Innovative Refractory Materials for Alternative Fuel Fired Kilns

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Hanoi, Vietnam, 21st - 24th April 2015

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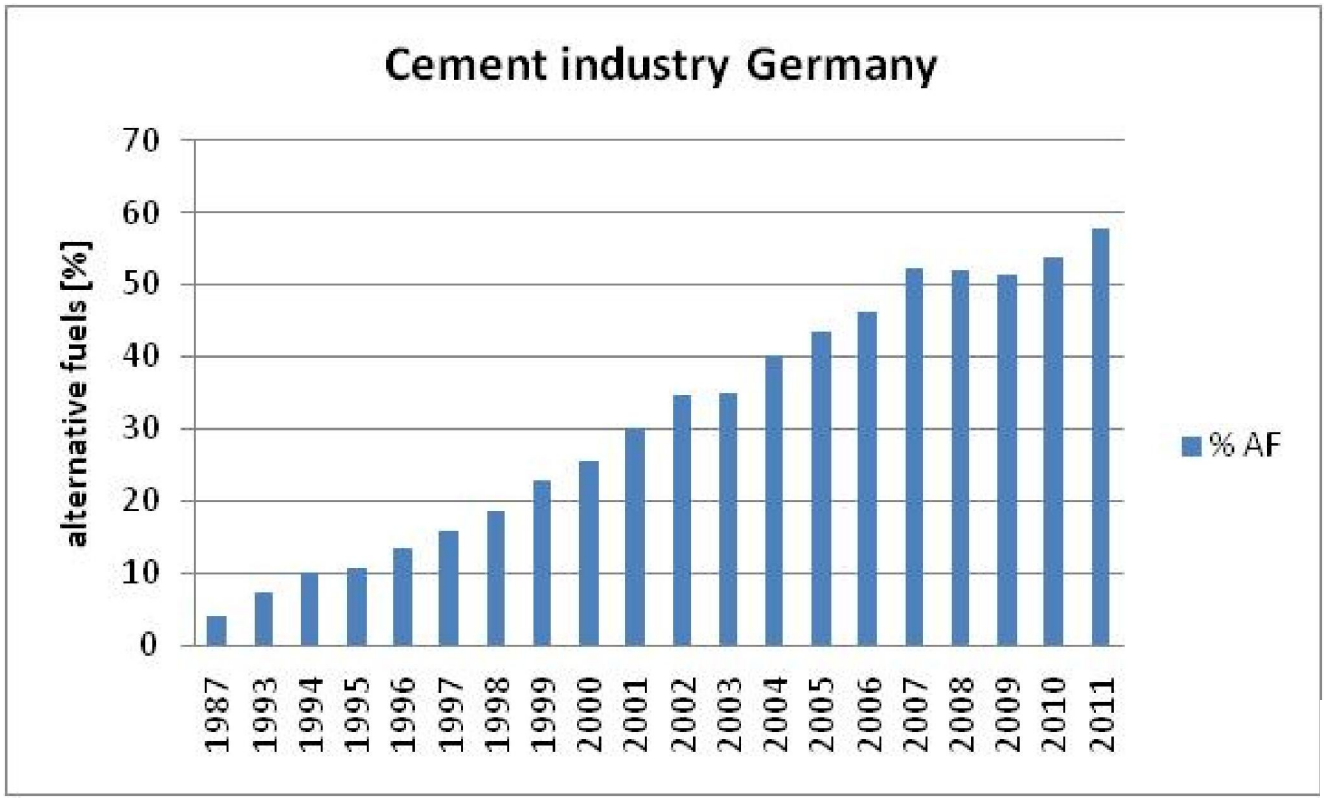
Alternative Fuels

The implementation of alternative not only helps to reduce energy costs but also makes an important contribution to an ecologically and economically sensible utilization of waste materials. Thereby also contributing to a sustainable production of cement.

In comparison with the use of conventional, fossil fuels, refractories are subject to significantly higher stresses when alternative fuels are used reducing kiln availability.

Based on long time experience with cement plants utilizing high levels of AF, RHI has developed products to cope with the requirements of AF use, able to increase kiln availability and productivity.

Percentage of alternative fuels in Germany 1987 – 2011



Source: www.vdz-online.de

Cost saving issues has lead in the last years to an increased use of alternative fuels. Substitution rates of up to 90% have already been achieved in individual kilns (share of AF for 2013 62,5%).

Innovative Refractories for AF Firing

COMPAC CARSIT SOL

fast dry and heat-up mixes by RHI

ANKRAL Q-SERIES

hybrid spinel technology by RHI

Innovative refractory concepts based on Sol bonded castables and the Q-Series allows to improve kiln availability despite the use of alternative fuels.

Sol Bonded Mixes

What are Sol-Gel Bonded Castables?

- The new product line named COMPAC SOL / CARSIT SOL are based on a completely different bonding system, based on nano-particle silica.

- This bonding system replaces the conventional cement as binder and its complex system of (hydrated) calcium-aluminate-phases.

- The binder is delivered separately from the mix.

This offers a variety of advantages:

Advantages

- easy to dry, no specific pre-drying required.
- Fast and easy heating-up procedure.
- Improved chemical resistance (e.g., alkali as well as sulphur) compared to equivalent cement-bonded products.
- Higher refractoriness compared to equivalent cement-bonded products.
- Reduced ambient temperature impact on final product properties.
- Reduced sensitivity to incorrect dosing of the mixing fluid.
- Easily adjusted to the desired setting time.
- 18 months shelf life – compared to 6 - 8 months for LCCs.

Difference Cement-/ Sol-Gel Bonded Castables

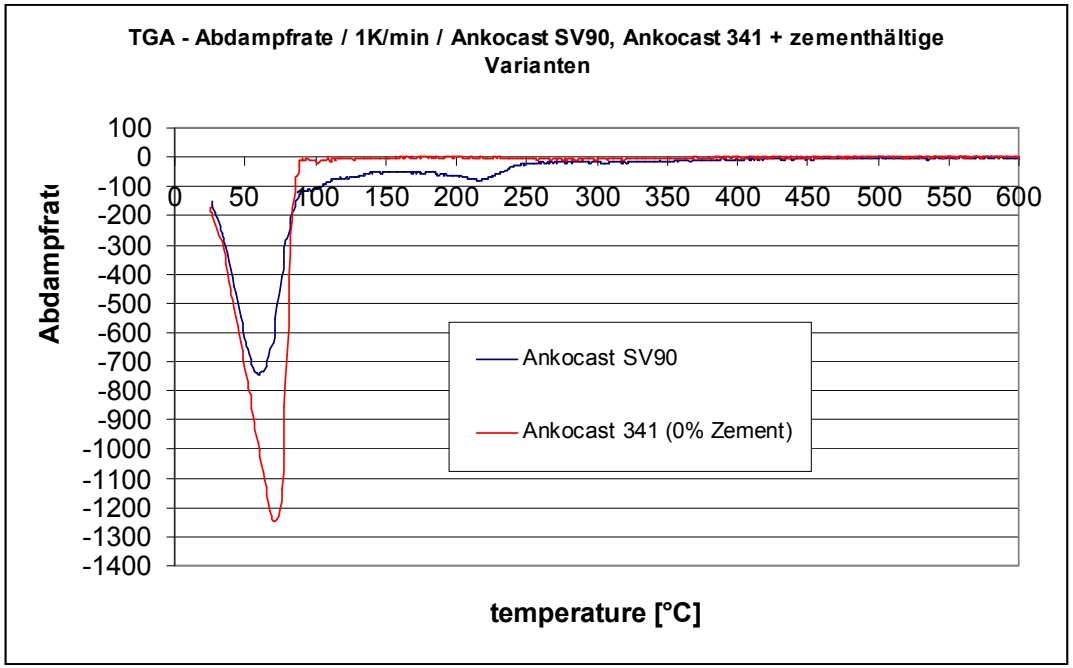
Sol-gel bonded castables:

