

Challenges in refractory design

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 - > RHI on one view
 - > Refractory consumption

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 - > Exposure and typical design concept
 - > Examples

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 - > Insulating materials
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- **Summary**

Inroduction

- **Refractory – Essential for all basic material industry**
- **RHI on one view**
- **Refractory consumption**

Refractory – Essential for all basic material Industry

refractory products



Refractory



unshaped



lining

- Ceramic refractory products are used in all **industrial high temperature applications** (>1.200°C). They protect persons and equipment from **thermal**, **mechanical** and **chemical** loads.
- **Main Raw materials** are magnesite and dolomite (melting point of pure MgO >2.800°C)



magnesite



dolomite

high temperature processes



steel



cement and lime



glass



non-ferrous metals

RHI is a vertical integrated global supplier of premium grade refractory products, systems and services, which are essential for industrial high temperature processes more than 1.200 °C

RHI on one view



Basic data

- Focus on production, sales and installation of premium grade refractory products
- Key figures see: http://www.rhi-ag.com/internet_en
- 32 production- and over 70 sales departments with app. 8.000 employees
- Global partner for over 10.000 customers in more than 180 countries
- Technology leadership with market-oriented R&D-facilities and made- to- measure products

selected key customer

steel	cement	glass	non ferrous
 ArcelorMittal	 Buzzi Unicem	 ArdaghGlass	 GLENCORE INTERNATIONAL AG
 Severstal	 COMEX	 CORNING	 bhpbilliton
 voestalpine <small>EINEN SCHRITT VORWAUS.</small>	 Holcim	 VITRO	 RioTinto
	 LAFARGE		

Refractory consumption



Materials used for a car:

- Steel
- Aluminum
- Glass
- Plastics
- Copper
- Electronics

Involved refractory consumers:

- Iron and steel industry
- Aluminum industry
- Glass industry
- Chemical industry
- Non-ferrous industry (base metals)
- Semiconductor and precious metals industry

Refractory consumption

Refractory consumption for 1 t product:

Steel	10-12 kg
Glass	4 kg
Cement	1 kg
Lime	0,7 kg
Copper (base metal)	6 kg
Waste	5,5 kg

Worldwide the total high quality refractory consumption is estimated to app. 20-25 billion t.

Demands on refractories

- **Definition: Refractory**
- **Availability of raw materials**
- **Raw materials and main users**
- **Exposure and typical design concept**
- **Examples**

Definition: Refractory

DIN 51060 / ISO/R 836

fire resistant	below	1.500 °C
refractory	min.	1.500 °C
highly-refractory	min.	1.800 °C

Most common: Materials which can withstand **T >600°C** are referred to refractory materials.

