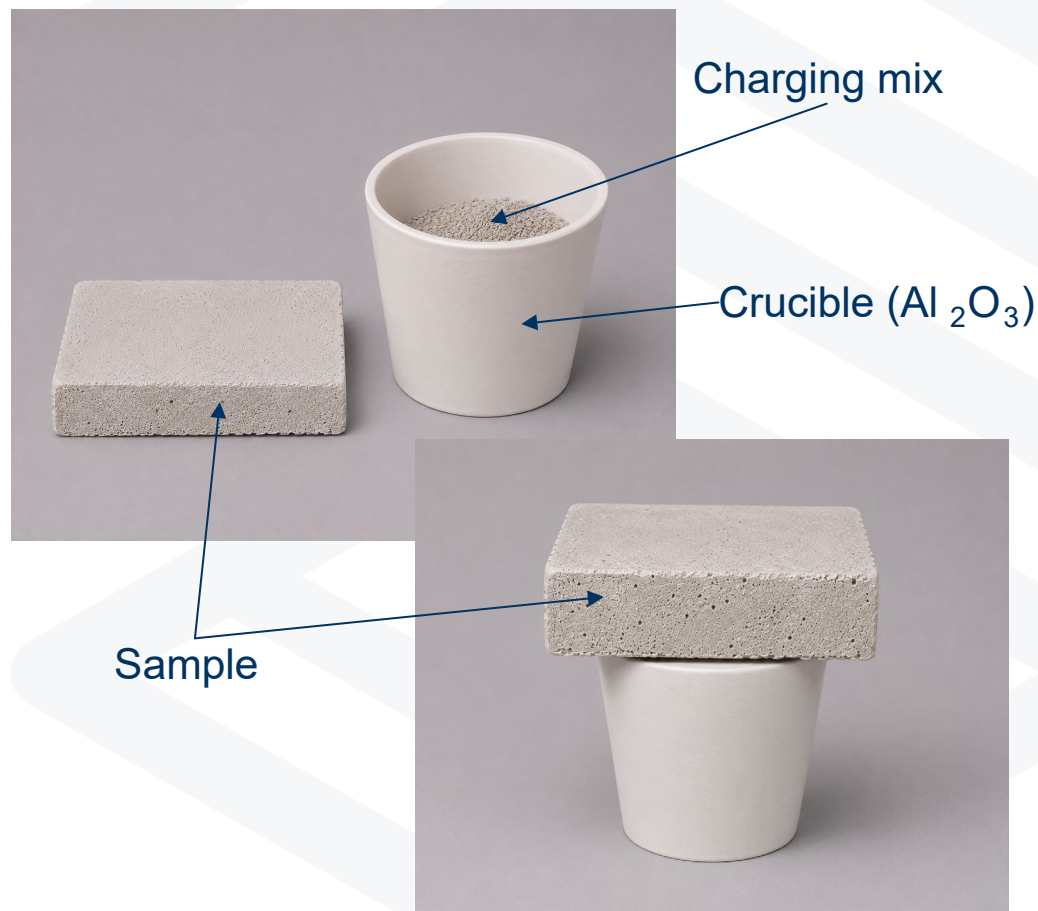
### Main findings

- ✓ No significant infiltration was detected in any of the tested samples.
- ✓ No significant Na -up-take for any test specimen.
- ✓ The observed mass loss in silica-based samples is mainly linked to surface reaction/material degradation rather than deep Na penetration.
- ✓ The higher mass loss in standard silica is expected, and it is related to the presence of CaO in the binder. CaO contributes with NaOH to the formation of the silicates melt .