- The setting and hardening of the concrete (jellying) is based on the formation of **Si-O-Si** - bonding
- **NO** chemically bonded water, no hydrate phases

  → easy drying and heating up

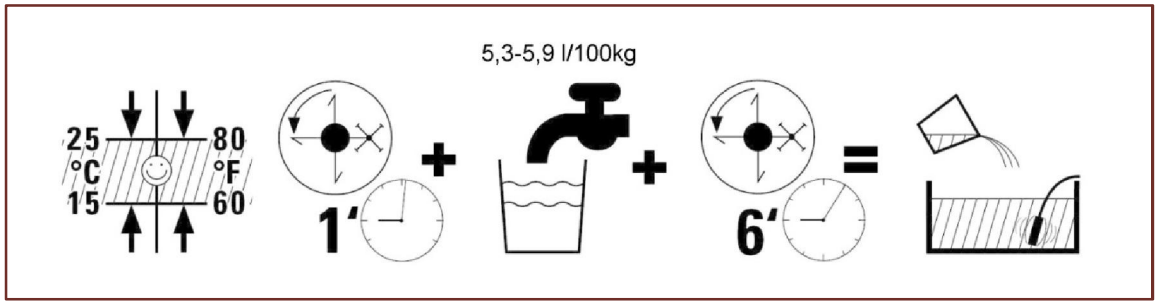
- **NO** chemical additives necessary in order to achieve a controlled and practice-oriented setting and hardening of LCC & ULCC

Disadvantages: separate binder, storage/processing only above + 5°C !

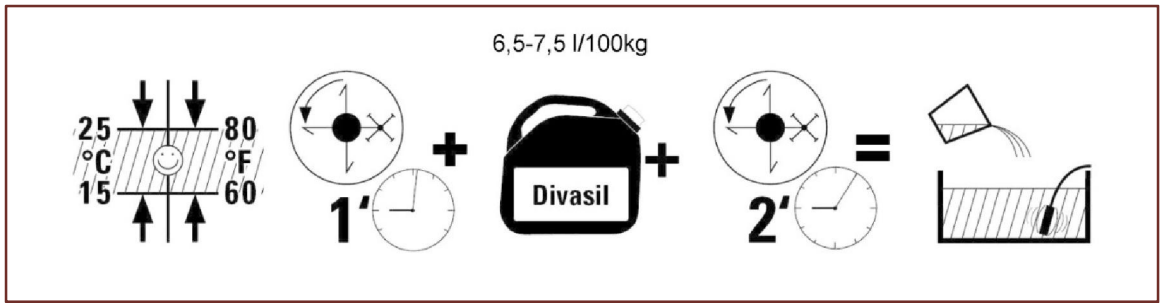


Processing of LCC vs. Sol Bonded Castables

CARSIT M10-6

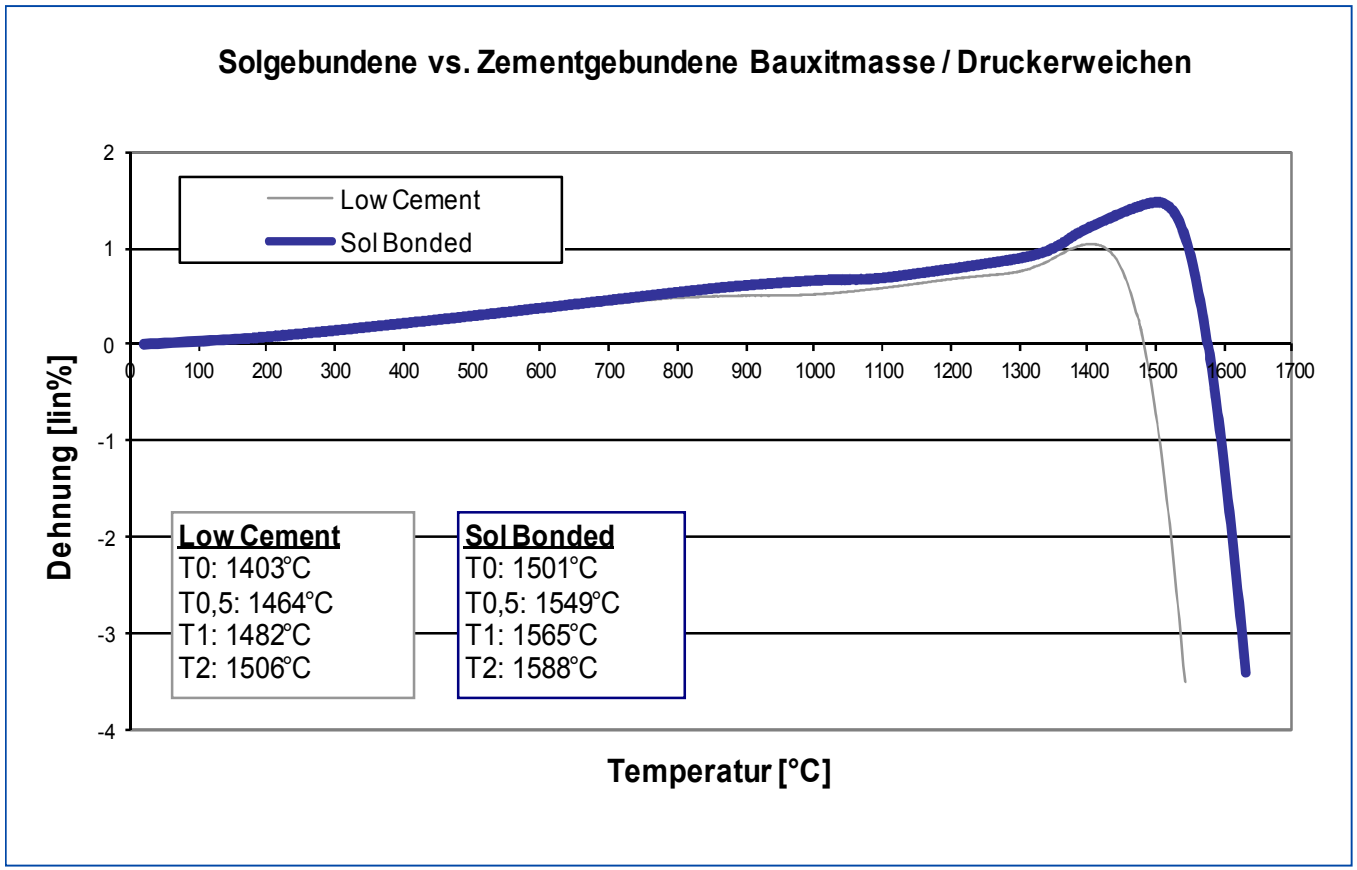


CARSIT SOL M10-6



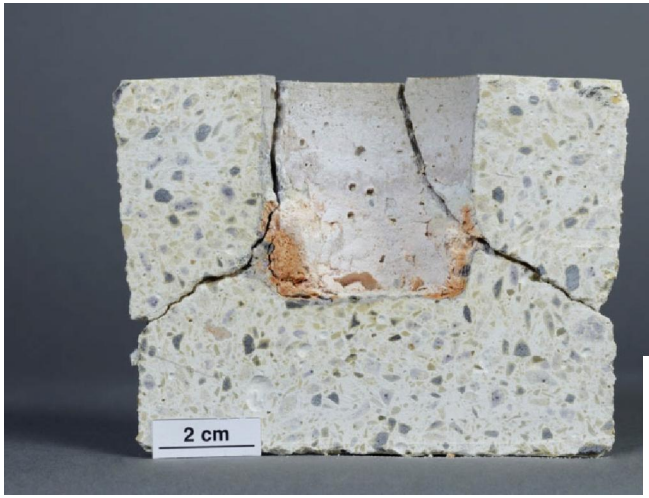
Processing of sol bonded castables is essentially the same as for cement bonded castables. Instead of water the special binder is added during mixing. The wet mixing time is shorter. Also the same equipment is used. All customers and also installation companies have rated sol bonded mixes as very easy to process.

