Refractories for aluminium
the industry behind the industries
the theory behind the refractories

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ir. drs. Marcel C. Franken

General
Any process at high T in a installation
need for refractory (Feuerfest)
• not only resistant to high temperatures (Feuer)
• resistant to interaction with process
• keep heat in installation

minimum heat loss

Process
high T

refractory

no interaction
In a process installation many partial processes each partial process different refractory solutions possible: bricks, castables, chemical composition,....

PROCESS
Search for the perfect match
REFRACTORY
“each advantage has its disadvantage”

Refractory industry - “industry behind industries”

Refractory Consumption in Consumers Industry of Europe

- Steel 65%
- Chemical and Others 18%
- Non-ferrous 4%
- Glass 5%
- Cement/Lime 8%
GOUDA refractories

Ref refractories consumption

Specific consumption in 1955, 1980, 2000 and 2010 in major industries:

<table>
<thead>
<tr>
<th>Industry</th>
<th>Specific consumption kg (refractory) per t (product)</th>
<th>Reduction Total in %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1955</td>
<td>1980</td>
</tr>
<tr>
<td>Iron and Steel</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>Cement, Lime</td>
<td>2.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Glass</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>Aluminium</td>
<td>25.5</td>
<td>20</td>
</tr>
</tbody>
</table>

* Japan 11, Europe 12, USA 12, China 30 kg/ton

Reduction refractory consumption:

• improved process control
• larger installation (A/V)
• improved refractory

GOUDA refractories

Ref refractories producers

In Europe 26.000 employees and turnover 3.1 billion Euro

Tendency conglomeration:

• RHI Refractories:
  Didier, Veitsch, Radex, Harbison & Walker
• Vesuvius:
  Premier, VGT-Dyko
• Saint Gobain:
  Carborundum, Savoie, Norton
• Calderys:
  Lafarge, Plibrico

Gouda Refractories (Vuurvast)
Private owned company since 1901
Gouda Refractories

Total refractory lining solutions for critical equipments in various industries (% of TO)
- Aluminium 45 %
- Petrochemical 35 %
- Power & Energy 55 %
- Steel 5 %
- Calcination 10 %

Global network

Manufacturing, design, installation
65,000 ton bricks, 25,000 ton castables, 2500 ton precast (range: 30-100% Al₂O₃)

Refractory is chemistry and physics “alchemy”

Basis chemistry:
- inorganic material
- oxidic components
- reactions “transformations”

Basis physics:
- material expands as it becomes hot

Refractories goes to the fire
Thermal expansion

<table>
<thead>
<tr>
<th>Length A-B</th>
<th>Uitzetting</th>
<th>Temperatuur</th>
<th>Length A-B</th>
<th>Buiging C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Staal</td>
<td>1000 mm</td>
<td>1.2 mm / 100°C</td>
<td>200°C</td>
<td>1002 mm</td>
</tr>
<tr>
<td></td>
<td>3000 mm</td>
<td>1.2 mm / 100°C</td>
<td>200°C</td>
<td>3007 mm</td>
</tr>
<tr>
<td>Vuurvast</td>
<td>1000 mm</td>
<td>0.6 - 1.0% &gt; 0.8%</td>
<td>1100°C</td>
<td>1008 mm</td>
</tr>
<tr>
<td></td>
<td>3000 mm</td>
<td>0.6 - 1.0% &gt; 0.8%</td>
<td>1100°C</td>
<td>3024 mm</td>
</tr>
</tbody>
</table>

Back to basic
Stable oxides
High melting temperature
Classification based on chemistry
Slagbasicty: CaO/\( \text{SiO}_2 \)

Basic Product
- Magnesia
- Cr\(_2\)O\(_3\)
- Doloma
- Forsterite

Special Product
- Graphite/Carbon
- Zircon/Spinel
- Siliciumcarbide
- Siliciumnitride
- SIA/ION

Alumina-silicates
- "acid" product
- Silica
- Chamotte (Fire clay)
- Sillimaniet/Andalusiet/Kyaniet/Mulliet
- Sinterbauxiet
- Corundum

Not used
- reaction with Al
- spinel formation
- high expansion
each material has its own properties: refractoriness, chemical resistance,...
What is refractory?

Grain Size Distribution:
“flow” properties and density

Grain type:
“chemical” properties

Due to grains: high compressive strength, less tensile strength (5:1)

<table>
<thead>
<tr>
<th>Brick</th>
<th>Castable</th>
</tr>
</thead>
<tbody>
<tr>
<td>clay bonding</td>
<td>cement bonding</td>
</tr>
<tr>
<td>(ceramic /phosphate)</td>
<td>semi-product</td>
</tr>
<tr>
<td>ready to use</td>
<td>made on site</td>
</tr>
<tr>
<td>is mixed, densified, fired</td>
<td></td>
</tr>
</tbody>
</table>

Raw materials: Bauxite

Origine: Les Baux-en-Provence (F)

Consists of boehmite (Al2O3.H2O) and/or gibbsite (Al2O3.3H2O).