DURITAL SP 70 remains stable under the selected test conditions

# Durital SP70

## Alkali and Boron Vapor test



### Test Conditions



T= 1600°C



Charging mix: 12,5 gr including 30%  $\text{B}_2\text{O}_3$  + 70%  $\text{Na}_2\text{CO}_3$



Holding time : 24h



Samples :  
Fused Mullite  
MA spinel brick  
Fused Alpha- Beta alumina  
Standard Silica



The different samples reflect the traditional materials used for glass furnace crowns

# Durital SP70

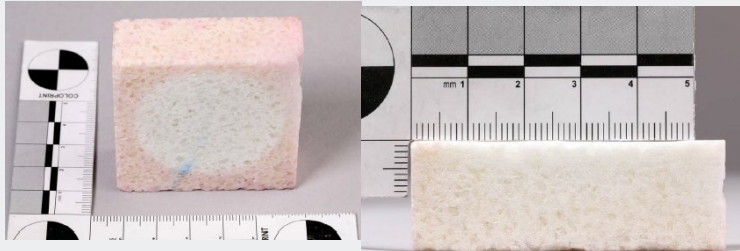
## Alkali and Boron Vapor test - Results

1



**BEST  
PERFORMANCE**

DURITAL SP 70

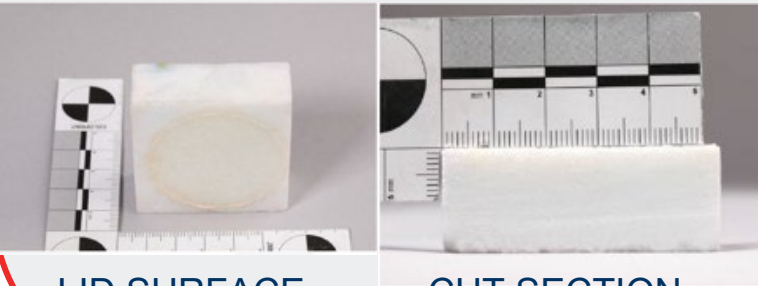


LID SURFACE

CUT SECTION

- ✓ Lid surface : no visible wear; discoloration outside the exposure area
- ✓ Cut Section: no visible wear;

FUSED ALPHA BETA ALUMINA



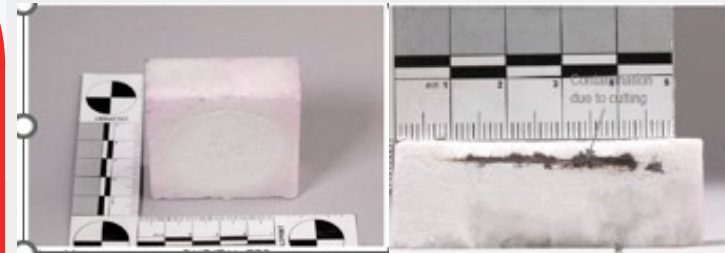
LID SURFACE

CUT SECTION

- ✓ Lid surface : minor build - up of charging material at interface between lid surface and crucible; slight discoloration
- ✓ Cut Section: no visible wear;

2

FUSED MULLITE



LID SURFACE

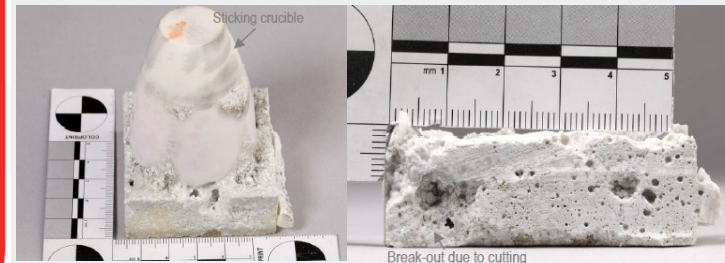
CUT SECTION

Lid surface : Slight wear at interface between lid surface and crucible; discoloration outside the exposure area

Cut Section: apparent reaction zone up to ~3mm from lid surface

3

STANDARD SILICA



LID SURFACE

CUT SECTION

Lid surface : sticking crucible; significant discoloration

Cut Section: apparent deformation of exp. Surface with wear at interface between lid surface and crucible

# Durital SP70

## New criteria for furnace crown design

| Property                                                                                                           | Unit               | DURITAL SP70        | No lime silica | Standard Silica |
|--------------------------------------------------------------------------------------------------------------------|--------------------|---------------------|----------------|-----------------|
|  Density                          | gr/cm <sup>3</sup> | 2.96                | 1.9            | 1.82            |
|  Thermal Expansion (1000 °C)      | %                  | 0.9 (1.5 at 1600°C) | 1.5            | 1.35            |
|  Cold Crushing Strength (CCS)     | MPa                | 85                  | 40             | 40              |
|  CuL(typical) Z <sub>5h-25h</sub> | 1650°C             | 0.025               | 0.021          | 0.001 (1550°C)  |