Increased Refractoriness



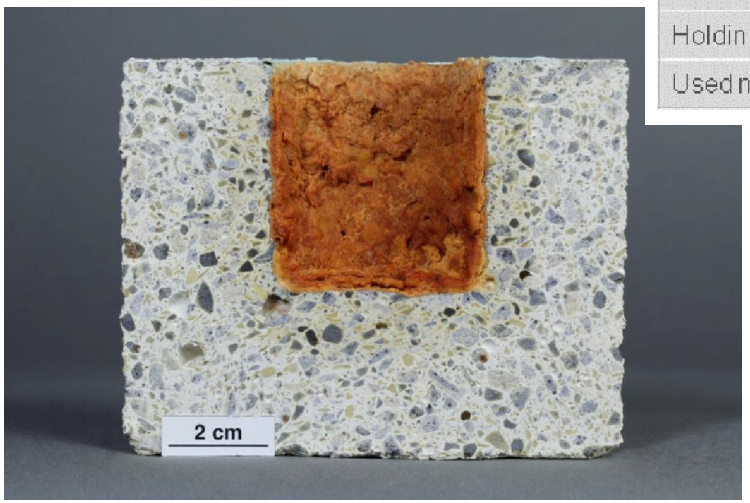
RuL about
90 - 100°C higher!

Alkali Resistance of LC vs. Sol Gel Castables



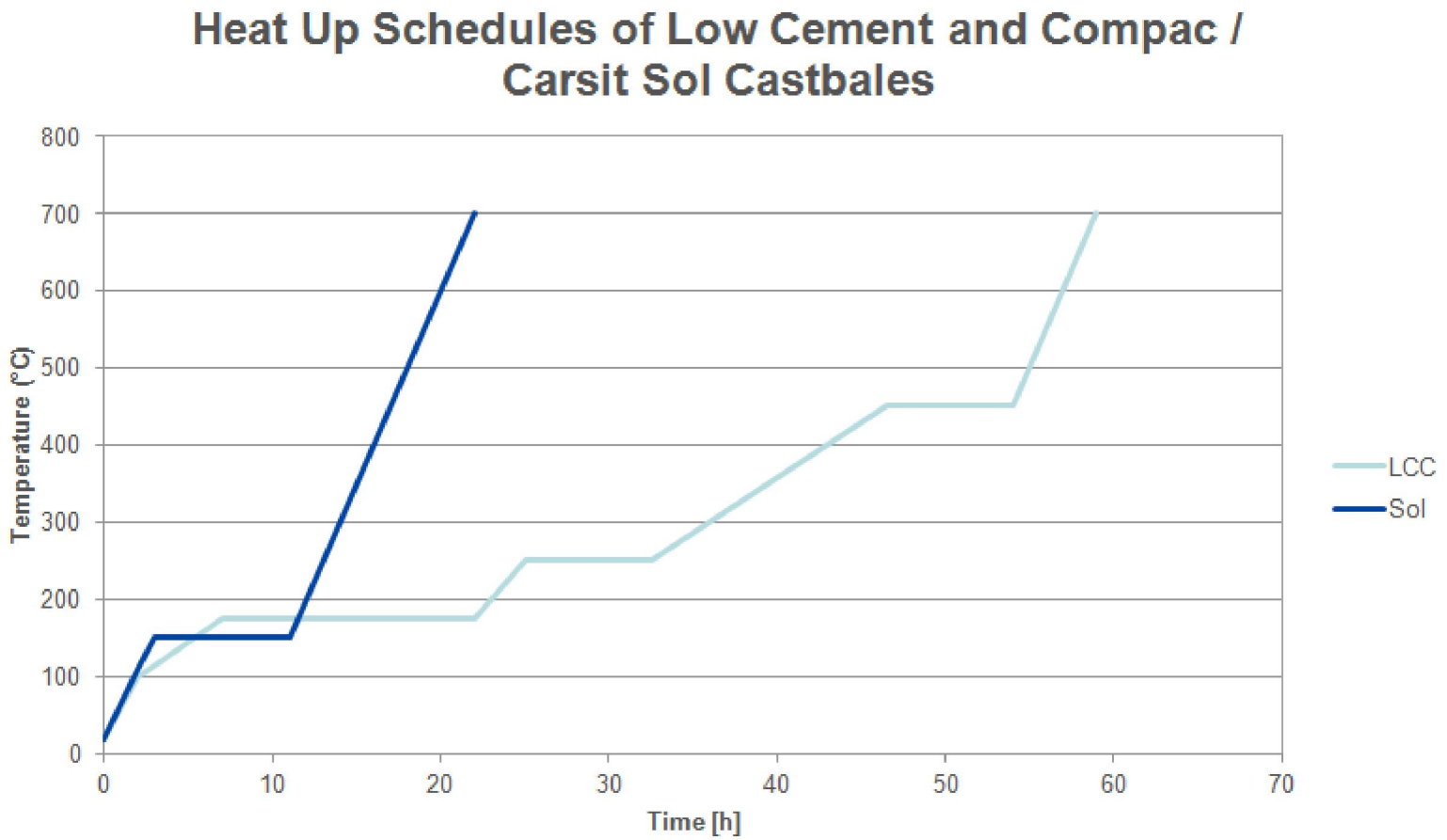
Low cement mullite based castable
60% Al_2O_3
7 cycles

Alkali cup testing parameters	
Temperature	1100°C
Heating rate	300 k/h
Holding time	5 h
Used material	20g K_2CO_3



