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Refractories for aluminium

the industry behind the industries

the theory behind the refractories

AMAP colloquium 11 June 2015

ir. drs. Marcel C. Franken

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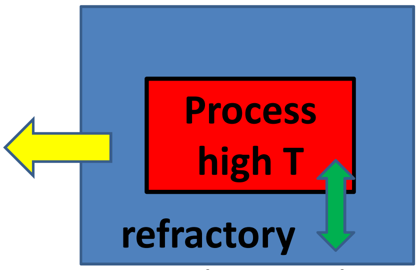
General

Any process at high T in a installation
need for refractory (Feuerfest)

- not only resistent to high temperatures (Feuer)
- resistent to interaction with process
- keep heat in installation

miniumum heat loss



no interaction

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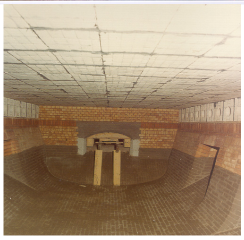
In a process installation many partial processes
each partial process different refractory solutions possible: bricks, castables, chemical composition,….



PROCESS

Search for the perfect match

REFRACTORY

“each advantage has its disadvantage”

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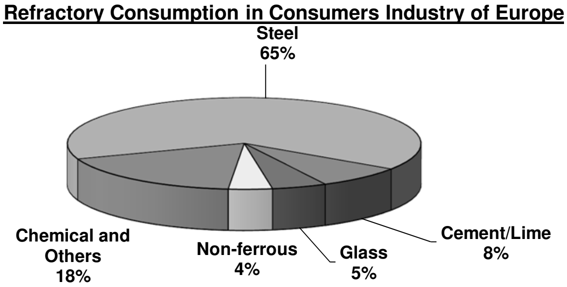
Refractory industry - “industry behind industries”

Refractory Consumption in Consumers Industry of Europe



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Refractory consumption

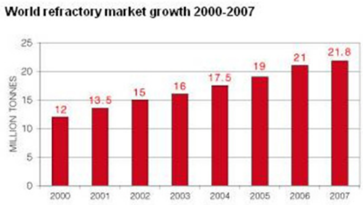
Specific consumption in 1955, 1980, 2000 and 2010 in major industries :

	Specific consumption kg (refractory) per t * (product)				Reduction
	1955	1980	2000	2010	Total in %
Iron and Steel	50	30	18	16*	68
Cement, Lime	2,2	1,2	0,9	0,7	68
Glass	15	12	6	5	66
Aluminium	25,5	20	14	10	60

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

***Reduction refractory consumption*:**

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



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Refractory producers

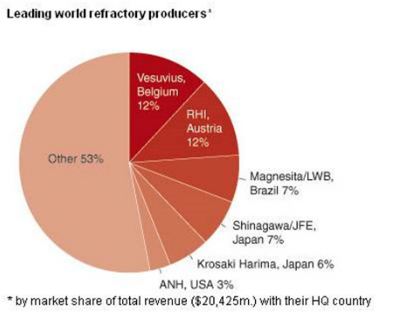
In Europe 26.000 employees and turnover 3.1 billion Euro

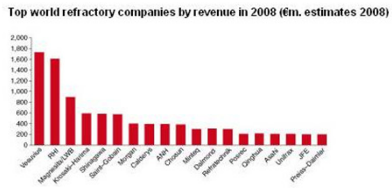
Tendency conglomeration:

- *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





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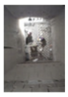
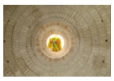
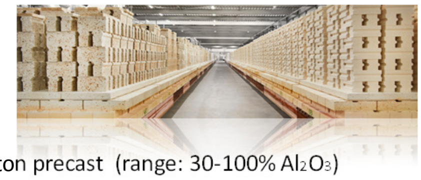
Total refractory lining solutions for critical equipments in various industries (% of TO)

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% Al_2O_3)

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Refractory is chemistry and physics *"alchemistry"*

Basis chemistry:

- inorganic material
- oxidic components
- reactions "transformations"

Basis physics:

- material expands as it becomes hot

Refractories goes to the fire

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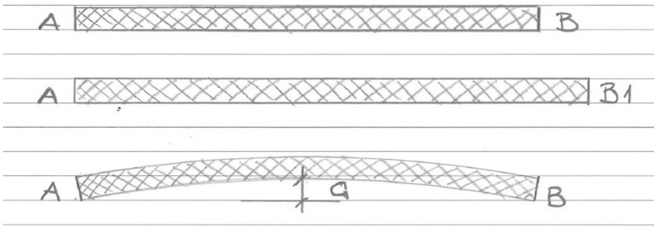
Thermal expansion



	Lengte A-B	uitzetting	temperatuur	Lengte A-B1	Buiging C
Staal	1000 mm	1,2mm / 100°C	200°C	1002 mm	32 mm
	3000 mm	1,2mm / 100°C	200°C	3007 mm	103 mm
Vuurvast	1000 mm	0,6 - 1,0 % **> 0,8%**	1100°C	1008 mm	**63 mm**
	3000 mm	0,6 - 1,0 % **> 0,8%**	1100°C	3024 mm	**190 mm**

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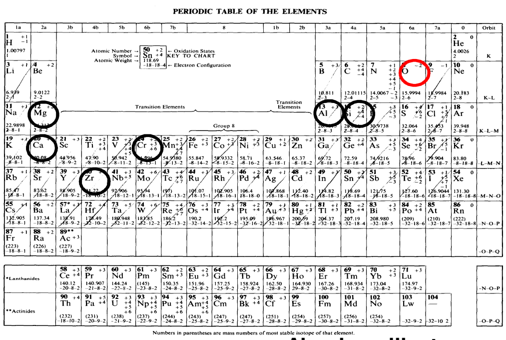

Back to basic

Stable oxides
High melting temperature

Classification based on chemistry

Slagbasicity: CaO/SiO_2

Basic Product

not used
reaction with Al
spinel formation
high expansion

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

Special Product
Graphite/Carbon
ZirconSpinel
Siliciumcarbide
Siliciumnitride
SiAlON

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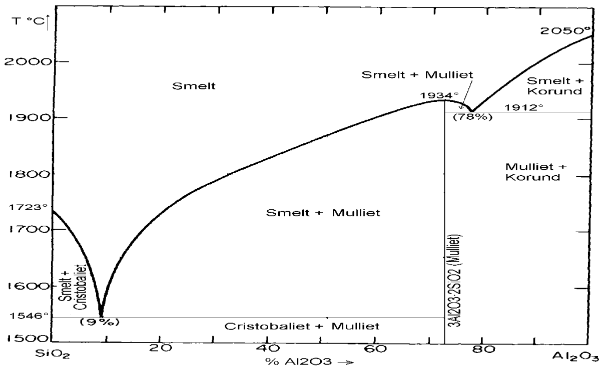
Al_2O_3-SiO_2 Phasediagram



each material has its own properties: refractoriness, chemical resistance,..

Silica
Chamotte
Andalusite
Sillimanite
Kyanite
Mullite
Bauxite
Corundum

Mineral name vs chemical composition

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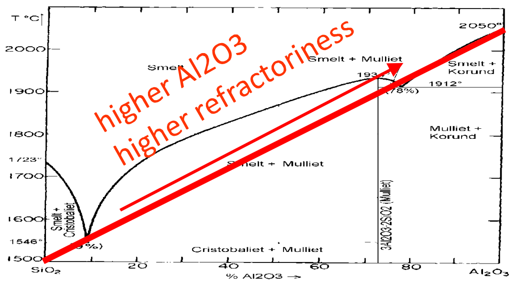
Al_2O_3-SiO_2 Phasediagram

Name of product

→ **Temperature,** eg

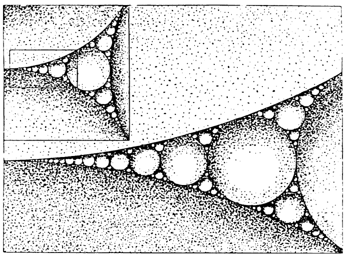
Group 23 = 2300 F

Curon 160= 16000 C



→ **percentage Al2O3,** eg AK46, AK85

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)

