Challenges in refractory design

DI Dr. Roland Nilica

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www.rhi-ag.com EXCELLENCE IN REFRACTORIES RHI

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  > RHI on one view
  > Refractory consumption

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  > Insulating materials
  > Overview of refractory insulating materials

- **Summary**

Inroduction

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

Refractory – Essential for all basic material Industry

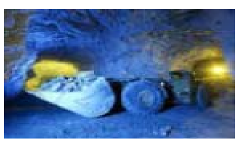
refractory products


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

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RHI on one view

- Marketing/Sales departments
- Production
- Headquarter
- Technology center
- Mining and raw material production
- Production site under construction

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	Ardagh Glass	GLENCORE INTERNATIONAL AG
SeverStal	Cemex	CORNING	bhpbilliton
voestalpine EINEN SCHRITT VORAUS.	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.

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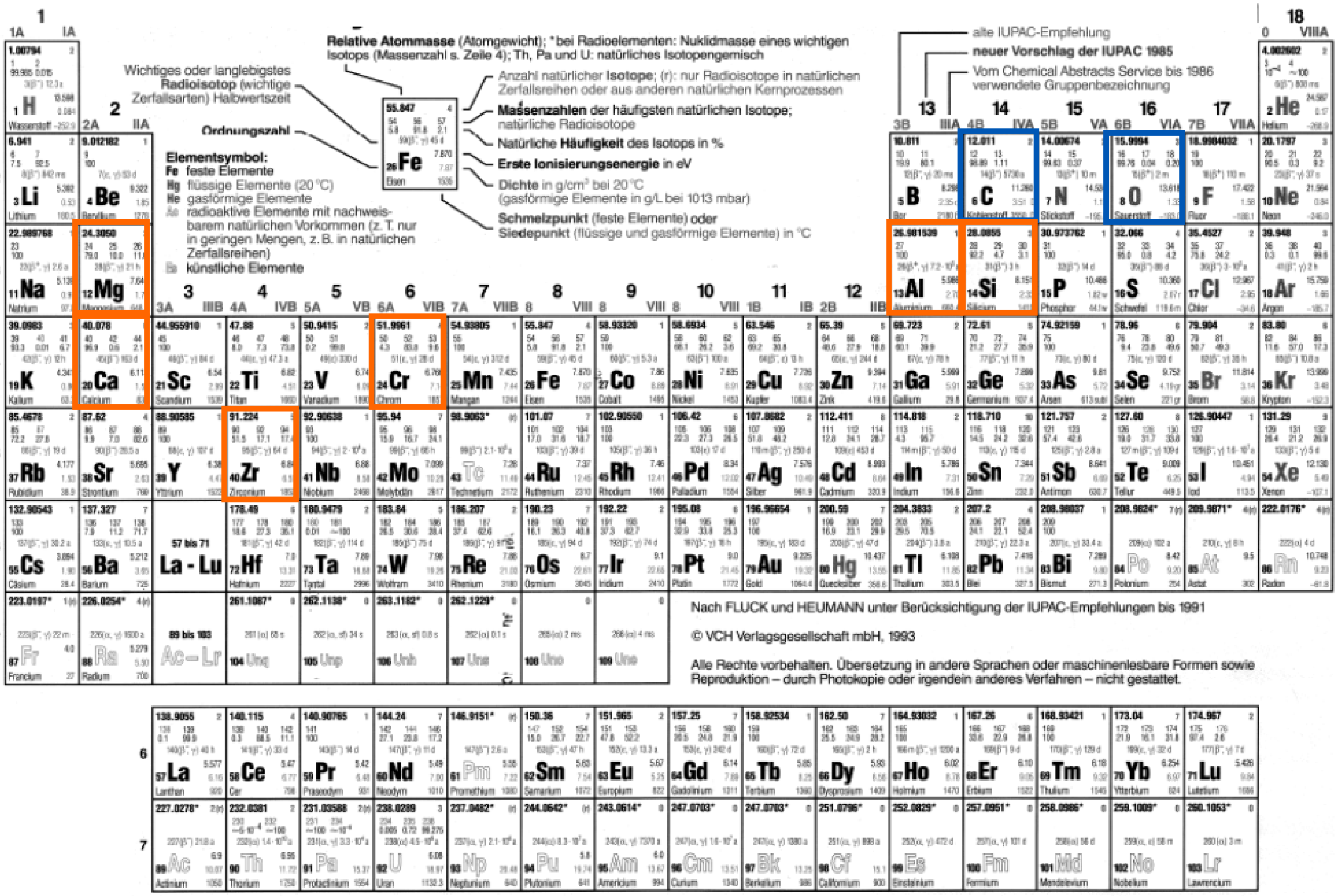
Availability of raw materials