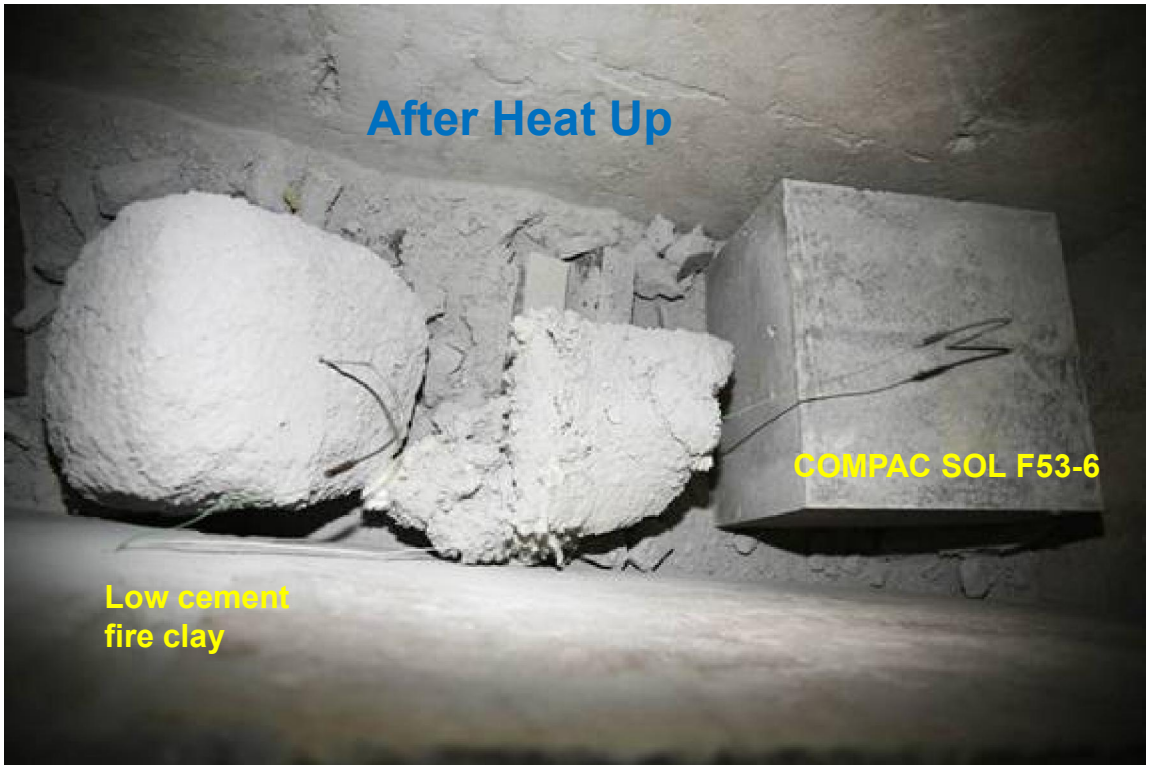
equivalent
sol bonded castable
COMPAC SOL M64-6
18 cycles

Aufheizkurve LCC vs Sol



Heat Up – LCC vs. Sol-Gel

Before Testing



Pictures of a **30K/h Heat Up Test** comparing a common LCC and the equivalent COMPAC SOL F53-6 with the same raw material base.

Innovative Refractories - Sol Mixes

COMPAC CARSIT SOL

fast dry and heat-up mixes by RHI

Cement free castables with fast drying and heating up properties

Product Range Sol Gel

Grade	Al2O3	SiO2	Fe2O3	SiC	SL	CCS		TL	TE	TC			Raw material
						110 °C	1000 °C		1000 °C	400 °C	800 °C	1200 °C	
	%	%	%	%	months	N/mm²	N/mm²	°C	%	W/m.K	W/m.K	W/m.K	
Sol Casting													
COMPAC SOL F53-6	52.2	44.0	0.8		18	70	110	1600	0.55	1.50	1.60	1.80	Fireclay
COMPAC SOL M64-6	64.0	32.0	0.9		18	70	115	1700	0.55	1.80	1.75	1.95	Mullite
COMPAC SOL B82-6	82.0	15.0	0.6		18	70	120	1750	0.55	2.10	2.15	2.25	Bauxite
COMPAC SOL B87-6	85.0	9.5	1.5		18	70	140	1700	0.60	2.20	2.30	2.40	Bauxite
CARSIT SOL F10-6	48.0	39.0	0.7	10	18	65	110	1550	0.55	1.70	1.80	1.80	Fireclay, SiC
CARSIT SOL F30-6	39.0	29.5	0.6	30	18	70	105	1550	0.55	2.70	2.68	2.62	Fireclay, SiC
CARSIT SOL M10-6	58.0	28.0	0.8	10	18	50	80	1650	0.55	1.84	1.77	2.13	Mullite, SiC
CARSIT SOL S30-6	46.5	22.0	0.5	30	18	70	110	1580	0.55	2.75	2.72	2.81	Andalusite, SiC
Clasil production													
CARSIT SOL M10-5 V	57.0	29.0	1.2	10	18	50	80	1650	0.55	1.84	1.77	2.13	Mullite, SiC
CARSIT SOL M30-5 V	47.0	21.0	0.6	29	18	70	110	1580	0.55	2.85	2.80	2.90	Mullite, SiC
Mullite Bonding (MB) Casting													
COMPAC SOL A100MB-15	99.5	0.0	0.1		18	80	180	1850	0.75	3.05	2.45	2.40	Tabular Alumina
CARSIT SOL MB A10-15	89.0	1.3	0.1	10	18	45	200	1650	0.75	3.15	2.54	2.49	Tabular Alumina, SIC

Product Range Sol Gel

						110 °C	1000 °C		1000 °C	400 °C	800 °C	1200 °C	
	%	%	%	%	months	N/mm²	N/mm²	°C	%	W/m.K	W/m.K	W/m.K	
Sol Gunning													
COMPAC SOL F53G-6	50.0	47.0	0.7		18	45	45	1570	0.50	1.30	1.40	1.60	Fireclay
COMPAC SOL M64G-6	61.0	34.0	0.7		18	55	65	1670	0.55	1.65	1.60	1.80	Mullite
COMPAC SOL S64G-6	63.0	36.0	0.5		18	55	60	1670	0.55	1.75	1.70	1.90	Andalusite
CARSIT SOL F10G-6	45.0	42.0	0.7	10	18	45	50	1550	0.50	1.40	1.50	1.70	Fireclay, SiC
CARSIT SOL F30G-6	38.0	31.0	0.7	30	18	45	45	1550	0.50	2.50	2.48	2.42	Fireclay, SiC
CARSIT SOL M10G-6	57.0	30.0	0.7	10	18	55	65	1650	0.55	1.65	1.57	1.94	Mullite, SiC
CARSIT SOL M30G-6	44.0	20.0	0.7	30	18	65	75	1580	0.55	2.56	2.51	2.61	Mullite, SiC
CARSIT SOL S10G-6	60.0	23.0	0.7	10	18	55	55	1650	0.55	1.69	1.63	1.97	Andalusite, SiC
CARSIT SOL S30G-6	44.0	22.0	0.7	30	18	55	55	1580	0.55	2.58	2.54	2.63	Andalusite, SiC
Sol Shotcreting													
CARSIT SHOT SB F30-6	39.0	30.0	0.6	30	18	63	65	1550	0.55	2.65	2.64	2.58	Fireclay, SiC
CARSIT SHOT SB M10-6	58.0	28.0	0.9	10	18	55	75	1650	0.55	1.83	1.75	2.12	Mullite, SiC

Sol References Worldwide

Algeria
Austria
Bulgaria
Canada
Chile
China
Colombia
Czech Republic
Denmark
Dominican Republic
Egypt
Finland
France
Germany
Honduras
India
Indonesia
Iran
Ireland
Italy
Jordan
Kenya
Luxembourg
Malaysia
Mexico
Morocco
Namibia
New Zealand
Nigeria
Norway
Oman
Pakistan
Poland
Romania
Saudi Arabia
Serbia
Slovakia
South Africa
Spain
Sweden
Switzerland
Taiwan
Tunisia
Turkey
Uganda
United Arab Emirates
United Kingdom
Venezuela
Zambia
Zimbabwe

References 1: Horse shoe

Horseshoe installation, Feb. 2010:

CARSIT SOL S30-6 showed excellent processing conditions at ambient temperatures around and slightly below 0°C.