Brick	**Castable**
clay bonding (ceramic /phophate)	cement bonding
ready to use	semi-product
is mixed, densified, fired	made on site

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

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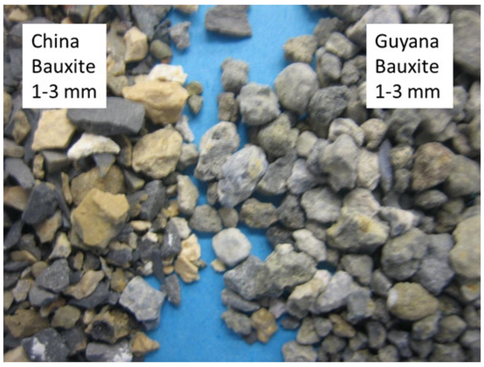
Raw materials: Bauxite



	China Bauxite	Guyana Bauxite
Al_2O_3	84 – 89%	84 – 89%
SiO_2	6 – 10%	6 – 10%
TiO_2	3 – 4,5%	2 – 3,5%
Fe_2O_3	1,5 – 2,5%	1,5 – 2,5%
CaO + MgO	< 0,5%	< 0,1%
$Na_2O + K_2O$	< 0,5%	< 0,2%
Abrasion Resistance	Good	Minor
Aluminium resistance	Minor	Good

Chemical similar
but different properties

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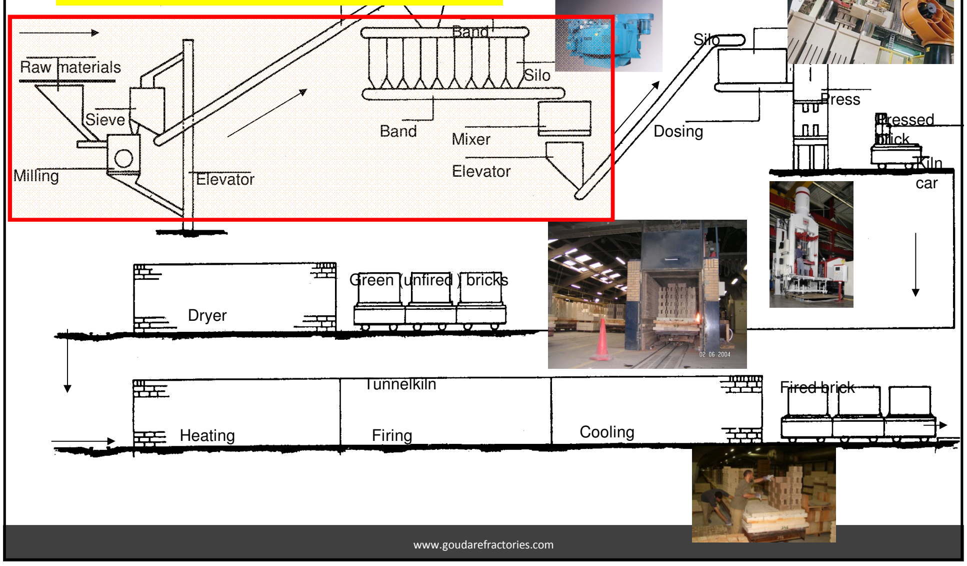
Manufacturing Refractory Brick

Castables are "semi"-products quality made during installation



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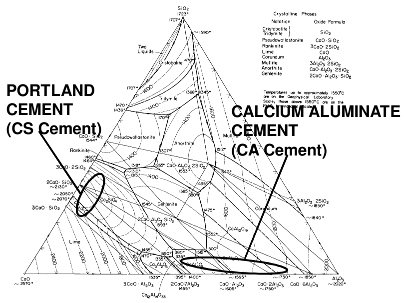
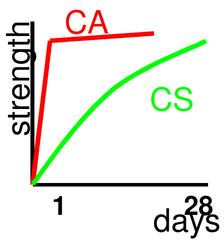
Refractory cement