Raw materials and main users

ACID				NEUTRAL		BASIC	
silica	chamotte	bauxite	chrome ore	corundum	zirkondioxide	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**

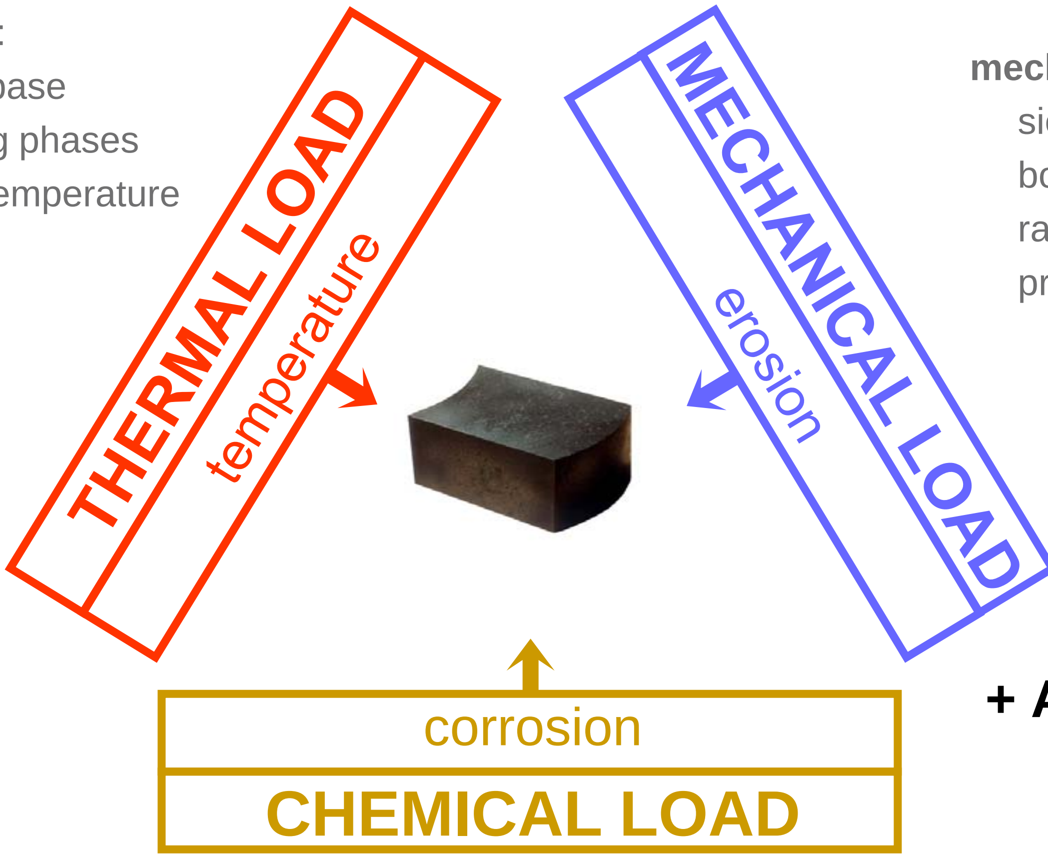
Exposure and typical design concept

refractoriness:

- material base
- coexisting phases
- liquidus temperature

mechanical properties:

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

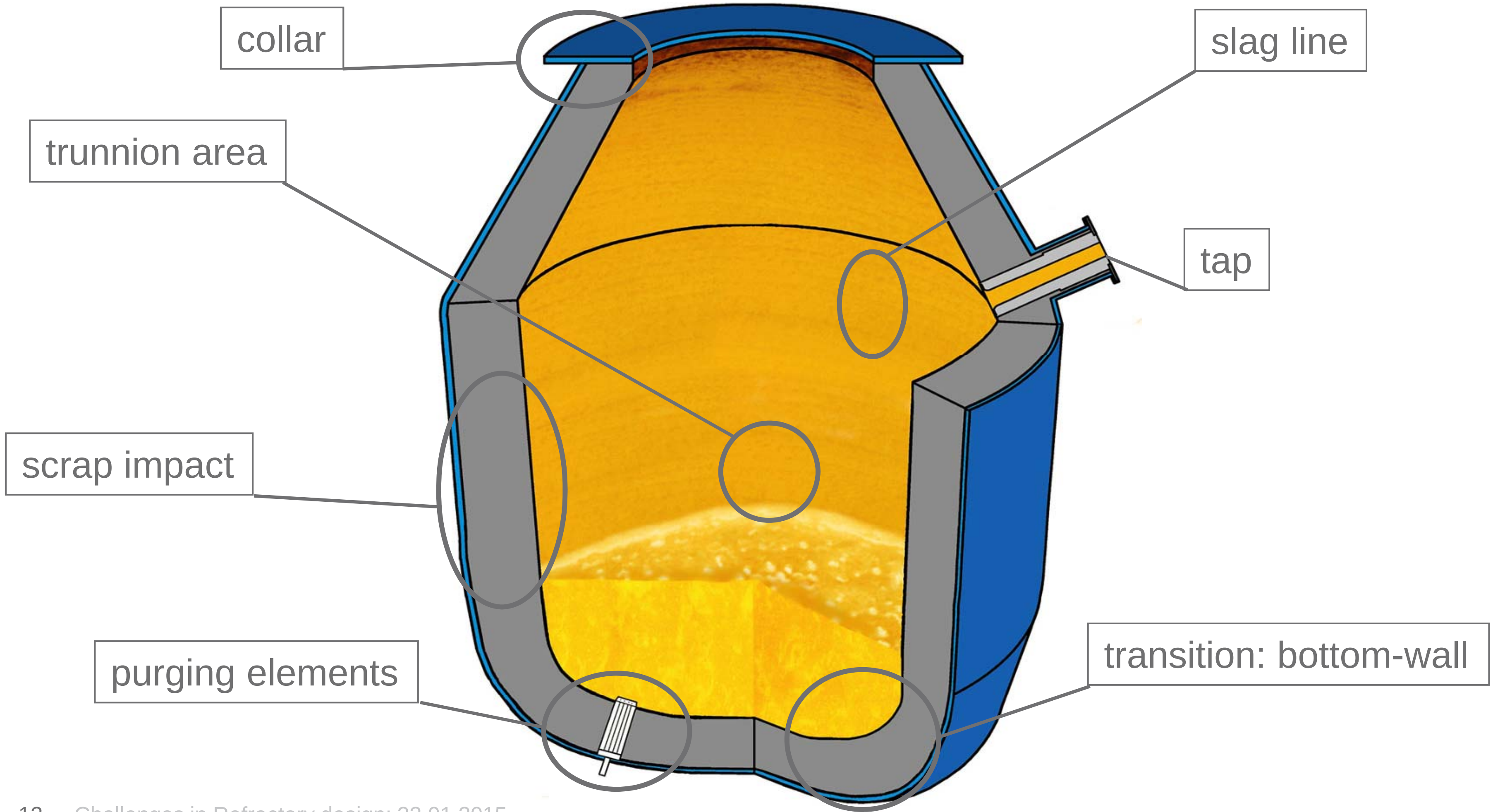


+ Availability and price of used materials!