For refractory high Al2O3 and low impurities

Dig up (aluminiumhydrate), drying and firing/sintering 1400-1600 °C in rotary- or shaftkiln, porosity 12-20 %

Sintered bauxite mineralogy: corundum, mullite, tialite and glass
Raw materials: Bauxite

<table>
<thead>
<tr>
<th>China Bauxite</th>
<th>Guyana Bauxite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>84 – 89%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>6 – 10%</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3 – 4,5%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1,5 – 2,5%</td>
</tr>
<tr>
<td>CaO + MgO</td>
<td>&lt; 0,5%</td>
</tr>
<tr>
<td>Na₂O + K₂O</td>
<td>&lt; 0,5%</td>
</tr>
<tr>
<td>Abrasion Resistance</td>
<td>Good</td>
</tr>
<tr>
<td>Aluminium resistance</td>
<td>Minor</td>
</tr>
</tbody>
</table>

Chemical similar but different properties

Manufacturing Refractory Brick

Castables are “semi”-products quality made during installation
Refractory cement

Bonding of castable: CaO-containing

Differs from civil concrete: calcium aluminate vs calcium silicate

<table>
<thead>
<tr>
<th>Type</th>
<th>40% CAC</th>
<th>50% CAC</th>
<th>70% CAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>37,5 – 41,5</td>
<td>50,8 – 54,2</td>
<td>68,7 – 70,5</td>
</tr>
<tr>
<td>CaO</td>
<td>36,5 – 39,5</td>
<td>35,9 – 38,9</td>
<td>28,5 – 30,5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>4,2 – 5,0</td>
<td>4,0 – 5,5</td>
<td>0,2 – 0,6</td>
</tr>
<tr>
<td>FeO + Fe₂O₃</td>
<td>14,0-18,0</td>
<td>1,0 – 2,2</td>
<td>&lt;0,4</td>
</tr>
<tr>
<td>Temp</td>
<td>1100 C</td>
<td>1300 C</td>
<td>1500 C</td>
</tr>
</tbody>
</table>

Types of castables

- **conventional castables** (regular cement, RCC)
  - cement content 15 - 20 %
  - fine fraction 0 - 0,5 mm
  - water added +/- 12 %

- **low cement castable** (deflocculated – low cement, LC, ULC, NC)
  - cement content +/- 5 %
  - ultrafine fraction up to 0,3 um microsilica – round spheres
  - water added +/- 5 %

Ball in Hand method

Vibrating method

Self flowing

www.goudarefractories.com
Castables become more dense (higher strength, more fines) risk on steam explosions

Explosion:
Water/vapor pressure > tensile stress refractory

Attack mechanisms wear of refractory
4 types:
• melting - liquidification of refractory, too high T
• spalling - “breaking” refractory due to ΔT (+ or -)
• corrosion - chemical attack
• erosion - abrasion, strength

Oft combination of mechanisms:
no individual failure but amplifying each other (1+1=3)
also known as cause for wear (failure mechanism):
- CHEMICAL: corrosion
- THERMAL: melting and spalling
- MECHANICAL: erosion and spalling
Thermodynamics

Refractory (Al₂O₃-SiO₂) can react with Al:

- Corundum formation:
  \[ 4\text{Al} + \text{SiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Si} \]
  \[ 2\text{Mg} + \text{SiO}_2 \rightarrow 2\text{MgO} + \text{Si} \]
  \[ \text{Mg} + 2\text{Al} + 2\text{SiO}_2 \rightarrow \text{MgAl}_2\text{O}_4 + \text{Si} \]
  \[ 4\text{Al} + 3\text{TiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + \text{Ti} \]

→ Volume change and destroying refractory.

Al₂O₃-SiO₂ used:
- Good thermal properties
- Reasonable chemical resistance
- "Low" cost

Diamond is thermodynamically NOT stable.

Tabular cement castable (no SiO₂) usable?

CaO will not react with Al:

\[ 3\text{CaO} + 2 \text{Al} \rightarrow 3 \text{Ca} + \text{Al}_2\text{O}_3 \quad \Delta G = +234 \text{ kJ} \]

But:

\[ 3\text{CaO} + 8 \text{Al} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Al}_2\text{Ca} \quad \Delta G = -234 \text{ kJ} \]

Seems like corundum formation but is intermetallic formation.
Reaction kinetic *speed of reaction*

Not only important if components react with each other but also the velocity (speed) of reaction.

Lower temperature will give slower reaction.

*“Best refractory is water”*

Keep process cold → kinetics will be slowed.

In aluminium

freeze line (solidification T) is at 2/3 of the hot face lining

Take care: change of Al-alloy – change of T solid?