Availability of raw materials

<p>1 1A 2 2A 3 3A 4 4A 5 5A 6 6A 7 7A 8 VIII 9 VIII 10 VIII 11 IB 12 IIB 13 14 15 16 17 18 0</p> <p>1 1A 2 2A 3 3A 4 4A 5 5A 6 6A 7 7A 8 VIII 9 VIII 10 VIII 11 IB 12 IIB 13 14 15 16 17 18 0</p>																	
<p>Relative Atommasse (Atomgewicht): * bei Radioelementen: Nuklidmasse eines wichtigen Isotops (Massenzahl s. Zeile 4); Th, Pa und U: natürliches Isotopengemisch</p> <p>Anzahl natürlicher Isotope; (r): nur Radioisotope in natürlichen Zerfallsreihen oder aus anderen natürlichen Kernprozessen</p> <p>Massenzahlen der häufigsten natürlichen Isotope; natürliche Radioisotope</p> <p>Natürliche Häufigkeit des Isotops in %</p> <p>Erste Ionisierungsenergie in eV</p> <p>Dichte in g/cm³ bei 20°C</p> <p>Schmelzpunkt (feste Elemente) oder Siedepunkt (flüssige und gasförmige Elemente) in °C</p>																	
<p>Wichtiges oder langlebigstes Radioisotop (wichtige Zerfallsarten) Halbwertszeit</p> <p>Ordnungszahl</p> <p>Elementensymbol:</p> <p>Fe feste Elemente</p> <p>flüssige Elemente (20°C)</p> <p>gasförmige Elemente</p> <p>radioaktive Elemente mit nachweisbarem natürlichem Vorkommen (z. T. nur in geringen Mengen, z. B. in natürlichen Zerfallsreihen)</p> <p>künstliche Elemente</p>																	
<p>alte IUPAC-Empfehlung</p> <p>neuer Vorschlag der IUPAC 1985</p> <p>Vom Chemical Abstracts Service bis 1986 verwendete Gruppenbezeichnung</p>																	
<p>1.00794 2 1.00794 2 1.00794 2</p> <p>1 1 H 1.00794 2 Wasserstoff -101.9</p> <p>6.941 2 6.941 2 6.941 2</p> <p>2 2 Li 6.941 2 Lithium 100.5</p> <p>23.00369 2 23.00369 2 23.00369 2</p> <p>3 3 Na 23.00369 2 Natrium 100.7</p> <p>39.0983 2 39.0983 2 39.0983 2</p> <p>4 4 K 39.0983 2 Kalium 100.9</p> <p>85.4678 2 85.4678 2 85.4678 2</p> <p>5 5 Rb 85.4678 2 Rubidium 100.9</p> <p>132.90543 2 132.90543 2 132.90543 2</p> <p>6 6 Cs 132.90543 2 Cäsium 100.9</p> <p>223.0187 2 223.0187 2 223.0187 2</p> <p>7 7 Fr 223.0187 2 Francium 100.7</p>																	
<p>4.002602 2 4.002602 2 4.002602 2</p> <p>2 He 4.002602 2 Helium -100.5</p> <p>12.011 2 12.011 2 12.011 2</p> <p>13 B 12.011 2 Bor 108.1</p> <p>26.981538 2 26.981538 2 26.981538 2</p> <p>13 Al 26.981538 2 Aluminium 108.1</p> <p>28.0855 2 28.0855 2 28.0855 2</p> <p>14 Si 28.0855 2 Silicium 108.1</p> <p>30.973762 2 30.973762 2 30.973762 2</p> <p>15 P 30.973762 2 Phosphor 108.1</p> <p>32.06 2 32.06 2 32.06 2</p> <p>16 S 32.06 2 Schwefel 108.1</p> <p>35.453 2 35.453 2 35.453 2</p> <p>17 Cl 35.453 2 Chlor 108.1</p> <p>36.461 2 36.461 2 36.461 2</p> <p>18 Ar 36.461 2 Argon 108.1</p>																	
<p>68.723 2 68.723 2 68.723 2</p> <p>13 Ga 68.723 2 Gallium 108.1</p> <p>72.61 2 72.61 2 72.61 2</p> <p>14 Ge 72.61 2 Germanium 108.1</p> <p>74.921595 2 74.921595 2 74.921595 2</p> <p>15 As 74.921595 2 Arsen 108.1</p> <p>78.96 2 78.96 2 78.96 2</p> <p>16 Se 78.96 2 Selen 108.1</p> <p>79.904 2 79.904 2 79.904 2</p> <p>17 Br 79.904 2 Brom 108.1</p> <p>83.80 2 83.80 2 83.80 2</p> <p>18 Kr 83.80 2 Krypton 108.1</p>																	
<p>101.07 2 101.07 2 101.07 2</p> <p>20 Ni 101.07 2 Nickel 108.1</p> <p>102.90550 2 102.90550 2 102.90550 2</p> <p>21 Cu 102.90550 2 Kupfer 108.1</p> <p>106.42 2 106.42 2 106.42 2</p> <p>22 Zn 106.42 2 Zink 108.1</p> <p>106.90 2 106.90 2 106.90 2</p> <p>23 Ga 106.90 2 Gallium 108.1</p> <p>107.8682 2 107.8682 2 107.8682 2</p> <p>24 Ge 107.8682 2 Germanium 108.1</p> <p>112.411 2 112.411 2 112.411 2</p> <p>25 As 112.411 2 Arsen 108.1</p> <p>114.818 2 114.818 2 114.818 2</p> <p>26 Se 114.818 2 Selen 108.1</p> <p>118.710 2 118.710 2 118.710 2</p> <p>27 Br 118.710 2 Brom 108.1</p> <p>121.757 2 121.757 2 121.757 2</p> <p>28 Kr 121.757 2 Krypton 108.1</p> <p>127.60 2 127.60 2 127.60 2</p> <p>29 Rb 127.60 2 Rubidium 108.1</p> <p>127.904 2 127.904 2 127.904 2</p> <p>30 Sr 127.904 2 Strontium 108.1</p> <p>132.90543 2 132.90543 2 132.90543 2</p> <p>31 Y 132.90543 2 Yttrium 108.1</p> <p>137.327 2 137.327 2 137.327 2</p> <p>32 Zr 137.327 2 Zirkon 108.1</p> <p>178.49 2 178.49 2 178.49 2</p> <p>33 Nb 178.49 2 Niobium 108.1</p> <p>180.9479 2 180.9479 2 180.9479 2</p> <p>34 Mo 180.9479 2 Molybdän 108.1</p> <p>183.84 2 183.84 2 183.84 2</p> <p>35 Tc 183.84 2 Technetium 108.1</p> <p>186.207 2 186.207 2 186.207 2</p> <p>36 Ru 186.207 2 Ruthenium 108.1</p> <p>190.23 2 190.23 2 190.23 2</p> <p>37 Rh 190.23 2 Rhodium 108.1</p> <p>192.22 2 192.22 2 192.22 2</p> <p>38 Pd 192.22 2 Palladium 108.1</p> <p>195.08 2 195.08 2 195.08 2</p> <p>39 Ag 195.08 2 Silber 108.1</p> <p>196.96654 2 196.96654 2 196.96654 2</p> <p>40 Cd 196.96654 2 Cadmium 108.1</p> <p>200.59 2 200.59 2 200.59 2</p> <p>41 In 200.59 2 Indium 108.1</p> <p>204.3833 2 204.3833 2 204.3833 2</p> <p>42 Sn 204.3833 2 Zinn 108.1</p> <p>207.2 2 207.2 2 207.2 2</p> <p>43 Sb 207.2 2 Antimon 108.1</p> <p>208.98037 2 208.98037 2 208.98037 2</p> <p>44 Te 208.98037 2 Tellur 108.1</p> <p>209.96964 2 209.96964 2 209.96964 2</p> <p>45 I 209.96964 2 Jod 108.1</p> <p>209.96964 2 209.96964 2 209.96964 2</p> <p>46 Xe 209.96964 2 Xenon 108.1</p>																	
<p>208.98037 2 208.98037 2 208.98037 2</p> <p>47 Ba 208.98037 2 Barium 108.1</p> <p>223.0187 2 223.0187 2 223.0187 2</p> <p>48 La-Lu 223.0187 2 Lanthan-Lutetium 108.1</p> <p>226.103 2 226.103 2 226.103 2</p> <p>49 Hf 226.103 2 Hafnium 108.1</p> <p>227.103 2 227.103 2 227.103 2</p> <p>50 Ta 227.103 2 Tantal 108.1</p> <p>231.036 2 231.036 2 231.036 2</p> <p>51 W 231.036 2 Wolfram 108.1</p> <p>232.037 2 232.037 2 232.037 2</p> <p>52 Re 232.037 2 Rhenium 108.1</p> <p>238.0289 2 238.0289 2 238.0289 2</p> <p>53 Os 238.0289 2 Osmium 108.1</p> <p>238.0289 2 238.0289 2 238.0289 2</p> <p>54 Ir 238.0289 2 Iridium 108.1</p> <p>238.0289 2 238.0289 2 238.0289 2</p> <p>55 Pt 238.0289 2 Platin 108.1</p> <p>238.0289 2 238.0289 2 238.0289 2</p> <p>56 Au 238.0289 2 Gold 108.1</p> <p>238.0289 2 238.0289 2 238.0289 2</p> <p>57 Hg 238.0289 2 Quecksilber 108.1</p> <p>238.0289 2 238.0289 2 238.0289 2</p> <p>58 Tl 238.0289 2 Thallium 108.1</p> <p>238.0289 2 238.0289 2 238.0289 2</p> <p>59 Pb 238.0289 2 Blei 108.1</p> <p>238.0289 2 238.0289 2 238.0289 2</p> <p>60 Bi 238.0289 2 Bismut 108.1</p> <p>238.0289 2 238.0289 2 238.0289 2</p> <p>61 Po 238.0289 2 Polonium 108.1</p> <p>238.0289 2 238.0289 2 238.0289 2</p> <p>62 At 238.0289 2 Astat 108.1</p> <p>238.0289 2 238.0289 2 238.0289 2</p> <p>63 Rn 238.0289 2 Radon 108.1</p>																	