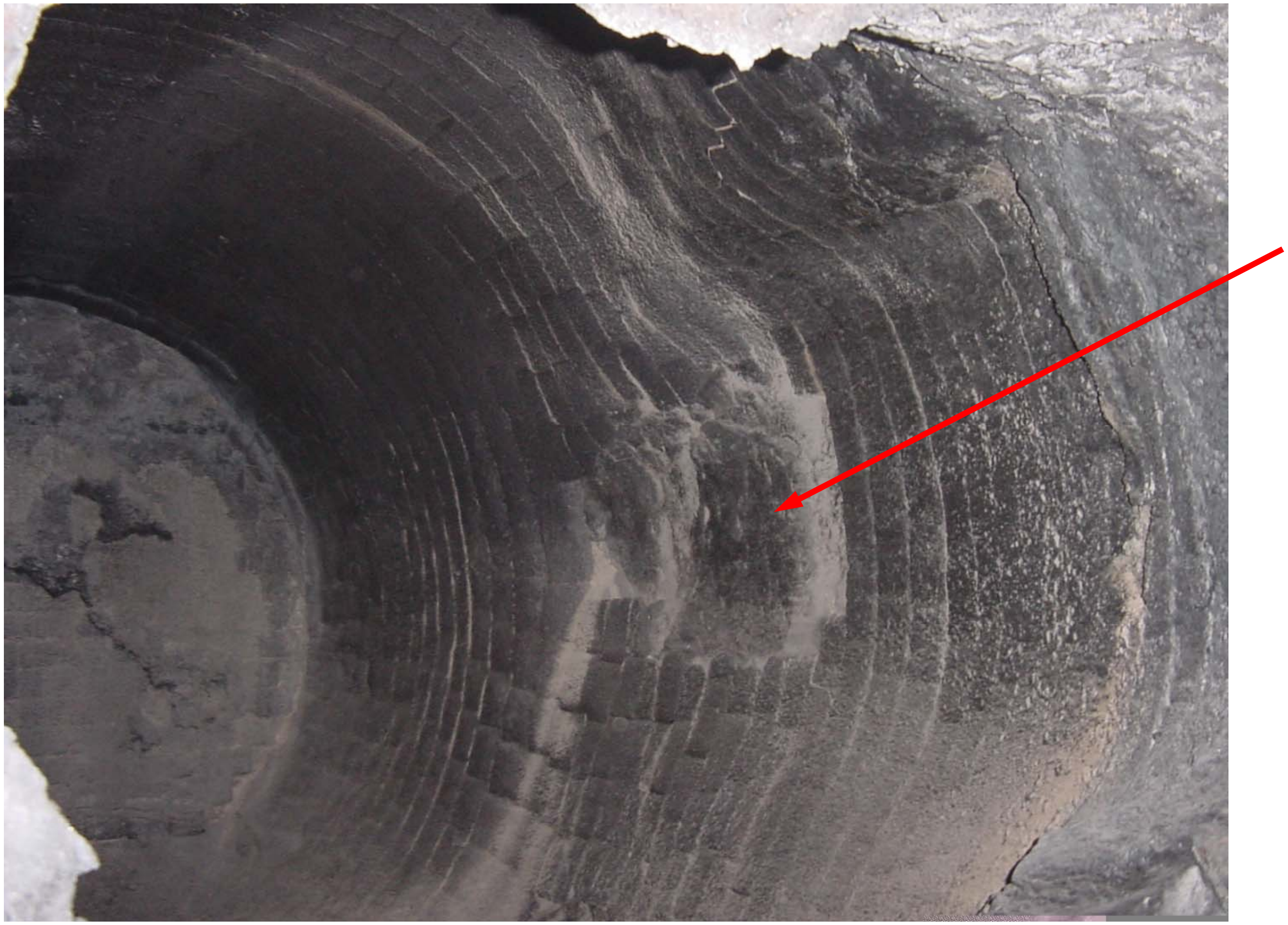
Chemical resistance:

- reactions with process media
- solubility

Example: wear of a steel converter

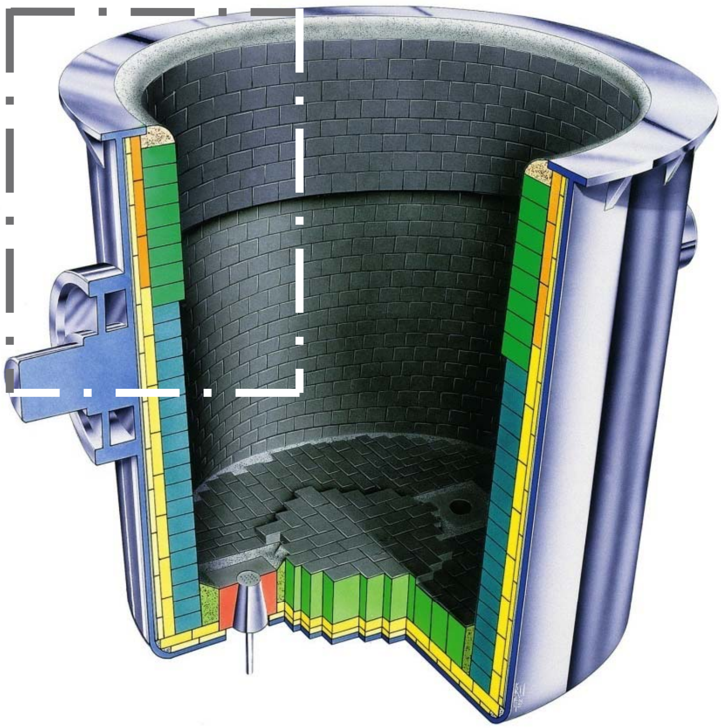


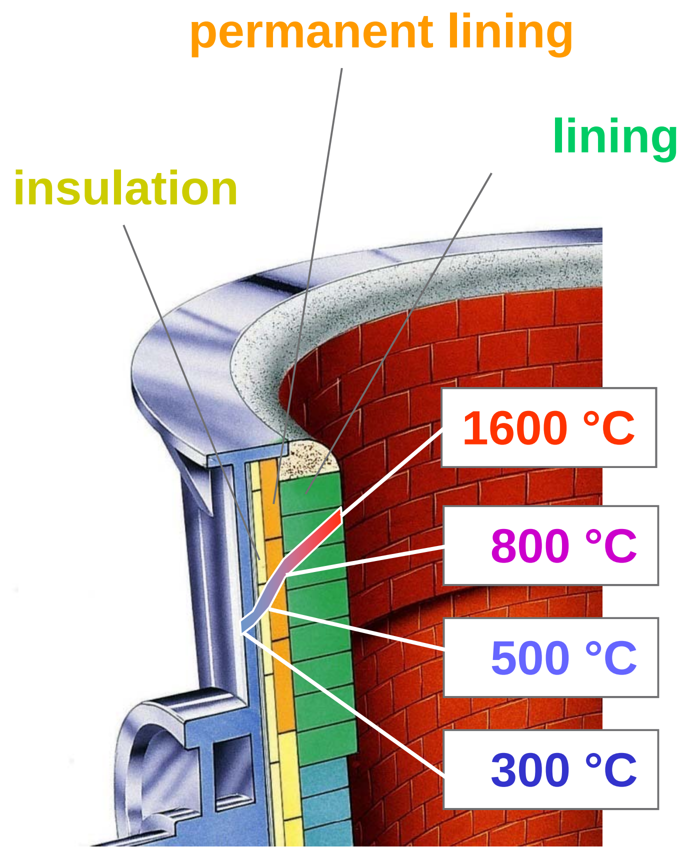
Example: wear of a steel converter



partial loss of wear lining

Example: complex lining of a steel ladle





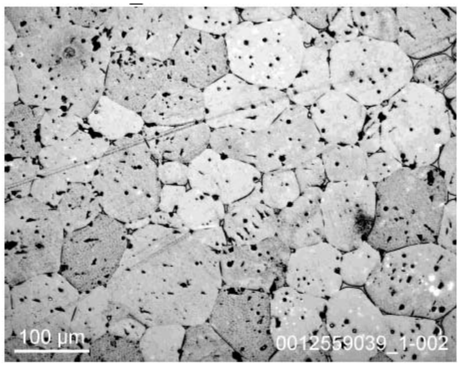
Important material properties of refractories

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

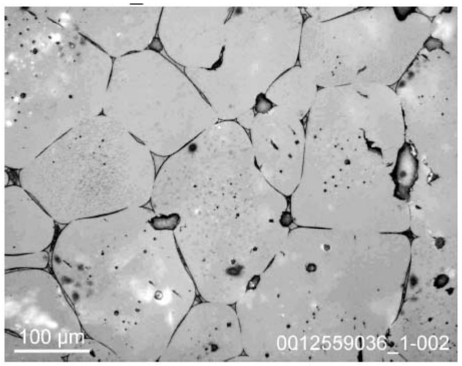
Chemical and mineralogical composition

- **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