As the castable was stored correctly it was possible to keep the temperature of the mix at about 10°C.

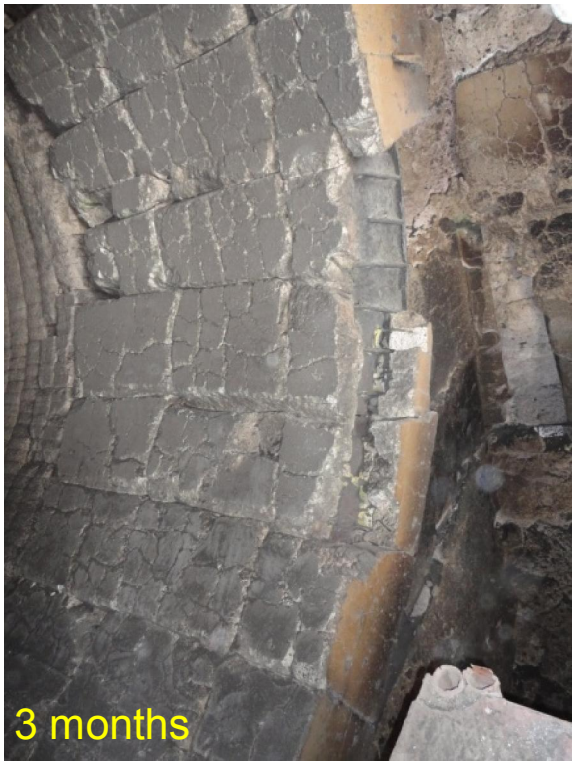
The castable was easy to pour into the moulds and also easy to vibrate and deaerate. The appearance of the fields were very homogeneous without formation of cavities.

References 1: Horse Shoe

Horseshoe installation, after **3** years in operation:

First repairs in Jan. 2015, main part still in operation

Reference
Titan Cement Beni Suef, Egypt: Nose Ring



Severely damaged monolithic outlet lining (high alumina low cement castable) after 3 months in operation.

CARSIT SOL M10-6 still in good condition after 12 months in operation.

published in World Cement Aug. 2013

Solnhofer PZW, Germany

KHD Suspension Pre-heater kiln 4 stages, 1150 tpd
Kiln: 3,8 x 59 m

Alternative fuels 60%: plastic rich residues (BPG), animal meal, fly ash

SM:	2,9 – 3,2
AM:	2,11 – 2,18
Kst:	97 – 99
LPC (1450°C):	22 – 24%
ASR (hot meal):	0,79 – 1,66

Lifetime in bullnose and clinker bed not more than 7 months
burner 6 – 10 weeks

publication in preparation

Reference
Solnhofer PZW, Germany: Bull Nose

Bauxite LC Gunning Mix with ZrO_2 and SiC after 4,5 months of operation, Maximum lifetime 7 months.

CARSIT SOL M10G-6 after 15 months in operation (July 2014). Lining still in service!

Due to the excellent results recently also the **kiln hood** was lines with SOL mixes.

published in World Cement Dec. 2014

Reference
Solnhofer PZW, Germany: Clinker Bed

LC Castable after 4,5 months of operation, Maximum lifetime 12 months.

CARSIT SOL S30-6 after 15 months in operation (July 2014).

Lining still in service!

published in World Cement Dec. 2014

Reference
Russia, Burner Lance

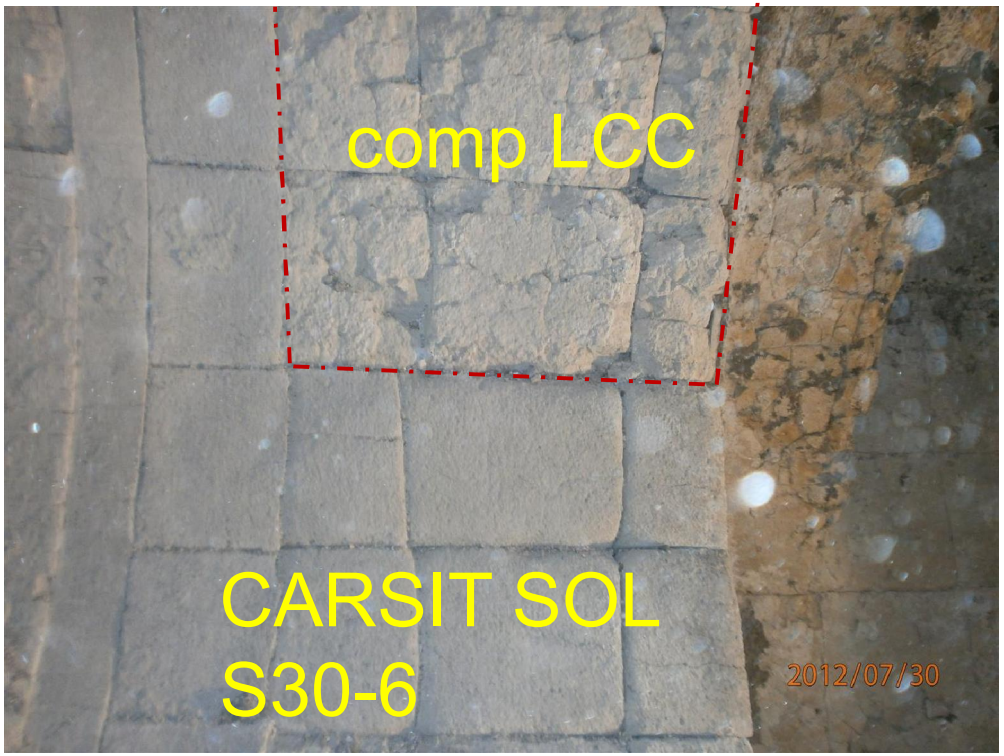
burner lance after 4 weeks in operation

High alumina conventional castable (95% Al_2O_3)

CARSIT SOL MB A10-15

Reference
Germany, Nosering

CARSIT SOL S30-6 compared to low cement castable (andalusite based with 30% SiC) at the nose ring after 6 months in operation.



Conclusions

All the applications so far have proved:

- In most of the applications the lifetime could be significantly increased.
- No need of pre-drying and easy heating up:
  Although the castables have not been pre-dried and where heated up with the same heating up curve as applied to basic bricks, there was no spalling or pre-damage of the castables.
- Perfect workability and setting also under extreme winter conditions.
- All customers rated the workability as good or very good.