Bonding of castable: CaO-containing

Differs from civil concrete:
calciumaluminate vs calciumsilicate





type	40% CAC	50% CAC	70% CAC
Al_2O_3	37,5 – 41,5	50,8 – 54,2	68,7 – 70,5
CaO	36,5 – 39,5	35,9 – 38,9	28,5 – 30,5
SiO_2	4,2 - 5,0	4,0 – 5,5	0,2 – 0,6
$FeO+Fe_2O_3$	14,0-18,0	1,0 – 2,2	<0,4
Temp	**1100 C**	**1300 C**	**1500 C**

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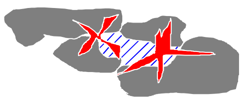
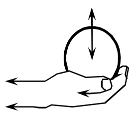
Types of castables

conventional castables
(regular cement, RCC)

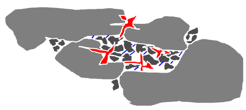


- cement content 15 - 20 %
- fine fraction 0 - 0,5 mm
- water added +/- 12 %



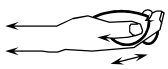
Ball in Hand method

low cement castable
(deflocculated – low cement, LC,ULC, NC)

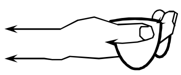


Mixing
very critical
Impurities very critical

- cement content +/- 5 %
- ultrafine fraction upto 0,3 um
  microsilica – round spheres
- water added +/- 5 %



Vibrating method



Self flowing

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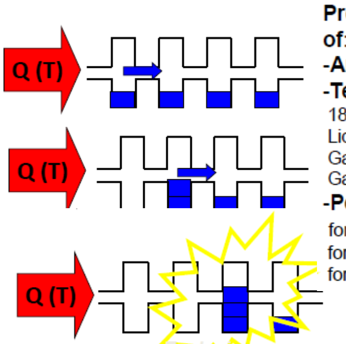
Castables become more dense (higher strength, more fines)
risc on steamexplosions



Pressure internal result of:
- **Amount water**
- **Temperature** V= f(T)
  - 18 gram water (1 mol)
  - Liquid 18 ml
  - Gas 22,4 liter at 20 C (293K)
  - Gas 30,5 liter at 127 C (400 K)
- **Permeability refractory**
  - for RCC high
  - for LCC low
  - for MCC very low

Explosion:
Water/vapor pressure > tensile stress refractory

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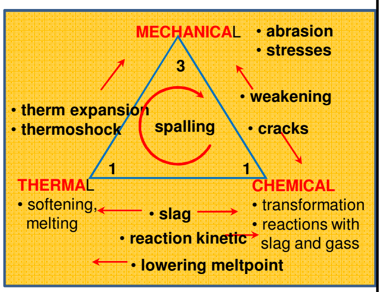
Attack mechanisms wear of refractory

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



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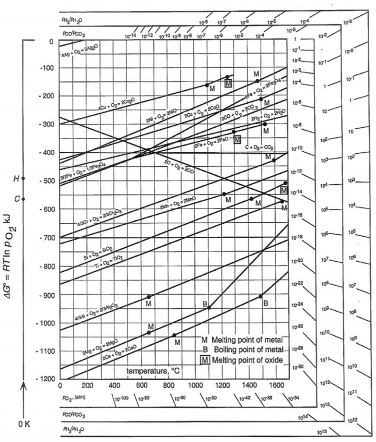

The Ellingham diagram for selected oxides.

Thermodynamics

refractory (Al_2O_3-SiO_2) can react with Al

Corundum formation:
$4Al + SiO_2 \rightarrow 2Al_2O_3 + 3Si$

$2Mg + SiO_2 \rightarrow 2MgO + Si$
$Mg + 2Al + 2SiO_2 \rightarrow MgAl_2O_4 + Si$
$4Al + 3TiO_2 \rightarrow 2Al_2O_3 + Ti$

→volume change and destroying refractory

Al_2O_3-SiO_2 used:

- good thermal properties
- reasonable chemical resistance
- "low" cost

diamond is thermodynamical NOT stable

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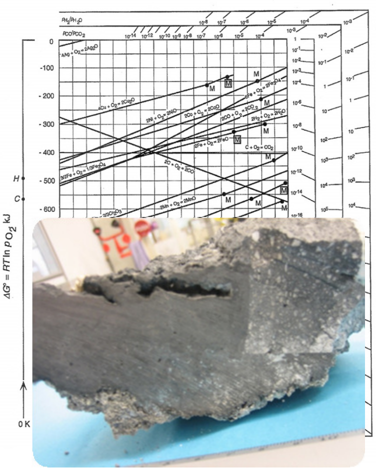

Thermodynamics

Tabular cement castable (no SiO_2) usable?