Nach FLUCK und HEUMANN unter Berücksichtigung der IUPAC-Empfehlungen bis 1991

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57 La 138.9055 2 Lanthan 100.9	58 Ce 140.115 4 Cer 101.1	59 Pr 140.90785 1 Praseodym 101.1	60 Nd 144.24 7 Neodym 101.1	61 Pm 146.9151 01 Promethium 101.1	62 Sm 150.36 7 Samarium 101.1	63 Eu 151.965 2 Europium 101.1	64 Gd 157.25 7 Gadolinium 101.1	65 Tb 158.92534 1 Terbium 101.1	66 Dy 162.50 7 Dysprosium 101.1	67 Ho 164.93032 1 Holmium 101.1	68 Er 167.26 6 Erbium 101.1	69 Tm 168.93421 1 Thulium 101.1	70 Yb 173.04 7 Ytterbium 101.1	71 Lu 174.967 2 Lutetium 101.1
227.0276 2 227.0276 2 227.0276 2	232.037 2 232.037 2 232.037 2	231.03688 2 231.03688 2 231.03688 2	232.037 2 232.037 2 232.037 2	237.0482 01 237.0482 01 237.0482 01	244.0642 01 244.0642 01 244.0642 01	243.0614 01 243.0614 01 243.0614 01	247.0703 01 247.0703 01 247.0703 01	247.0703 01 247.0703 01 247.0703 01	251.0789 01 251.0789 01 251.0789 01	252.0829 01 252.0829 01 252.0829 01	257.0951 01 257.0951 01 257.0951 01	258.0966 01 258.0966 01 258.0966 01	259.1009 01 259.1009 01 259.1009 01	260.1053 01 260.1053 01 260.1053 01
88 Ac 227.0276 2 Actinium 100.7	90 Th 232.037 2 Thorium 100.7	91 Pa 231.03688 2 Protactinium 100.7	92 U 232.037 2 Uran 100.7	93 Np 237.0482 01 Neptunium 100.7	94 Pu 244.0642 01 Plutonium 100.7	95 Am 243.0614 01 Americium 100.7	96 Cm 247.0703 01 Curium 100.7	97 Bk 247.0703 01 Berkeleium 100.7	98 Cf 251.0789 01 Californium 100.7	99 Es 252.0829 01 Einsteinium 100.7	100 Fm 257.0951 01 Fermium 100.7	101 Md 258.0966 01 Mendelevium 100.7	102 No 259.1009 01 Nobelium 100.7	103 Lr 260.1053 01 Lawrencium 100.7