ANKRAL Q-Series

Product Portfolio, Q – Series:

Due to the success of the bricks based on the "Q-concept", a complete product line has been implemented, based on this concept:

Q - Series

top grade
special solutions

ANKRAL QF

top grade

ANKRAL Q1

high grade

ANKRAL Q2
ANKRAL QC

economic grade

ANKRAL QE

Use of Q-Concept Bricks Worldwide

Albania
Algeria
Austria
Belgium
Brazil
Bulgaria
Canada
Chile
China
Colombia
Costa Rica
Croatia
Cuba
Czech Republic
Denmark
Ecuador
Egypt
Estonia
Finland
France
Georgia
Germany
Greece
Hungary
India
Indonesia
Iran
Iraq
Ireland
Israel
Italy
Jordan
Kazakhstan
Kenya
Lebanon
Lithuania
Luxembourg
Mexico
Morocco
Namibia
Nigeria
Norway
Pakistan
Panama
Peru
Portugal
Puerto Rico
Romania
Saudi Arabia
Serbia
Slovakia
Slovenia
South Africa
Spain
Sweden
Switzerland
Togo
Tunisia
Turkey
United Arab Emirates
United Kingdom
USA
Uzbekistan
Venezuela

Vietnam

The Q-Concept

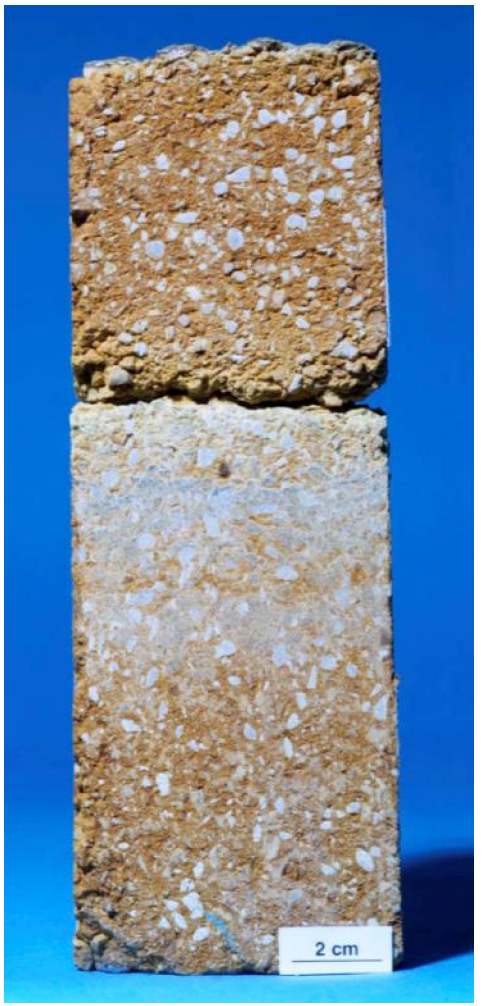
Chemical Wear

Chemical wear is characterized by **two effects**:

Thermo-Chemical Load

1. **Corrosion of the brick structure, ceramic bonding**

2. **Densification of the brick structure, loss of flexibility**



Dynamic E-Modul – Increased Flexibility

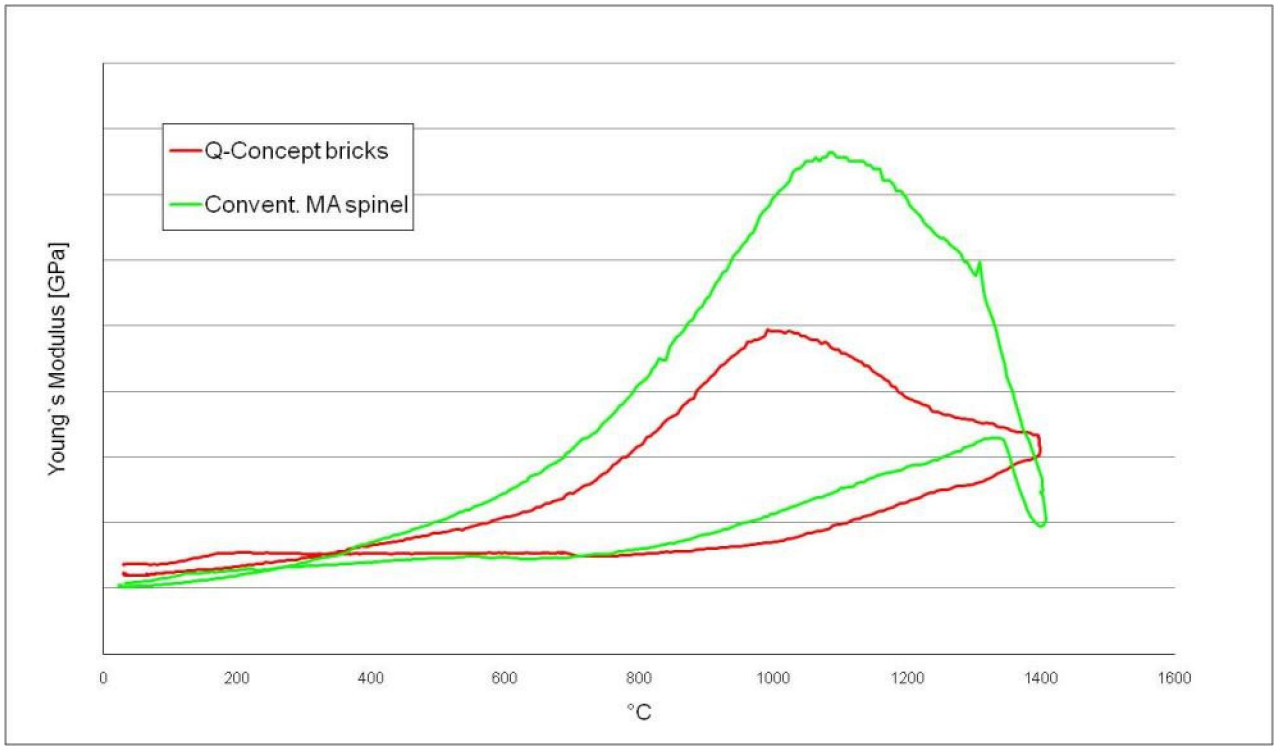
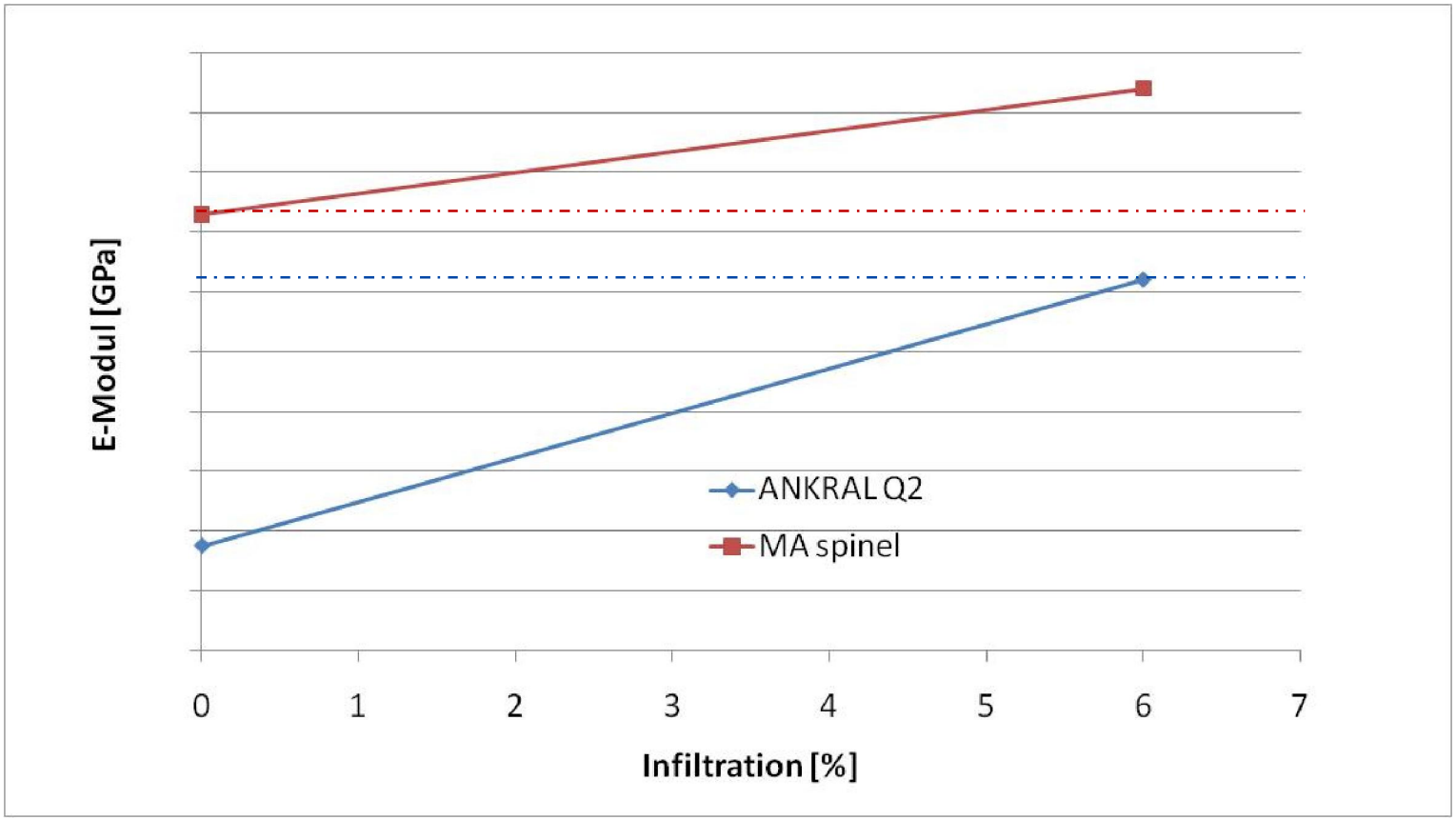