CaO will not react with Al

$3CaO + 2Al \rightarrow 3Ca + Al_2O_3$ $\Delta G = +234$ kJ

But:

$3CaO + 8Al \rightarrow Al_2O_3 + 3Al_2Ca$ $\Delta G = -234$ kJ

seems like corundum formation but is intermetallic formation

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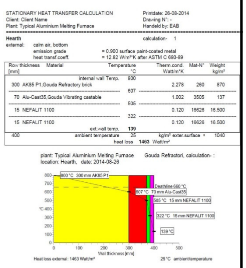
Reaction kinetic *speed of reaction*

Not only important if components reacts wich 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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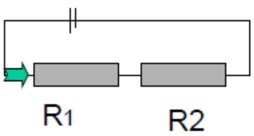
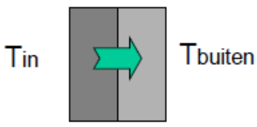
T-profile calculations – thermal resistance (d/λ)

Several layer system - serial system





$V = I.\ R_{tot}$

$R_{tot} = R_1 + R_2$

$\Delta T = Q.R$

$R_{tot} = R_1 + R_2$

$\Delta T = Q.(R_1 + R_2)$

$Q = \Delta T/\ (d_1/\lambda_1 + d_2/\lambda_2)$

per layer $\Delta T_1 = Q.R_1$

$\Delta T_1 = R_1/R_{tot}{}^{*}\ \Delta T_{tot}$

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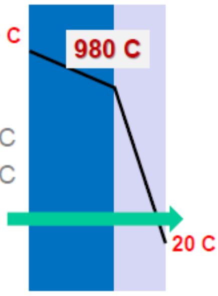
T-profile calculations – thermal resistance (d/λ)

Assume furnace 1220 C inside, 20 C outside:
chamotte layer 230 mm and λ=1,15 W/m.K
→ R1= d/λ = 0,23/1,15 = 0,2 m^2K/W
insulating layer 80 mm and λ=0,1 W/m.K
→ R2= d/λ = 0,08/0,1 = 0,8 m^2K/W
→ Rtot = 1 m^2K/W

T-drop per layer:
ΔT1 = R1/Rtot* ΔTtot = 0,2/1*1200= 240 C
ΔT2 = R2/Rtot* ΔTtot = 0,8/1*1200= 960 C

Heat loss: Q=ΔT/Rtot =1200/1=1200 W/m^2

Most T-drop over the highest R



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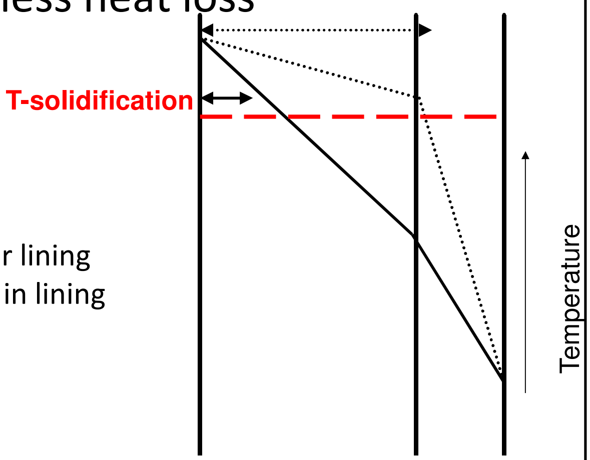
More insulation - less heat loss



Disadvantage:
- Less T-profile over wear lining
- Solidification-T deeper in lining
- More attack
- Risc of Al- outbreak

