Developments in Monolithic Products
For the Portland Cement Industry

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Content

- Introduction

- Cement Bonded Monolithics
  - Mix-Crete Monolithic Concept
    - SiC Mixes
    - SiC – ZrO₂ Mixes

- Chemically Bonded (No Cement) Monolithics
  - Phosphate bonded
  - Sol Gel (Nanobond) bonded
  - Geopolymer bonded

- Lining Concepts

- Conclusions
Consumption of Monolithic Refractory Material

- **Graph Title**: Consumption of Monolithic Refractory Material
- **Y-axis**: Share (%)
- **X-axis**: Years (1950 to 2010)
- **Graph Lines**:
  - **Red Line**: all industries
  - **Blue Line**: cement industry

The graph shows the increasing share of monolithic refractory material consumption in all industries and the cement industry over the years from 1950 to 2010.
Cement Industry: Areas of Application
Material Classes

- VIBRATION Castables
- SELF-LEVELING Castables
- PUMPABLE Castables
- DRY GUNNITES
- SHOTCRETES (Wet Gunning)
CALCIUM – ALUMINATE Cement Bonded Monolithics

- **Medium & Regular Cement**  \(2.5\% < CA < +6\%\)
- **Low Cement**  \(1\% < CA \leq 2.5\%\)
- **Ultra – Low Cement**  \(0.2\% < CA \leq 1\%\)
- **No Cement**  \(CA \leq 0.2\%\)
Products with SiC - Riser Duct (after approximately 1 year)

reaction zone
silicate-rich protective layer

unaffected microstructure
Improved Alkali Resistance

- 87% bauxite
- 60% andalusite
- 40% fireclay
- 25% fireclay

Alkali cup test / 1100 °C / K₂CO₃
Mix-Crete Monolithics
Case Study - Alkali Cup Test Results

40% Fireclay - Alumina LCC (No SiC)

3:1

2:1

1:1

50% SiC LCC
Case Study - Alkali Cup Test Results

85% Bauxite - Alumina LCC (3 – 7% SiC)

50% SiC LCC
SiC Mixcrete – Clinker Cooler Curbs

85% Bauxite - Alumina LCC + 50% SiC LCC (1:1)

Cooler Curbs after 6 months

Cooler Curbs after 4 months
SiC Mixcrete – Kiln Nose Ring

nose-ring after 12 months
Case Study - Alkali Cup Test Results

<table>
<thead>
<tr>
<th>Product</th>
<th>RLY 40</th>
<th>Ratio</th>
<th>RZN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material basis</td>
<td>Fireclay</td>
<td>1:1</td>
<td>ZrAR</td>
</tr>
<tr>
<td>Physical properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water addition %</td>
<td>6.0 - 7.5</td>
<td>5.5 - 6.5</td>
<td>5.0 - 6.0</td>
</tr>
<tr>
<td>Material requirement t/m³</td>
<td>2.35</td>
<td>2.70</td>
<td>3.05</td>
</tr>
<tr>
<td>After firing at 1000 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk density g/cm³</td>
<td>2.25</td>
<td>2.57</td>
<td>2.90</td>
</tr>
<tr>
<td>Apparent porosity %</td>
<td>19.0</td>
<td>19.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Thermal expansion lin.-%</td>
<td>0.50</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>Permanent linear change after firing lin.-%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 1000 °C</td>
<td>-0.30</td>
<td>-0.15</td>
<td>0.00</td>
</tr>
<tr>
<td>at 1200 °C</td>
<td>-0.20</td>
<td>-0.10</td>
<td>+0.10</td>
</tr>
<tr>
<td>at 1400 °C</td>
<td>+0.35</td>
<td>+0.30</td>
<td>+0.20</td>
</tr>
<tr>
<td>Cold crushing strength after firing N/mm²</td>
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<td></td>
</tr>
<tr>
<td>at 1000 °C</td>
<td>80</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>at 1200 °C</td>
<td>80</td>
<td>90</td>
<td>110</td>
</tr>
<tr>
<td>at 1400 °C</td>
<td>80</td>
<td>100</td>
<td>140</td>
</tr>
<tr>
<td>Maximum service Temperature °C</td>
<td>1500</td>
<td>1500</td>
<td>1550</td>
</tr>
<tr>
<td>Thermal conductivity W/m-K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 300 °C</td>
<td>1.6</td>
<td>1.9</td>
<td>2.1</td>
</tr>
<tr>
<td>at 700 °C</td>
<td>1.7</td>
<td>1.8</td>
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</tr>
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<tr>
<td>Chemical analysis Weight %</td>
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<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>43 - 47</td>
<td>43 - 47</td>
<td>43 - 47</td>
</tr>
<tr>
<td>SiO₂</td>
<td>48 - 60</td>
<td>35 - 39</td>
<td>22 - 26</td>
</tr>
<tr>
<td>SiC</td>
<td></td>
<td>3 - 7</td>
<td>7 - 11</td>
</tr>
<tr>
<td>ZrO₂</td>
<td></td>
<td>7 - 11</td>
<td>16 - 20</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>&lt; 1.5</td>
<td>&lt; 1.5</td>
<td>&lt; 1.0</td>
</tr>
</tbody>
</table>
## Case Study - Alkali Cup Test Results