Diagram showing the development of E-modul during heating up and cooling down. There is a reduction in flexibility (increase in E-modul) during cooling down at around 1100°C. This effect can be reduced significantly by use of the Q-concept technology, resulting in an overall higher flexibility.

E-Modul Comparison



ANKRAL Q2 shows even infiltrated a lower E-modul compared to conventional MA spinel brick of type e.g. ANKRAL R2, ALMAG 85 or MA11.

ANKRAL QF, Germany

Kiln: ∅ 5,2 x 87m SP with satellite coolers, 2.500 tpd
Lining area: UTZ tyre between rm 31,6 and 35,6
Tyre creep within campaign: about 40mm/rev

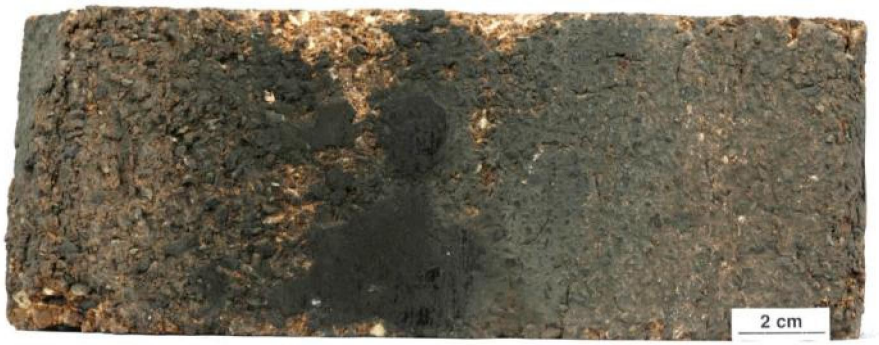
Fuels:

Main burner:	bituminous coal, plastics, solvents (AF approx 70%)
Inlet:	tyre chips

Situation:

The usual lining life until now has been limited to 4 months due to strong mechanical and chemical load in the tyre section.

ANKRAL QF, Germany:
Result after Full Campaign of 12 Months



Brick shows nearly full residual thickness (205mm from original 220mm) with clear signs of severe chemo-thermal and mechanical load (scratch marks and damages on the cold face).

Furthermore there are reducing operation conditions.

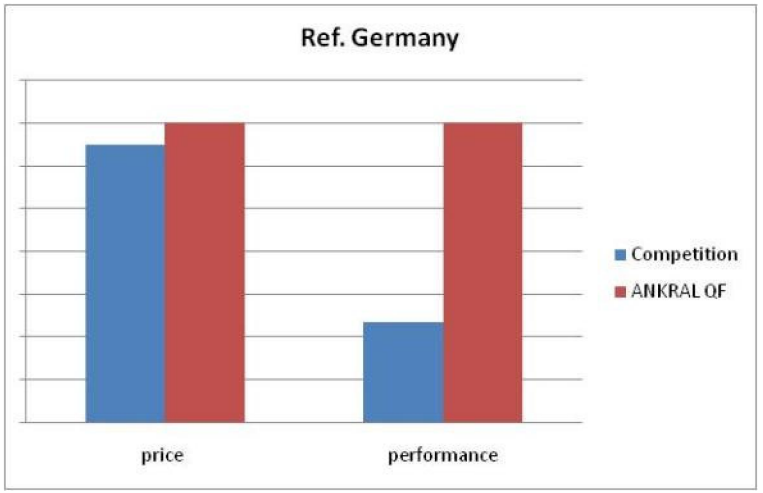
ANKRAL QF, Germany:
Result after Full Campaign of 12 Months

Severe chemical attack and mechanical load !!

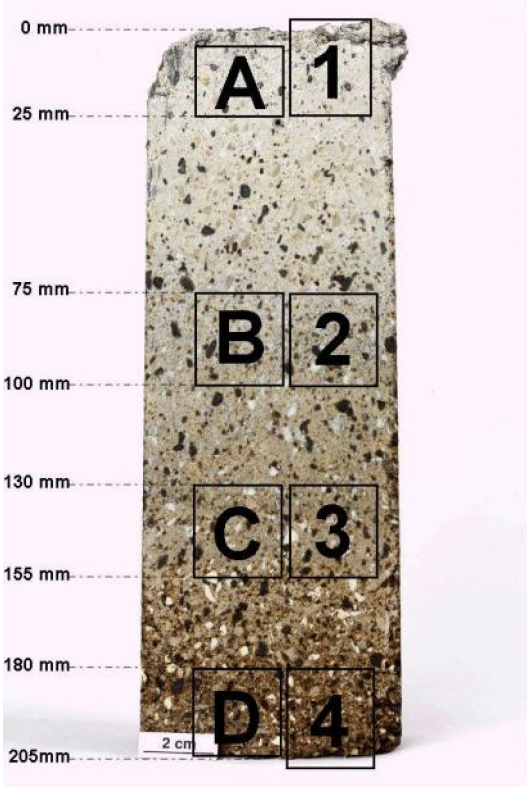
The colour is gone,

but nothing serious happened.

Increase of life time from 4 to 12 months !