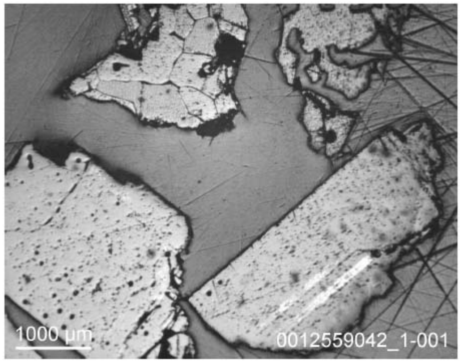
Example MgO:



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 Crystal 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_2O_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/cm^3

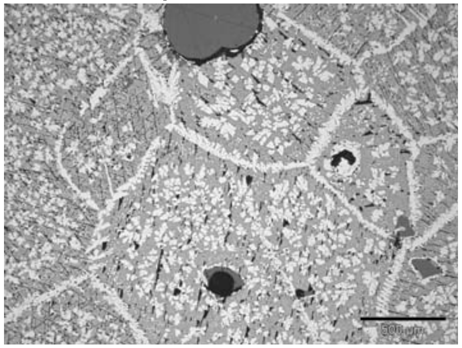
Mechanical properties

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

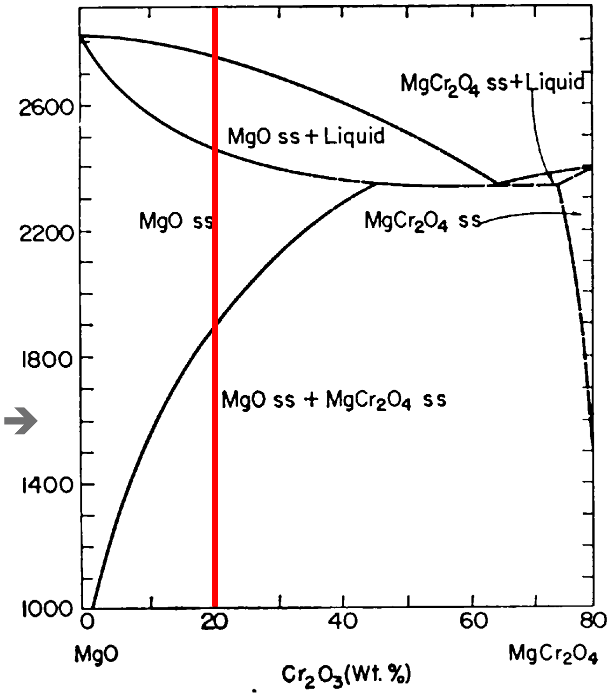
- **At „service“ conditions**:
  - > Unknown in many cases
  - > Difficult to measure (temperature)
  - > Complex interactions of properties on wear resistance

