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KEY FIGURES

Sales
€ 41 bn

Present in
64 countries

More than
180,000 employees

Almost
4,400 sales outlets

79% of sales on the habitat market

One of the world’s 100 most innovative companies*

Production sites

*Source: Thomson Reuters
REFRACTORIES BACKGROUND
REFRACTORY CHEMISTRY

Al₂O₃ - high melting T, chemically inert
SiO₂ - cheap and abundant, structurally good
MgO - basic, steel industry
CaO - good low T properties, usually mixed
ZrO₂ - high melting T, good insulator
Cr₂O₃ - corrosion / abrasion resistant
SiC - high heat transfer, abrasion resistant

Sourced from mined clays and minerals, or chemically derived
REFRACTORY MANUFACTURING

Pressing

Casting

Fusion Casting

Extrusion

... processing may be similar after forming
REFRACTORY TYPES

- Bricks and Special Shapes
- Castables (Cements & Mortars)
- Plastics (Ramming)
- Fibers (Blankets, etc.)
- Ramming Mixes and Loose Fill Powders
Chromia-Alumina Brick Shapes
Castables & Monolithics
## BRICKS & SHAPES V. CASTABLES

<table>
<thead>
<tr>
<th></th>
<th>Bricks &amp; Shapes</th>
<th>Castables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shaping limits</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Size limits</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Density</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Erosion</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Volume Stability</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Manuf. Quality</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Install Quality</td>
<td>+</td>
<td>--</td>
</tr>
<tr>
<td>Drying &amp; Curing</td>
<td>++</td>
<td>--</td>
</tr>
<tr>
<td>Cost</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>
Process Risks

From a refractory standpoint:

- High temperature excursions
- Rapid thermal cycles
- Chemical instability, contamination
- Slagging parameters
- Expansion stresses
- Water / steam leaks
- Improper curing

... can lead to forced shutdowns, expensive maintenance, hot spots, and worse...
Refractories are ceramic materials that are able to contain high temperature processes by providing thermal, structural, chemical, and corrosion barriers for a variety of industrial applications.
REFRACTORIES FOR GASIFICATION
PROPERTY TRADE-OFFS

Al₂O₃ - Cr₂O₃ - ZrO₂ system

Corrosion resistance (slag, glass)

Cr₂O₃

ZC900

ZC750

ZC60

ZC400

CC12

Hot mechanical strength

Al₂O₃

ZrO₂

Thermal shock resistance
THERMAL CYCLING

Rapid changes in operating temperature (>100 degC per hour) cause increased mechanical stresses, crack growth, and spalling.

Care must be taken when heating and cooling a refractory lining. A controlled schedule must be followed.

(Source: DOE ARC presentation, GTC 2002)
ACCURATE PREDICTIONS
Selective penetration of the elements

- Deep penetration of Ca, Si, Mg
- Concentration of V, Fe, Mg in surface layer ~ 1-2 mm
DENSE LAYER
OPTICAL & ELECTRONIC MICROSCOPY

SEM/EDS: dense layer/refractory interface

Optical microscopy: slag/dense layer/Refractory

No sign of microcracks in the dense layer or hot face  ➔ No spalling
## PETCOKE SLAG ANALYSES

<table>
<thead>
<tr>
<th>Material</th>
<th>Literature</th>
<th>Sample 1A</th>
<th>Sample 1B</th>
<th>Sample 2</th>
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<tbody>
<tr>
<td>SiO2</td>
<td>18.9</td>
<td>3.1</td>
<td>14.1</td>
<td>8.7</td>
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<tr>
<td>Al2O3</td>
<td>9.4</td>
<td>0.5</td>
<td>4.8</td>
<td>2.8</td>
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<tr>
<td>Fe2O3</td>
<td>31.6</td>
<td>1.2</td>
<td>7.2</td>
<td>9.3</td>
</tr>
<tr>
<td>CaO</td>
<td>11.9</td>
<td>2</td>
<td>5.4</td>
<td>3.8</td>
</tr>
<tr>
<td>MgO</td>
<td>5.1</td>
<td>0.3</td>
<td>1</td>
<td>1.6</td>
</tr>
<tr>
<td>K2O</td>
<td>0.7</td>
<td>0.3</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>Na2O</td>
<td>2.3</td>
<td>0.3</td>
<td>0.6</td>
<td>4</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.6</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
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<tr>
<td>NiO</td>
<td>11.4</td>
<td>2.9</td>
<td>8.4</td>
<td>3.2</td>
</tr>
<tr>
<td>V2O5</td>
<td>79.4</td>
<td>30.2</td>
<td>57</td>
<td>19.5</td>
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<tr>
<td>Cr2O3</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>P2O5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Fe2+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Fe total</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Fe2+/Fe Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% FeO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% C (Brut)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

**Note:** The table provides analysis data for various materials in terms of % wt, with references to specific samples and literature for comparison.
REFRACTORY DEVELOPMENTS
REFRACTORY ASSESSMENT PROGRAM – PRODUCT DEVELOPMENT

Lab performance tests II
• Infiltration kinetics
• Structural stability

Pilot Production
• Industrial feasibility
• Mix validation (compared to lab results!)

Test panel with customer
• Performance in operations
• Several months

Performance evaluation
• Corrosion resistance
• Thermal shock resistance

Final evaluated product
Ready for commercial operations
RESEARCH & DEVELOPMENT OF NEW MATERIALS

Initial Performance Improvement

Run Hours

C.R.E.E. R&D Center
Cavaillon, France

Northboro R&D Center
Massachusetts, USA
EXAMPLES OF REFRACTORY DEVELOPMENTS

- Transition from alumina monolithics to fired shapes
- Saint-Gobain patents related to addition of zirconia
- DOE ARC NETL development of phosphate additions to Cr$_2$O$_3$
- DOE ORNL studies on MgO aluminate spinels
- Frauenhofer Institute studies on SiC/AlN refractories
- GE Gen II Advanced Refractory
THE FUTURE OF REFRACTORIES FOR GASIFICATION
HEXAVALENT CHROMIUM CONCERNS

Indication in MSDS

<table>
<thead>
<tr>
<th>Measurement according NF EN 689</th>
<th>France 8h VME (mg/m³)</th>
<th>USA (ACGIH) 8h TWA (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non specific dust</td>
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<td></td>
</tr>
<tr>
<td>-Total dust</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>-Respirable dust</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Chromium (hexavalent compound)</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Chromium (hexa) soluble in water</td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>Chromium (hexa) insoluble</td>
<td></td>
<td>0.01</td>
</tr>
</tbody>
</table>
Raw Material Prices

USD Per Tonne

Date

May-09Mar-06Jan-07Nov-07Sep-08Jul-09May-10Feb-11Dec-11Oct-12

Source – Industrial Minerals magazine

RAW MATERIAL VOLATILITY
ALTERNATIVE SOLUTIONS

What else can be done in the field of thermal management?

- More matching of refractory qualities to life by zone
- Non-chromia containing refractories
- Fused cast refractories? Composites? Coatings?
- Thin membrane refractory barriers
- Systems with no refractories
- Better slag treatment for solid feed units
- Coal beneficiation
MAIN CONSIDERATIONS

- Always weigh cost vs. performance
- Manufacturability
- Raw material availability
- Slag compatibility
CHANGES IN GASIFICATION TECHNOLOGY

- Traditional Process Evolution
- Hydrogen economy – smaller, distributed units
- Biomass gasification/pyrolysis
- Plasma gasification
- Domestic waste processes
- Hazardous waste processes
Thank You!