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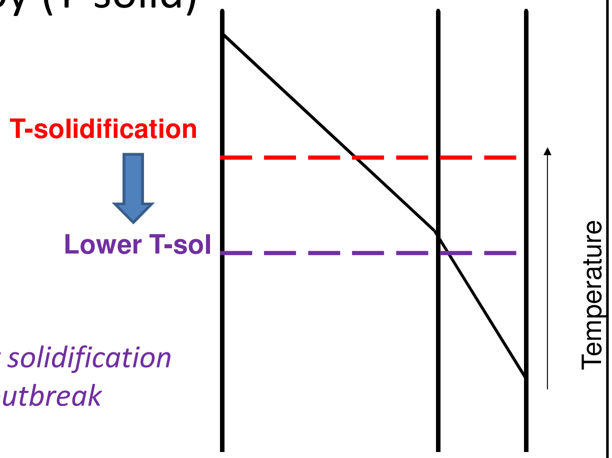
Change of Al-alloy (T-solid)



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

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Reaction kinetics – less surface

minimize surface reactions (less penetration by)

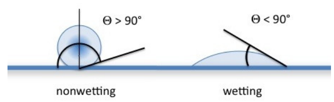
- lower porosity
- decrease wettability

use of anti-wetting agents:

- CaF_2
- $BaSO_4$
- ….

Potential disadvantage:

- CaF_2 lowers melting T → reduction in strength at T>900 C
- $BaSO_4$ decomposes (disappears) T>1150 C



equation of capillary action:

$h = 2\gamma\cos\vartheta / \rho g r$

Where:

- h **- height the liquid is lifted,**
- γ **- liquid-air surface tension,**
- ρ **- density of the liquid,**
- r **- radius of the capillary,**
- g **- acceleration due to gravity,**
- ϑ **-the angle of contact**

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

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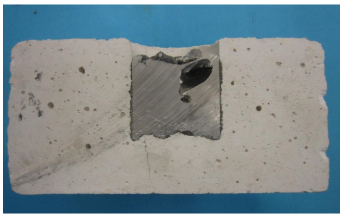
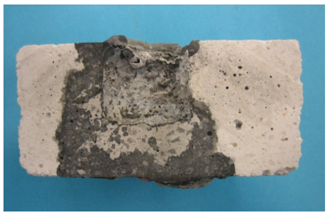
Corrosion by Aluminium

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)

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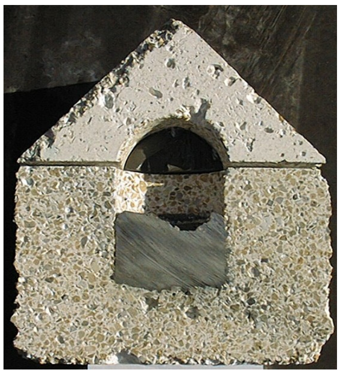
Effect of Al-alloy on refractory

Cup test, 72 hours, 1050 °C

Alloy 5083, Mg-rich



Alloy 7020, Zn-rich

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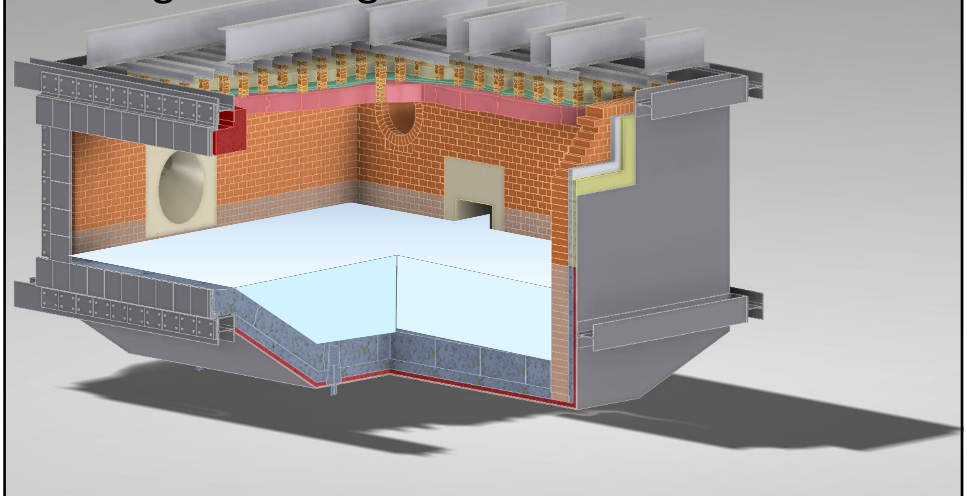
Melting & Holding Furnaces