### 36% Higher density

- ~30% higher weight
- Stronger steel to hold the weight including buckstays, steel skew, pressure bolts
- It is not critical since the steel structure can be easily dimensioned with structural calculations
- Similar steel structures are already adopted and in operation for melting crowns in alpha-beta alumina materials



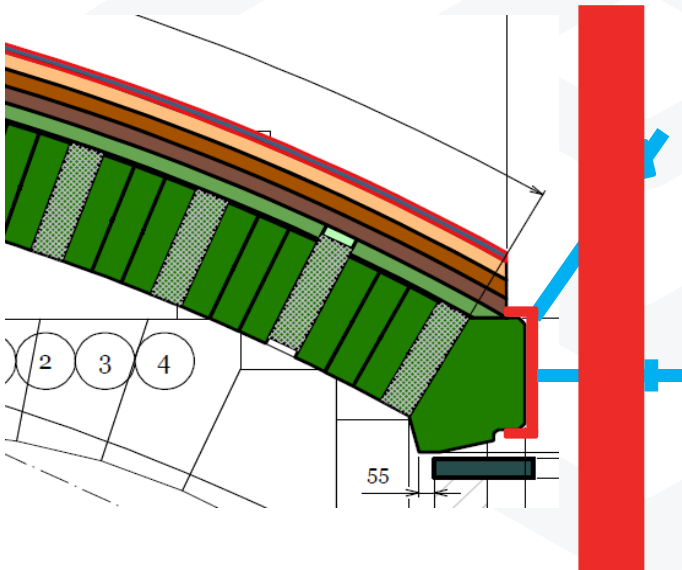
### Joints design

- Thermal expansion is similar to traditional crown materials, so the joints dimension will be similar.
- Silica TE reaches a stability above 600°C, so the crown expansion is not sensitive to changes at high temperatures (i.e. pull changes, boosting increase, etc.).
- DURITAL SP 70 has a linear TE coefficient, and it is more sensitive to temperature changes



### Superior creep resistance

- Creep is a critical parameter for a melting crown (risk of sagging)
- DU SP70 maintains a low creep at very high temperatures, assuring an optimal thermomechanical stability



# Durital SP70

## New design criteria for crown insulation

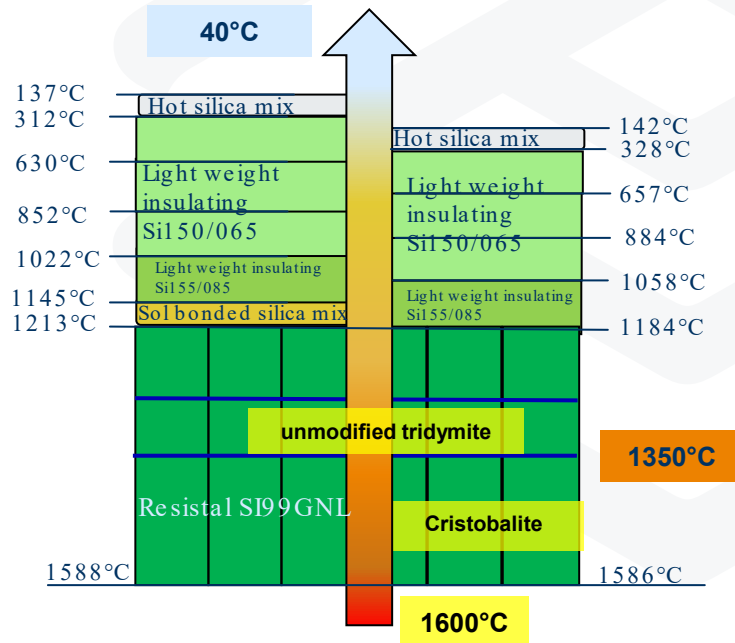


Thermal Conductivity W/mK (via Laser flash analysis)