**Product**
- RME 63
- LCC

**Raw material basis**
- Andalusite
- Andalusite/ZrO₂
- Zirconium oxide/alumosilicate

**Physical properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>5.0 - 6.0</th>
<th>5.0 - 6.0</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Water addition %</td>
<td>2.63</td>
<td>2.84</td>
<td>3.05</td>
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<tr>
<td>Material requirement t/m³</td>
<td></td>
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<td>18.0</td>
<td>19.0</td>
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<td>Thermal expansion lin.-%</td>
<td>0.60</td>
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<td></td>
<td></td>
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<tr>
<td>at 1000 °C</td>
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<td>140</td>
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<tr>
<td>Maximum service Temperature °C</td>
<td>1700</td>
<td>1600</td>
<td>1550</td>
</tr>
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</table>

**Thermal conductivity W/m-K**

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<tr>
<th>Temperature °C</th>
<th>1.6</th>
<th>1.9</th>
<th>2.1</th>
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</table>

**Chemical analysis Weight %**

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<th>Material</th>
<th>57 - 61</th>
<th>50 - 54</th>
<th>43 - 47</th>
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<tbody>
<tr>
<td>Al₂O₃</td>
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**REFRA TECHNIK**

![Image: 63% Andalusite - Alumina LCC]
Chemically Bonded Monolithics
Phosphate Bonded Monolithics

- Alumino – Orthophosphate (AlPO₄) Bond
  - Heat Setting T > 500 °C (930 °F)
- Plastics
- Ramming Mixes
- 2 Component Castables / Dry Gunning Mixes
- Will bond to existing alumino-silicate refractories
Sol-Gel (Nanobond) Introduction

Nanobond name derived from the chemical Liquid Binder

- Aqueous colloid dispersion / suspensions of amorphous SiO$_2$
- Uncured spherical particles 5 – 75 nm
- Solutions with different particle size, particle distribution and solid phase content $\rightarrow$ different reactivity
Sol-Gel Polymerization Reaction

Sol-gel reaction /
- System contains one or more components → cause gelling and hardening

- Gelification: colloidal Silica → 3-dimensional network → Si-O-Si bonds → water solvent

- Formation of Si-O-Si binding system
  - thermal drying
  - changing the pH value
  - addition of ion soluble salts

- → Sol-Gel-Bond
Sol-Gel Performance Characteristics

Storage, curing and drying

• 2 or 3 component packaging (dry & wet) → storage up to 24 months (CA < 12 months)

• Short & controllable curing / hardening time → no exothermic reaction!
  • CA takes longer to form complete CAH-phases

• Less sensitive to ambient installation temperatures than CA bonded materials

• Liquid component water content is not part of bonding chemical reactions
  • CA bonded systems can trap water in C-A-hydrate phases
  • NB → easy water evaporation <150°C / 302°F
  • NB Dry out schedules with heating rates up to 100°C / hr (212°F / hr)
  • CA: 3 to max. 50°C / hr

• Easy water evaporation helps avoid explosive steam spalling during hot repair or initial heat up
Sol-Gel Performance Characteristics

Hydraulic bond (CA)
Sol-Gel Performance Characteristics

Initial heat-up of a 250 mm thick lining

22 Hour Savings
Sol-Gel Performance characteristics

CCS, CMOR, PLC

cold modulus of rupture

cold crushing strength

permanent linear change

60% LC Shotcrete
60% Sol- Gel
Sol-Gel Performance Characteristics

Sticking properties to other surfaces, MACARBON brick

Broken MACARBON brick with rough, dusty surface

- Treatment: thermal shock: 10 x 1200°C (200°C/h)
- Both materials still joined

60% SiC NB
magcarbon brick

No cracks

60% SiC NB
magcarbon brick
Sol-Gel Performance Characteristics

Sticking properties to other surfaces, high alumina castable surface after temperature treatment:
MOR (N/mm$^2$), test regarding “sticking strength”