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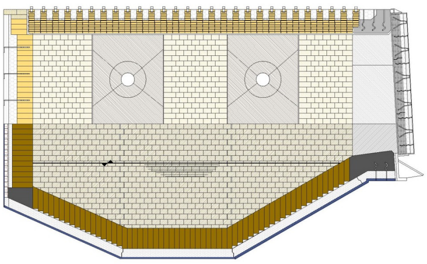
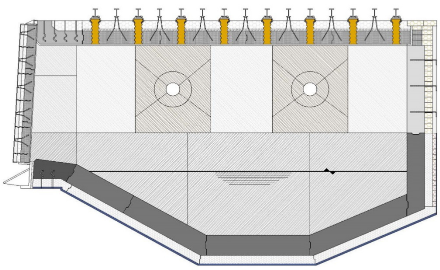
Lining Posibilities

- Castable for Back-up layer bath
- Hot face bricks bath
- Insulation castable roof
- Hot face brick upper wall
- anchor brick



Bricks refractory lining

- Hot face castable bath special
- Hot face castable upper wall
- Hot face castable bath
- Hot face castable roof
- Hot face castable upper wall special
- Hot face castable burner



Castable refractory lining

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GOUDA *refractories* an ANDUS *group* company

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

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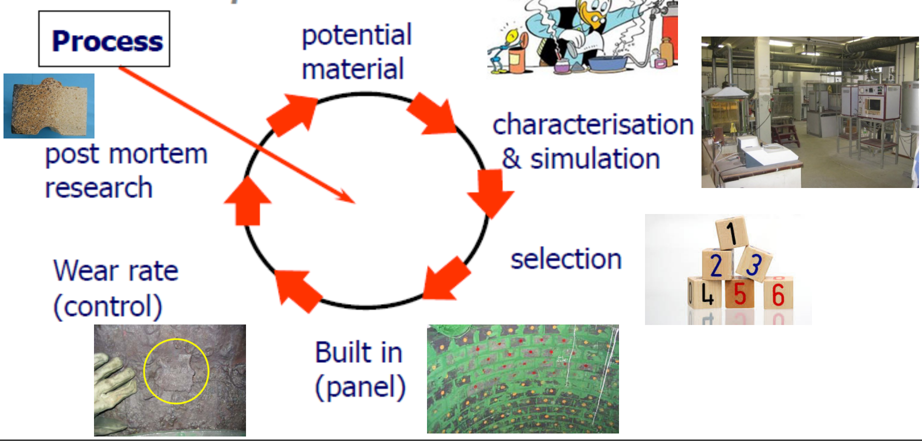
Improve refractory to adapt to changing process