Raw materials and main users

silica	chamotte	bauxite	chrome ore	corundum	zirkondioxi de	doloma	magnesia
quartz	refractory clay	mix	chromite	aluminiumdi -oxide	baddeleyite	dolomite	magnesite
glass- industry	all industry	all industry	steel, glass, cement, non- ferrous	all industry	steel industry	steel industry	steel, cement, non- ferrous
1600 °C	1300 °C	1500 °C	1700 °C	1650 °C	1800 °C	1750 °C	1800 °C
ACID				NEUTRAL		BASIC	

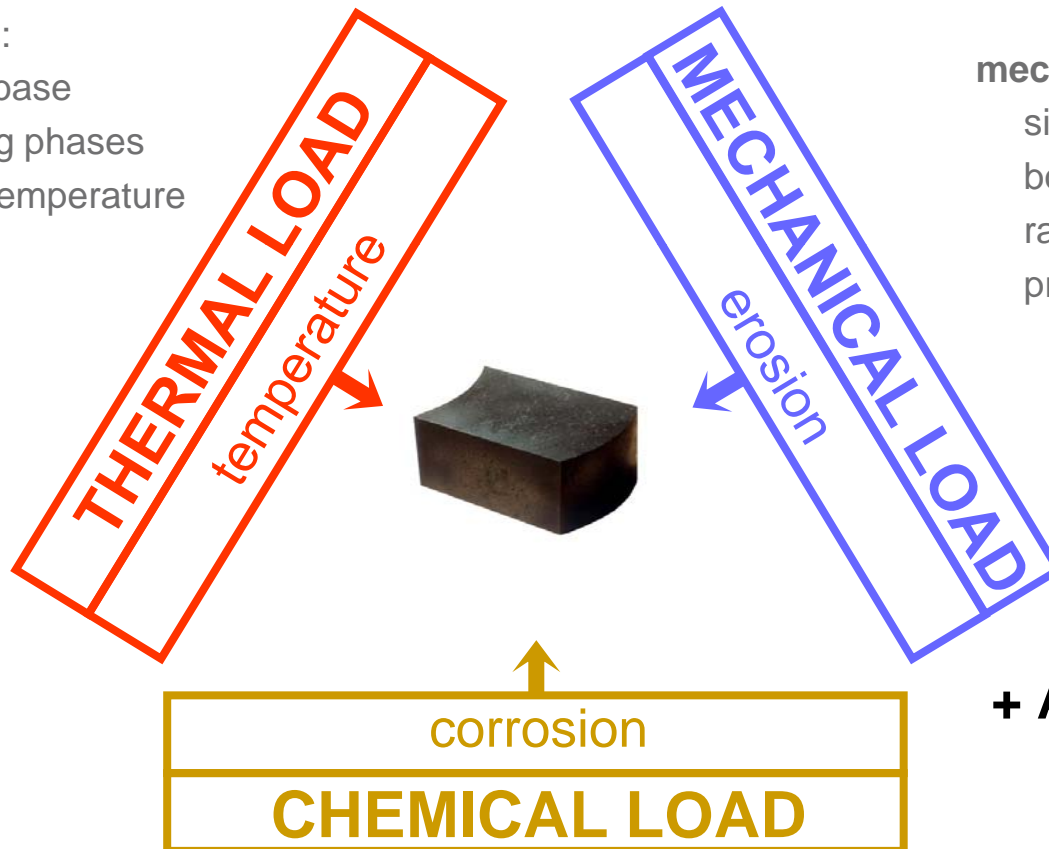
Exposure and typical design concept

refractoriness:

- material base
- coexisting phases
- liquidus temperature

mechanical properties:

- sieve analyses
- bonding type
- raw materials
- process parameters

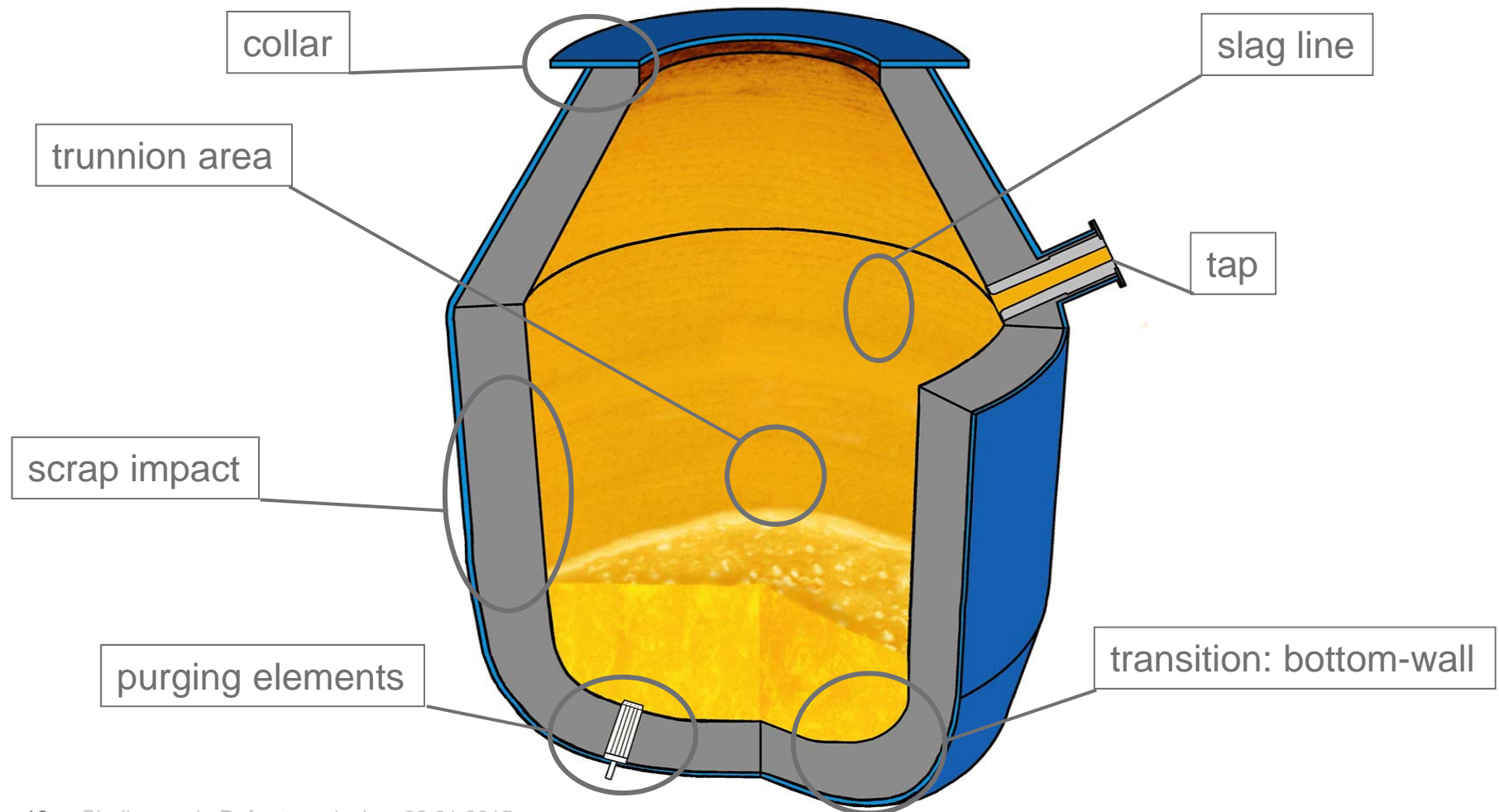


+ Availability and price of used materials!

Chemical resistance:

- reactions with process media
- solubility

Example: wear of a steel converter

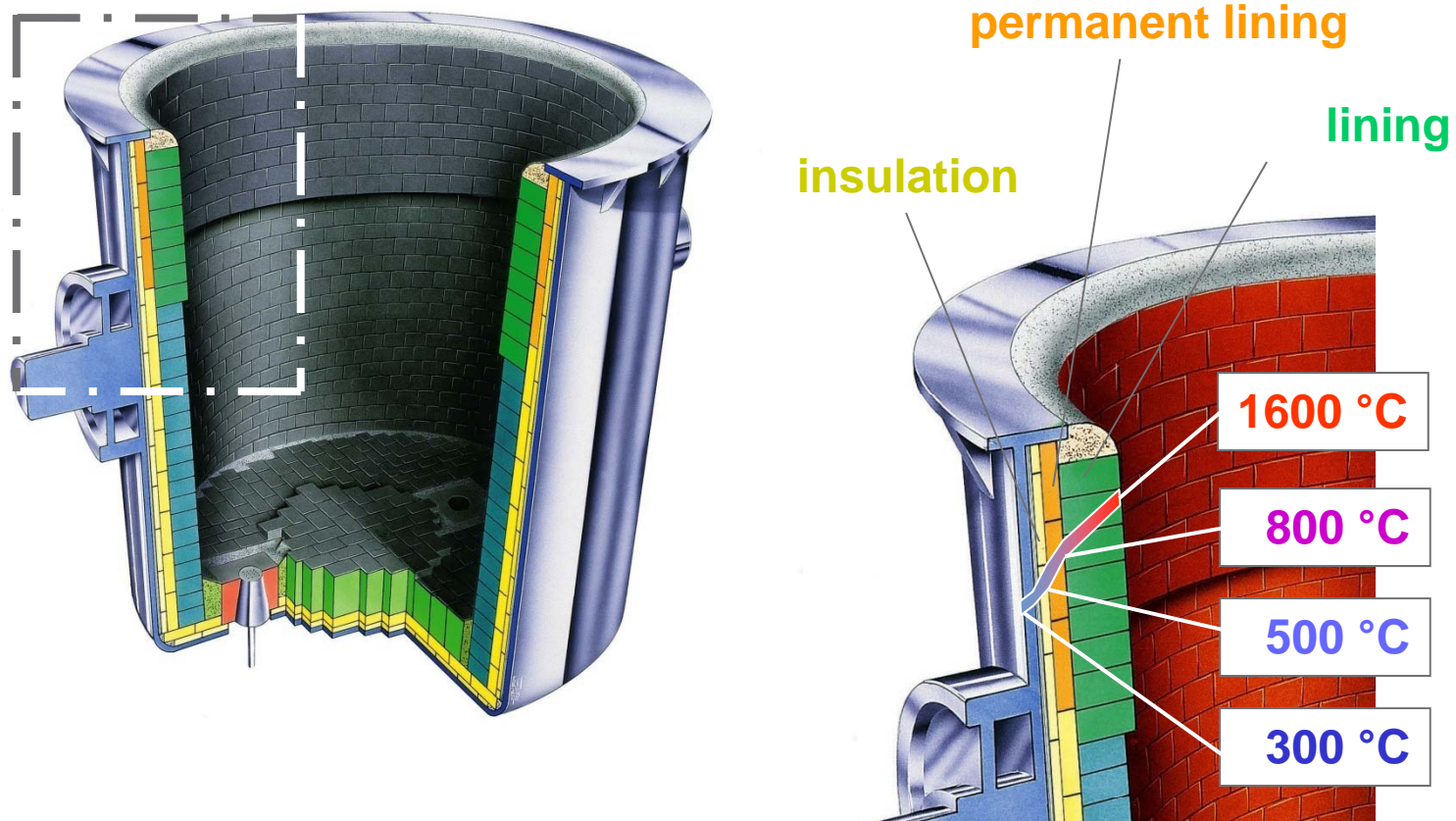


Example: wear of a steel converter



partial loss of wear
lining

Example: complex lining of a steel ladle



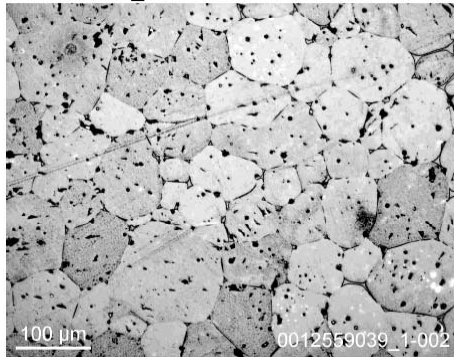
Important material properties of refractories

- Chemical and mineralogical composition
- Density and porosity
- Mechanical properties
- Alteration behaviour

Chemical and mineralogical composition

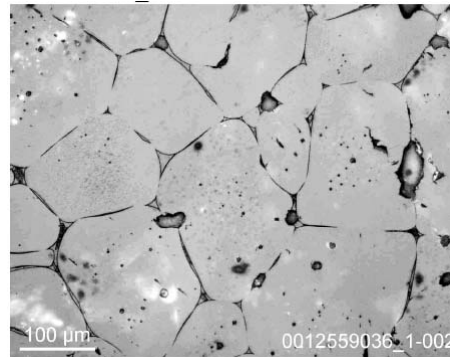
- **Material selection according to application:**
 - > Reduction of chemical wear: coexistent phases of refractory and process media
- **Purity**
 - > Impurities lower liquidus temperature
 - > Impurities along grain boundaries promote diffusion and corrosion

Example MgO:



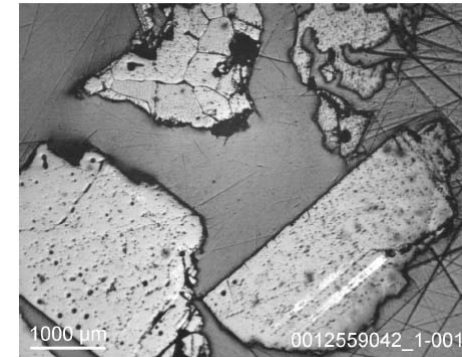
standard sintered magnesia

density > 3,38 g/cm³
 PCS* 60–120 μm
 MgO-content > 95%



large crystal sintered magnesia

density > 3,41 g/cm³
 PCS* > 150 μm
 MgO-content > 97%



fused magnesia

density > 3,50 g/cm³
 PCS* > 500 μm
 MgO-content > 96%

*PCS= Periclase Cystal Size

Density and porosity

- Targeted values are dependent on application:

- > **High density:**

- > good wear resistance
 - > High toughness
 - > Bad insulation behaviour
 - > Alterations: low risk of infiltration

target: **theoretical density** of raw materials used

pure MgO brick	2,96 g/cm ³ (limit 3,56 g/cm ³)
pure Al ₂ O ₃ brick	3,23 g/cm ³ (limit 4,00 g/cm ³)
fused cast ZrO ₂	5,29 g/cm ³ (limit 5,50 g/cm ³)

- > **Low density**

- > Low wear resistance
 - > High thermal insulation
 - > Low toughness
 - > Danger of strong alterations during service

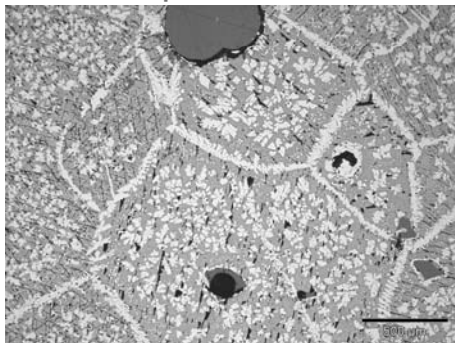
target **as low as possible**: < 1,00 g/cm³