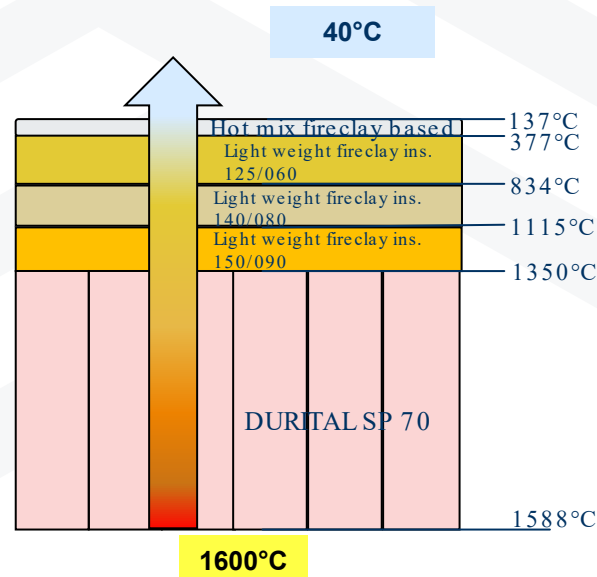
| Temperature (°C) | DURITAL SP70 | No lime silica | Standard Silica |
|------------------|--------------|----------------|-----------------|
| 25               | 10.26        | 1.02           | 1.32            |
| 200              | 6.8          | 0.86           | 1.24            |
| 400              | 5.36         | 1.02           | 1.52            |
| 600              | 4.61         | 1.12           | 1.62            |
| 800              | 4.04         | 1.21           | 1.72            |
| 1000             | 3.74         | 1.39           | 1.92            |
| 1200             | 3.54         | 1.58           | 2.08            |

- ✓ Specific Mg-Al spinel mortar required; soon available!
- ✓ Higher thermal conductivity, more insulation is needed!
- ✓ No need of sealing layer (no ratholing!)
- ✓ No need to apply silica insulating bricks
- ✓ Lightweight fireclay insulation package can achieve the same performance with reduced number of layers (less expensive!)

Silica crown concept



Mg-Al spinel crown concept



| Concept                                        | Layer Description                                                                                                                                                                     | Heat Loss W/m <sup>2</sup> | Cold Face Temp °C |
|------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------|-------------------|
| RHI Magnesita Brick Concept                    | 450 mm no lime silica<br>64mm light weight ins. SI155/085<br>3x64mm light weight ins. SI150/065<br>30mm hot Si mix                                                                    | 1998                       | 142               |
| RHI Magnesita Brick Concept with sealing layer | 450mm no lime silica<br>50 mm sol bonded sealing Si mix<br>64mm light weight ins. SI155/085<br>3x64mm light weight ins. SI150/065<br>30mm hot silica mix                              | 1874                       | 137               |
| Mg-Al Spinel RHIM concept                      | 450 mm DURITAL SP 70 brick<br>64 mm lightweight ins. F.clay 150/090<br>64 mm lightweight ins. F.clay 140/080<br>64 mm lightweight ins. F.clay 125/060<br>30 mm hot mix fireclay based | 1865                       | 137               |

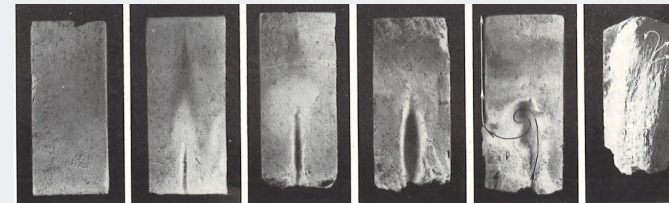
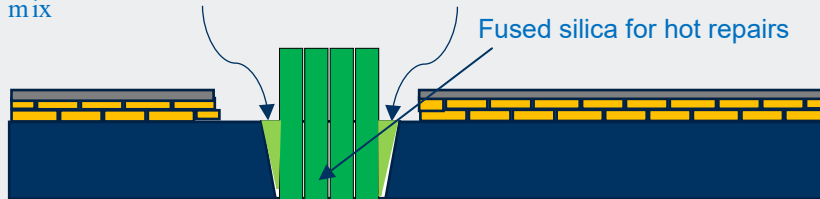
# Durital SP70