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

room temperature



← fused magnesia-chromite →

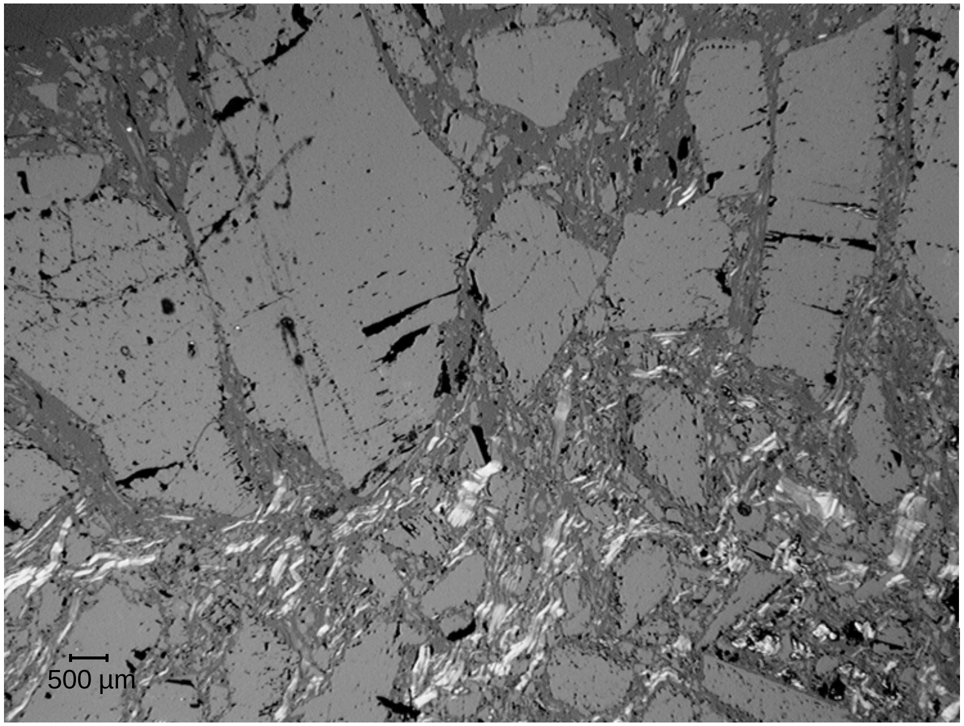


Alteration behaviour

- **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

Dense refractories

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

- **Wear and permanent lining**
- **Enables process**
- **Guarantees safety**

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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_2O_3	Al_2O_3	Fe_2O_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/cm³]	EN 993-1
Apparent Porosity		17,5	[vol%]	EN 993-1
Cold Crushing Strength		60,0	[N/mm²]	EN 993-5
Hot Crushing Strength (1500 °C / 2732 °F)		10,0	[N/mm²]	
Hot Modulus of Rupt. (1400 °C / 2552 °F)		8,0	[N/mm²]	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

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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

LEGRAL 40/08

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_2O	Fe_2O_3	CaO	K_2O	TiO_2	SiO_2
0.7%	1.0%	1.0%	1.1%	1.3%	38.0%
Al_2O_3					
56.0%					
Determination on fired substance (1025 °C / 1877 °F) acc. to EN ISO 12677					

Physical properties				
Bulk Density		1,12	[g/cm³]	ISO 5016
Cold Crushing Strength		3,5	[N/mm²]	ISO 8895
Permanent Linear Change		1,20	[%]	ISO 2477
Temperature for PLC		1 400	[°C]	
Modulus of Rupture		4,0	[N/mm²]	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/cm³
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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