Mechanical properties

- **At room temperature**
 - > Can be measured to a certain degree
 - > Most time: destructive testing
 - > Important: damage tolerance

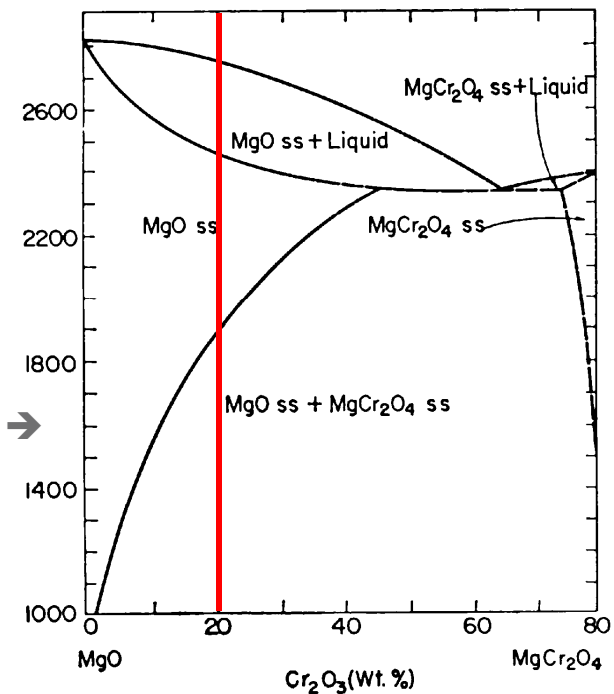
- **At „service“ conditions:**
 - > Unknown in many cases
 - > Difficult to measure (temperature)
 - > Complex interactions of properties on wear resistance

room temperature



← fused magnesia-chromite →

- **Cold crushing strength**
 - > Dense refractory
40 -150 N/mm²
 - > Lightweight insulating brick
0,5 – 5 N/mm²

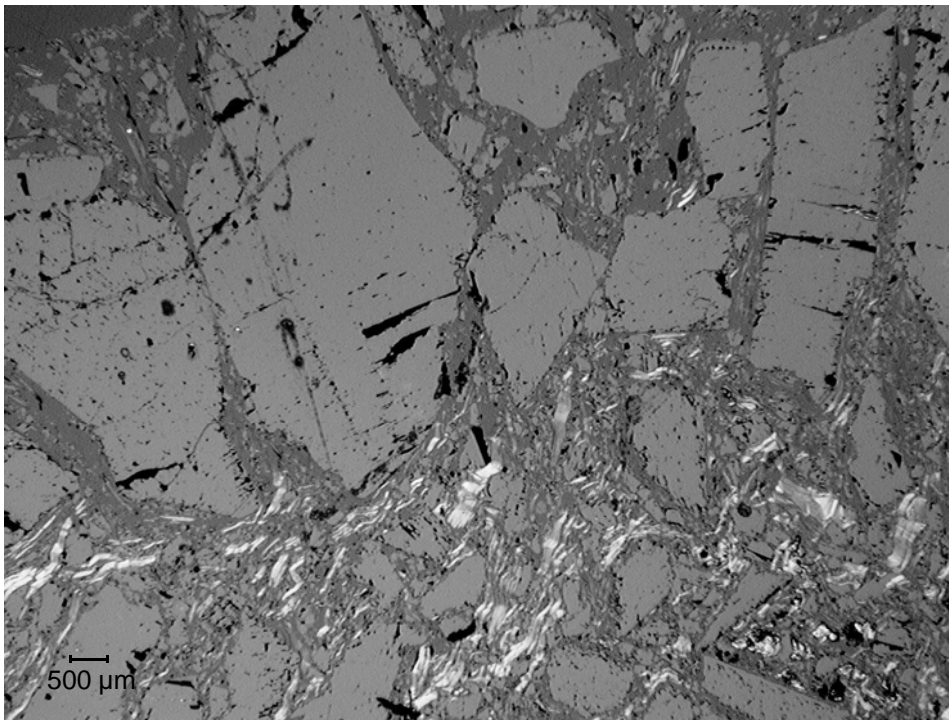


Alteration behaviour

- **Alteration appears due to:**
 - > Temperature load: further sintering, re-crystallisation
 - > Chemical reactions with process media
 - > Infiltration by melts like: metals, slags, glass, salts, condensates

- **Result:**
 - > Change of physical and chemical properties
 - > Anisotropy may occur

Alteration behaviour



MgO-C brick showing carbon burn off, loss of binding matrix and elongated MgO-grains



“alkalibursting” on the wall of a cement cooler; big areas fall off due to irreversible expansion

Important material properties of refractories

- Dense refractories
- Insulating materials
- Overview of refractory insulating materials

ANKROM B65

Dense refractories

- Defined porosity < 45%
- Bonding type:
 - > ceramic
 - > organic (carbon bond)
 - > hydraulic