## Reduced maintenance

### Silica corrosion mechanism

- ✓ Tightness of the joint is crucial; the application of a monolithic layer is recommended to seal the joints
- ✓ Alkalis evaporate from the glass bath, infiltrate through the open joints, condensate when they reach a  $T < 1350^{\circ}\text{C}$  and corrode the bricks. Gas recirculation increases the corroded area
- ✓ The corroded bricks may cover large areas requiring the application of hanging bricks for the repair

High purity silica ramming mix, Sol bonded silica ramming mix or Zircon silicate ramming mix



**Result:** the silica crown requires more maintenance.



Mg -Al spinel is much less sensitive to alkali attack, reducing the frequency of the repairs

# Durital SP70

## Crown Heat up

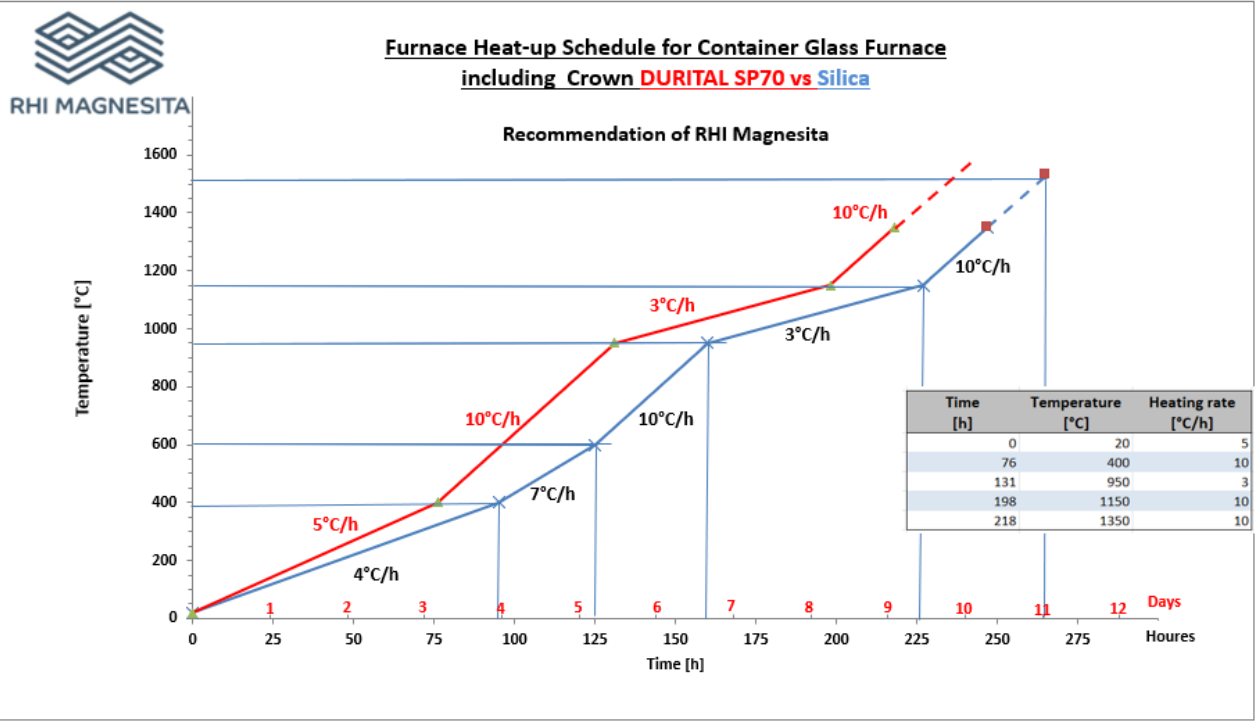
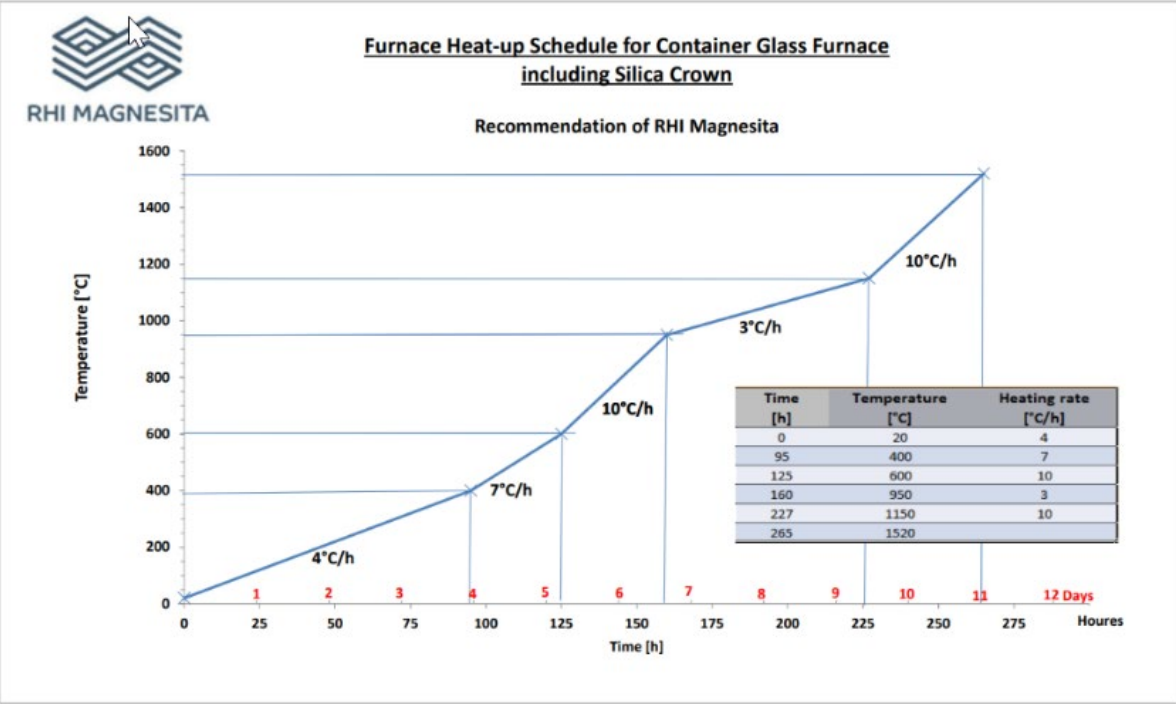
### Silica