Route of improvement



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NAME	RAW MATERIAL	MAIN ADDITION	SEQUEL ADDITION	
DENSE BRICKS		Al_2O_3 %	A	Strong & Erosion resistant
A	Fireclay	35 - 42 %	B	Special raw material
B	< Al2O3 %	33 - 29 %	D	High Thermal Shock Resistant / Ductile
C	<< Al2O3 %	25 - 27 %	FM	Fused Mullite
AK	High Alumina	$Al_2O_3 \geq$ 42 %	K	Corundum
LP	Low Porosity	$Al_2O_3 \geq$ 42 %	M	Mullite bonded
AC	Chrome / Corundum	$Al_2O_3 + Cr_2O_3$ %	P	Phosphate bonded
ACZ	Chrome / Zircon / Corundum	$Al_2O_3+Cr_2O_3$%	S	Special Raw Materials
SIC	Silicon Carbide	SiC %	Sp	Special
Saffier	Cordierite		X	Low Creep
PRE-CAST tiles only dried and /or fired at high temperature				
C xxx	Pre-cast specialty	Max.Temp / 10 of Castable		Regular Castable
V xxx	Pre-cast specialty	Max.Temp / 10 of Castable		Low, Ultra low & No cement castable
INSULATION BRICKS		Classification		
GI	ASTM classification	xxxx° Fahrenheit / 100		
FI	Improved ASTM Classification	°C-1000/10 – kg/m³ /100		
CASTABLES		Max.Temp. / 10	B	Special Raw Materials
Dense Regular Castable CURON	Low Grade Fireclay	100 - 140	C / CC	Coarse / Extra Coarse
	Cordierite	130	C / G	Casting / Gunning
	Fireclay	145 – 150H	F / FF	Fine / Extra Fine
	Bauxite	150 / 170	G	Special Bauxite
	Andalusite / Sinter Mullite	160 / 160H	GM	Gunning Mix (conventional dry-gunning)
	Andalusite / Corundum	175	GS	Pumpable / Shotcrete
	Corundum	180 & 185	H	High Thermal Shock Resistant
			K	Silicon Carbide Percentage (Kxx)
LC & ULC Vibration Castable VIBRON	Cordierite	130 - 135	L	Lower Weight
	Fireclay	140 - 145	LW	Light Weight
	Bauxite	150 - 155	M	Fused Mullite
	Andalusite / Sinter Mullite	160 – 165 / 160H	MD	Maintenance Delay
LC & ULC Self flowing Castable FLUCON	Fused Mullite	170 - 175	Mg	Spinel
	Corundum	180 - 185	MW	Medium Weight
			N	SS-Needles (Stainless Steel)
ULC Rapid Heating Castable VELOX		Classification Based on Percentage Al_2O_3	P	Phosphate Bonded
			R	Low Iron
Aluminium resistant Castable ALU-CAST			S	Strong / Erosion & Slag Resistant
			SV	Erosion Resistant (only Curon)
			Sp	Special
Insulation Regular Castable GOLITE	Vermiculite / Perlite	90 - 100	T	Tabular Alumina
	Expanded Clay (Haydite)	120 - 125	XLW	Extra Light Weight
	Light Weight Fireclay	120 - 155	Z	Zircon
Insulating Self flowing Castable Flowlite	Special Light Weight Fireclay	155 - 160	ZV	Acid resistant
	Bubbled Corundum	180		
Insulation Mix Castable GOLITE	Ratio L : H : V Lumnite : Haydite : Vermiculite	Samples 1:0:6 / 1:2:4 / 1:4:0		
RAMMING & PLASTIC MOULDABLE		Al_2O_3 %	P	Phosphate Addition
CURAS & CURASBOND	Fireclay	40	D	Dry material
	Andalusite / Sinter Mullite	60	GM	Gunning Mix
	Bauxite	85	PBK	Phosphate Bonded Corundum
	Corundum	90	Repair	Repair material
MORTAR & COATING		Max.Temp. / 10	Al	Aluminium Metal Resistant
HS	Heat-Setting (dry)	A / 150-185 / K	Hy	Hydraulic Bonded
ADHESIET	Air-Setting (dry)	A / 150-185 / K	P	Phosphate bonded
HS N xxx	Heat-Setting Wet (pre-mixed)	A / 150-185 / K	ZV	Acid resistant
ADHESIET N xxx	Air-Setting Wet (pre-mixed)	A / 150-185 / K	Sp	Special
Cohesiet	Coating Chemical / Air-Setting		L	Low Porosity
			K	Silicon Carbide Percentage (Kxx)

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)

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GOUDA refractories

an ANDUS group company

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***”.

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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"

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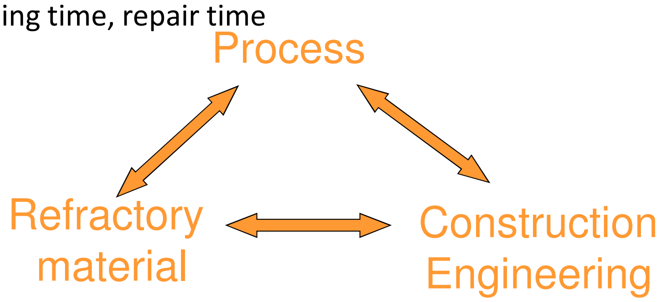
INTEGRATED REFRACTORY APPROACH

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"

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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

PROCESS

REFRACTORY

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