- Wear and permanent lining
- Enables process
- Guarantees safety

General information

Classification	Magnesia-chromite product type MCr50 ISO 10081-2
Main raw material components	Chrome ore, Sintered magnesia
Bonding type	Ceramic
Main Application(s)	Copper, Nickel, Lead

Chemical analysis

MgO	Cr ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	CaO	SiO ₂
58.0%	19.0%	6.5%	14.0%	1.4%	0.9%
Determination on fired substance (1025 °C / 1877 °F) acc. to EN ISO 12677					

Physical properties

Bulk Density		3,21	[g/cm ³]	EN 993-1
Apparent Porosity		17,5	[vol%]	EN 993-1
Cold Crushing Strength		60,0	[N/mm ²]	EN 993-5
Hot Crushing Strength (1500 °C / 2732 °F)		10,0	[N/mm ²]	
Hot Modulus of Rupt. (1400 °C / 2552 °F)		8,0	[N/mm ²]	EN ISO 1927-6
Thermal Expansion	500 °C / 932 °F	0,41	[%]	EN 993-19
	750 °C / 1382 °F	0,65	[%]	EN 993-19
	1000 °C / 1832 °F	0,94	[%]	EN 993-19
	1200 °C / 2192 °F	1,20	[%]	EN 993-19
	1400 °C / 2552 °F	1,47	[%]	EN 993-19
	1600 °C / 2912 °F	1,70	[%]	EN 993-19
Refractoriness under Load T _{0,5}		> 1700	[°C]	ISO 1893
Res. to Thermal Shocks Air		> 45	[cycles]	
Thermal Conductivity	500 °C / 932 °F	2,70	[W/mK]	DR. KLASSE
	750 °C / 1382 °F	2,60	[W/mK]	DR. KLASSE
	1000 °C / 1832 °F	2,60	[W/mK]	DR. KLASSE
	1200 °C / 2192 °F	2,60	[W/mK]	DR. KLASSE

LEGRAL 40/08

Insulating materials

- **Challenges**
 - > High mechanical strength
 - > Low thermal conductivity
 - > High and defined porosity
 - > High classification temperature
 - > Volume stability at high temperature
 - > Should be resilient like ceramic fibres

General information	
Classification	Insulating refractory brick type 140-1,0-L ISO 2245
Main raw material components	Fireclay, Kyanite
Bonding type	Ceramic
Temp. limit for application	1.425 °C

Chemical analysis					
Na ₂ O	Fe ₂ O ₃	CaO	K ₂ O	TiO ₂	SiO ₂
0.7%	1.0%	1.0%	1.1%	1.3%	38.0%
Al ₂ O ₃					
58.0%					
Determination on fired substance (1025 °C / 1877 °F) acc. to EN ISO 12677					

Physical properties			
Bulk Density		1,12	[g/cm ³] ISO 5018
Cold Crushing Strength		3,5	[N/mm ²] ISO 8895
Permanent Linear Change		1,20	[%] ISO 2477
Temperature for P.L.C.		1 400	[°C]
Modulus of Rupture		4,0	[N/mm ²] EN 993-6
Thermal Conductivity	500 °C / 932 °F	0,55	[W/mK] DR. KLASSE
	750 °C / 1382 °F	0,65	[W/mK] DR. KLASSE
	1000 °C / 1832 °F	0,70	[W/mK] DR. KLASSE

Overview of refractory insulating materials

property	fibres	ceramic foams	light weight refractory bricks	insulating monolithics
density	ultra low density	low density	medium density	
heat capacity	low thermal mass → less energy consumption → higher cycling rates		somewhat higher heat capacity	
insulation	very good	good	good / medium	
resilience	Resilience → flexible	no resilience	no resilience	no resilience
risks	hazardous (carcinogenic)	No	no, only if fibres contained	
compressive strength	no compressive strength	low / good	good	low / good

Overview of refractory insulating materials

material base	Typical classification temperature °C	density g/cm ³
light weight alumina	1800	0,5-0,6
alumina hollow spheres	1800	0,8-0,9
light weight chamotte	1350-1600	0,65-1,00
light weight mullite	1600	1,0-1,1
calciumaluminate (CA ₆)	1830	0,75
perlite	1300 (<1000)	0,07-0,12
vermiculite	1200 (<1000)	0,08-0,14
fly ash	1250	0,75-0,90
glass/mineral fibers*	<<1000	0,09
ceramic fibers*	1650	0,10
diatomaceous earth	900-1000	0,5-0,8
silica aerogel	800	0,1

* density strongly depends on final product (wool, fibre moduls, fire boards...)

Summary

- **Wide spread properties effort multilayered linings**
 - > Wear lining
 - > Permanent lining (safety lining)
 - > Insulation

- **Combinbation of insulation and permanent lining needs:**
 - > Material compatability at high temperature
 - > Minimum compression strenght or resilient behaviour of insulation material
 - > Similar thermal expansion of insulation and permanent lining

- **Potentials for improvement:**
 - > Thermal stable microstructure of refractory
 - > Avoidance of alterations (e.g. due to infiltration, further sintering...)
 - > Reduction of brittleness
 - > Realization of big shapes

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