MOR = 21,7 N/mm$^2$

Failure not in the contact area MCC – Nanobond
No cracks in the bond area
Sol-Gel Product Types

Material Types & Installation Methods

• Vibration Cast
  Activator in Dry Component

• Self-Leveling Castable
  Activator in Dry Component

• Dry Gunite
  Activator in Dry Component

• Pump Cast
  Dry Activator added in Mixer

• Shotcrete
  Liquid Activator added at Nozzle
Geopolymer Concept

Product Philosophy:

- no cement technology (<0.2 % CaO)
- only one component-system for castables
- only two component-system for shotcrete applications
- easy installation with water comparable to CAC containing refractory concretes
- storage and installation comparable to LC-refractory concretes
  - reduced water addition of 5.5 - 7.5 %
  - typical wet mixing time of 3 - 5 min for vibration and shotcrete applications
- chemically activated bonding
- safe and faster dry out and heating up-procedure
- physical properties comparable to LC-refractory concretes
- refractoriness comparable to LC-refractory concretes
- alkali resistance comparable to LC-refractory concretes
Geopolymer Product Types

- Vibration Cast
- Pumpcast
- Shotcrete
Geopolymer Monolithic in Cooler Bullnoses

New Installation

After 250,000 Tons Clinker Production
## No Cement Systems Comparison

<table>
<thead>
<tr>
<th>Application cement industry:</th>
<th>Low Cement</th>
<th>Sol-Gel</th>
<th>Geopolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature sensitivity storage + installation</td>
<td>(water)</td>
<td>(silica sol ≥ 5 °C)</td>
<td>(water)</td>
</tr>
<tr>
<td>Drying out and heating-up safety</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apparent porosity / alkali resistance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permanent linear change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microstructural strength / abrasion resistance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microstructural elasticity / TSR</td>
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<td></td>
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</tr>
<tr>
<td>Ratio microstructural strength/elasticity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refractoriness / hot modulus of rupture</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Improved**
- Comparable respectively high level of properties
- **Worse**
No-Cement - Drying Out and Heating-Up

The drying out and heating-up procedure can be started after demoulding.

- Max. 50 °C/h
- Up to the temp. of application

- 8 h
- 250 °C
- 10 h / 150 °C
- Max. 50 °C/h

Time after setting / h

02.2014
Lining Concepts
Dual vs Single Layer Linings

Increasing Temp

$T_P$

$T_L$

$T_S$

Lining Thickness

Lining Thickness
Single Layer Linings

- Similar Thermal Conductivities to Dual Layer Linings
- Similar Abrasion Resistance
- Similar Thermal Expansion
- Less Thermal Stress on Metallic Anchoring Components
- Lower Overall Weight / Unit Volume
- Less Support Structure Loading => Lower Cost
- Potential to be made from Recycled Ceramics => Sustainability
- Suitable for Retrofit Installations
Conclusions
Cement Bonded Monolithics Conclusions

- High Initial Strengths at Room Temperature
- Single Component Castable Mixes — Just add Potable Water
- Two Component Shotcrete Mixes
- 6-12 Month Shelf Life
- Long Dry-Outs (Temp Holds at 500, 1000 & 1500 °F)
- Material Temp > 50 °F to Install Properly
- Can be Difficult to Install at Low Temps
- Need to Add SiC / Zirconia / AZS to increase Alkali Resistance
Conclusion

- Two Component Material: Dry Mix + Liquid Binder → Extended Shelf Life
- Short Setting Time → Hardening Time → Start Heating Up
- No Chemical Bonded Water → Very Easy Dry Out → Up to 100°C /Hr Heatups
- Same CCS and CMOR like CA-Bonded Materials > 800°C (1500 °F)
- Less Problems with Difficult Application Conditions (humidity, temperature)
- Excellent Sticking Properties to Other Refractory Materials → Hot and Cold Repair
- Storage of Liquid Binder Always > 5°C!
- Wet mixing with Liquid Binder → NO Additional Water
- Different Accelerators as Activators for Different Installation Methods
**Geopolymer Monolithics Conclusions**

- High Initial Strengths at Room Temperature
- Single Component Castable Mixes – Just add Potable Water
- Two Component Shotcrete Mixes
- 6 Month Shelf Life
- Short Dry-Out Schedules
- Chemically Activated Bonding
- Physical Properties Comparable to LC-Refractory Concretes
- Refractoriness Comparable to LC-Refractory Concretes
- Alkali Resistance Comparable to LC-Refractory Concretes
Thank You