requires special care during the heat-up.

Silica expansion starts at lower temperature and is fast → The temperature increase should be very slow, also to permit the correct management of the steelworks , to avoid joint openings and uncontrolled crown expansion

### Durital SP70

expands slowly and the volume increase is linear →  
The heat up can be faster in the range of temperatures 20-950°C



# Durital SP70

## Conclusions

- 1** Modern furnace atmospheres are more demanding  
Hybrid, oxy-fuel and hydrogen firing can increase humidity and alkali activity in crown and superstructure areas
- 2** Durital SP70 shows high thermo -mechanical stability  
Durital SP70 exhibits very low creep at high temperatures over extended periods, effectively addressing the requirement for thermo -mechanical stability especially for melter crowns applications
- 3** Durital SP70 shows high chemical stability  
In alkali vapor test, Durital SP 70 showed no mass loss and no significant sodium up -take; in alkali -boron vapor test, Durital SP 70 showed no visible chemical attack and a behavior like fused alpha -beta alumina
- 4** New criteria for the furnace crown design  
DU SP70 features require a different approach for the furnace crown design, operation, maintenance and heat up, providing that the joints design do not need modifications, the same insulation can be achieved and less maintenance is required
- 5** High purity MA spinel is a credible solution  
The combination of chemical stability, creep resistance and stable microstructure makes Durital SP70 suitable for selected high duty furnace areas.
- 6** Other applications
  - ✓ Float furnaces (cooling zones );
  - ✓ Glass fiber furnaces (superstructure and crown of “C” glass)
  - ✓ Special glasses

DURITAL SP 70 is a long-lasting lining solution in alkali and alkali-boron rich glass furnace environments



RHI MAGNESITA

# Thank you for your attention

## Get in Touch

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