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T-profile calculations – thermal resistance (d/λ)

Several layer system - serial system

\[
V = I \cdot R_{\text{tot}} \\
R_{\text{tot}} = R_1 + R_2
\]

\[
\Delta T = Q \cdot R \\
R_{\text{tot}} = R_1 + R_2 \\
\Delta T = Q \cdot (R_1 + R_2) \\
Q = \frac{\Delta T}{(d_1/\lambda_1 + d_2/\lambda_2)} \\
\]

per layer

\[
\Delta T_1 = Q \cdot R_1 \\
\Delta T_1 = R_1/R_{\text{tot}} \cdot \Delta T_{\text{tot}}
\]
T-profile calculations – thermal resistance (d/λ)

Assume furnace 1220°C inside, 20°C outside:
- chamotte layer 230 mm and λ=1.15 W/m.K
  \[ R_1 = \frac{d_1}{\lambda_1} = \frac{0.23}{1.15} = 0.2 \text{ m}^2\text{K/W} \]
- insulating layer 80 mm and λ=0.1 W/m.K
  \[ R_2 = \frac{d_2}{\lambda_2} = \frac{0.08}{0.1} = 0.8 \text{ m}^2\text{K/W} \]
  \[ R_{tot} = 1 \text{ m}^2\text{K/W} \]

T-drop per layer:
- \[ \Delta T_1 = R_1 \Delta T_{tot} = 0.2/1 \times 1200 = 240 \text{ C} \]
- \[ \Delta T_2 = R_2 \Delta T_{tot} = 0.8/1 \times 1200 = 960 \text{ C} \]

Heat loss:
\[ Q = \Delta T / R_{tot} = 1200/1 = 1200 \text{ W/m}^2 \]

Most T-drop over the highest R

More insulation - less heat loss

Disadvantage:
- Less T-profile over wear lining
- Solidification-T deeper in lining
- More attack
- Risc of Al- outbreak
### Change of Al-alloy (T-solid)

- **T-solidification**
- **Lower T-sol**

Change Al-alloy to lower solidification temperature → risk of outbreak

### Reaction kinetics – less surface

**minimize surface reactions** (less penetration by)
- lower porosity
- decrease wettability

**use of anti-wetting agents:**
- CaF2
- BaSO4
- ....

**Potential disadvantage:**
- CaF2 lowers melting T → reduction in strength at T>900 C
- BaSO4 decomposes (disappears) T>1150 C

Take care: change of Al-alloy – change of wettability?

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**Equation of capillary action:**

\[ h = \frac{2y \cos \theta}{\rho g r} \]

Where:
- \( h \) - height the liquid is lifted,
- \( y \) - liquid-air surface tension,
- \( \rho \) - density of the liquid,
- \( g \) - acceleration due to gravity,
- \( \theta \) - the angle of contact
Corrosion by Aluminium

*Cup test, 72 hours*

1050 °C  
1200 °C

*Figures are indicative (not typical Gouda Refractories products)*  
Critical T> 1100 °C, some additives “disappear”  
Melting furnace T higher than holding furnaces  
Often problems at burners (regenerative)

Effect of Al-alloy on refractory

*Cup test, 72 hours, 1050 °C*

Alloy 5083, Mg-rich  
Alloy 7020, Zn-rich
Melting & Holding Furnaces

Lining Possibilities

- Bricks refractory lining
- Castable for back-up layer bath
- Insulation castable roof
- Hot face brick upper wall
- Hot face brick bath
- Anchor brick
- Hot face castable upper wall
- Hot face castable roof
- Hot face castable burner
- Hot face castable wall special
- Castable refractory lining

www.goudarefractories.com
Melting and Holding Furnaces

- Continuous push for more metal output
- Higher operational temperatures
- More mechanical abuse
- More thermal shock
- Increase of different alloys
- More recycling of scrap

*Higher performance requirements of refractories*

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Failure Mechanisms

**Thermal stresses**

- Due to charging of the furnace there are in some areas of the furnace serious temperature fluctuations.
- The critical area’s are doorjambs and lintel

**Abrasion resistance**

- Charging of the furnace with big pieces of aluminium.
- Cleaning of the furnace with heavy equipment

**Refractory design**

- Refractory material with good thermal shock resistance/low thermal expansion (mineralogy)
- Refractory material with high abrasion resistance / castable good installation
Gouda Refractories has many products:

- > 100 types of bricks (dense, insulating)
- > 50 types of mortar (air, heat setting)
- > 400 types of castables (dense, insulating)
- > 100 type of precast blocks (dried, fired)
Refractory – General

Life time determined by:
- Quality - material and installation
- Design - good quality on the right place “zoning”
- Handling - (ab)use of refractories during operation

Gouda Refractories has many products, good refractory know-how but limited process know-how

Only by *mutual effort* (user and supplier) and *several disciplines* (process/operator, engineering, installation, refractory), it is possible to improve lining and to obtain “*best value in use*”.
You know all about the process, 
I will give you some information on refractories 
or better give the theory behind refractories 
so you better choose (know) your refractory for your 
process 
Or know the pros and cons of the refractory 
“each advantage has its disadvantage”
INTEGRATED REFRACTORY APPROACH

Best value in use:
• Life time, installing time, repair time
• Availability
• Capacity
• Safety & health
• Environment
• ......

Focus:
not on price per ton refractory but “best value in use”
Material choice
• know process conditions
• know material properties
match material on process (and vice versa)

Search for the perfect match

Application

Properties

Chemical composition  Microstructure