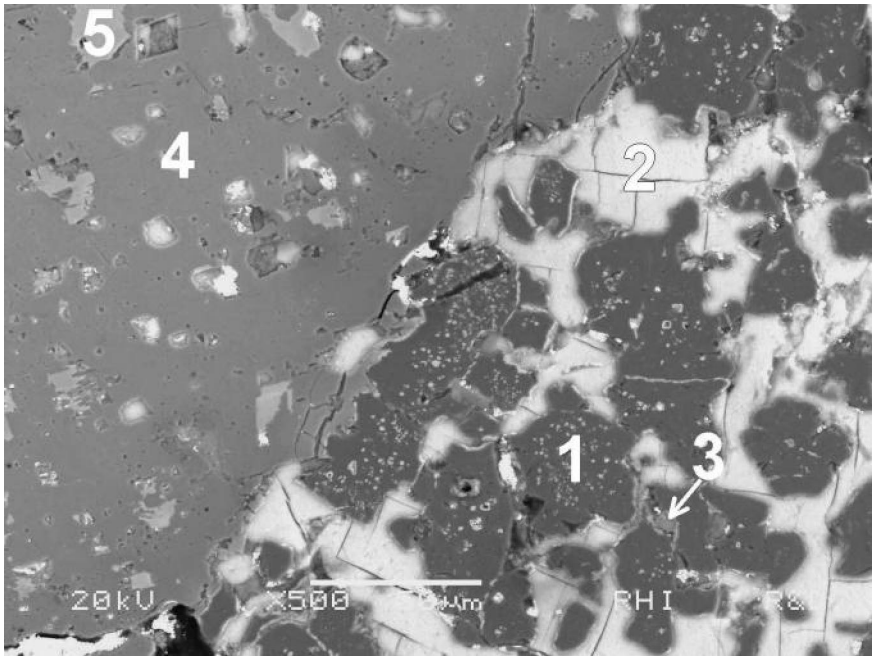
ANKRAL QF, Germany: Chemical Investigation



Despite severe chemical load no spalling or crack formation.

Brick grade	ANKRAL QF				
Area	A	B	C	D	Technical data sheet
Sampling for chemical analyses (distance from hot face)	5 - 25 mm	75 - 100 mm	130 - 155 mm	180 - 205 mm	
Chemical analysis (wt.%)					
MgO	83,80	80,40	83,60	86,8	87
Al_2O_3	9,69	9,73	8,80	9,26	9,3
SiO_2	0,26	0,25	0,27	0,26	0,3
CaO	0,47	0,74	1,30	0,76	0,7
MnO	0,12	0,12	0,13	0,12	
Fe_2O_3	2,33	2,97	2,73	2,71	2,7
Loss on ignition	4,18	7,09	3,62	-0,08	
SO_3	0,03	0,60	0,60	0,13	
Cl	1,84	3,24	1,51	0,07	
K_2O	1,07	1,88	0,92	0,05	
Na_2O	0,05	0,08	0,11	0,05	
$Cl + SO_3 + K_2O + Na_2O$	2,99	5,80	3,14	0,30	
Molar alkali sulphur ratio (ASR)					
$\frac{(K_2O/94)+(Na_2O/62)-(Cl/71)}{(SO_3/80)}$	-43,92	-3,25	-1,30	0,23	

ANKRAL QF, Germany: Mineralogical Investigation



Microstructural detail from sampling area 2 showing severely densified brick structure but no corrosion or degeneration of hercynite. Formation of monticellite as corrosion product of dicalcium-silicate.

Magnesia (1), potassium chloride (2), monticellite (3), hercynite (4), complex spinel (5).

ANKRAL QF, Germany II

Kiln: ∅ 5,3 x 80m SP, 3.500 tpd

Lining area: UTZ, rm 28 – 33, middle tyre (creep ranges between 5 and 30mm due to changing coating conditions)

Installation: Jan 2014 – Jan 2015
Residual thicknesses between 150 – 190mm

The lining is exposed to strong mechanical stresses due to the partly high tyre migration. Additional there is strong chemothermal load due to the use of about 70% of alternative fuels and thermal shocks due to the changing coating conditions.

Previous campaigns with competitive Mag Spinel bricks resulted in campaigns of 3 – 4 months. ANKRAL QF outperformed also neighboring lining.

ANKRAL QF, Germany II

Residual thickness 190 mm

0-95 mm from hot face, strongly brightened structure, infiltrated up to the cold face brick end

C1, C2, C3 samples for chemical investigation

ANKRAL QF, Germany II
Chemical analysis

Brick Grade	ANKRAL QF			
Lining area	UTZ rm 28 - 33			
Sampling area	C1	C2	C3	Data
	5-25mm	45-70mm	140-165mm	Sheet
Chemical analysis [wt. %]				
L.O.I (1050 °C) 2) (DIN 51081)	1,56	1,37	3,70	
Determination by XRF [1] (ISO 12677)				
MgO	79,15	78,39	79,59	87,00
Al_2O_3	8,36	7,86	8,78	9,30
SiO_2	0,31	0,28	0,29	0,30
CaO	1,02	0,82	1,57	0,70
TiO_2	0,01	0,01	0,01	
MnO	0,05	0,05	0,05	
Fe_2O_3	2,54	2,53	2,95	2,70
Determination by elemental analysis (DIN 51085)				
SO_3	4,00	4,32	3,07	
Determination by Titration [2]				
Cl	0,45	0,43	1,31	
Determination by ICP-OES [2), 3)] (ISO 26845)				
K_2O	4,990	5,940	4,690	
Na_2O	0,290	0,290	0,220	
Sum salts				
$K_2O+Na_2O+SO_3+Cl$	9,73	10,98	9,29	
Molar alkali sulphate ratio				
	1,03	1,14	0,91	

[1] on ignited sample (1050 °C) by x-ray fluorescence

[2] on original sample

[3] Optical Emission Spectroscopy by Inductively Coupled Plasma

ANKRAL Q2: UK

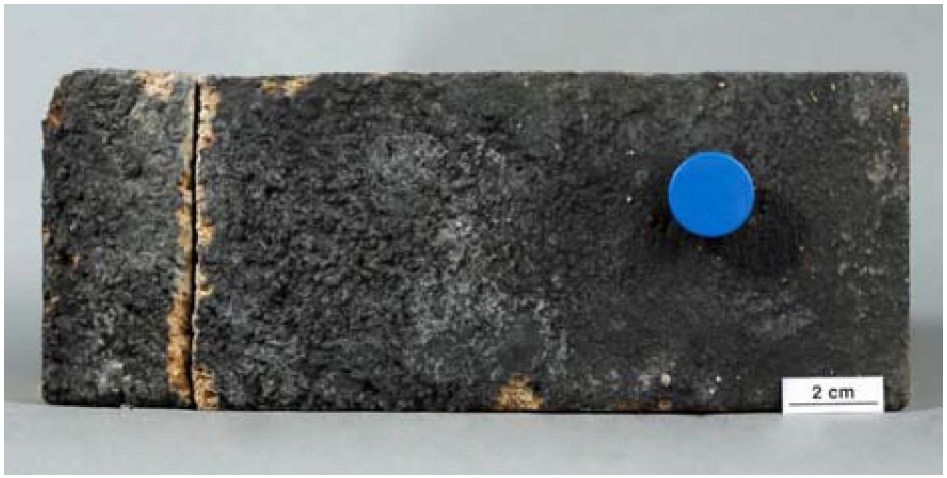
FLS, PC kiln, 2450 tpd
3,950 x 58 m

50% alternative fuels: pelletized sewage sludge
tyre chips
recycled liquid fuel with coal.

ANKRAL Q2 installed in Jan. 2011 1rm (23,8 - 24,8) trial field

After a full campaign the brick was in most parts **almost full depth** although for part of the panel infiltration spall was noted.
The customer is satisfied with performance and will install 5 metres of Q2 over the front tyre during this stop.

ANKRAL Q2: UK

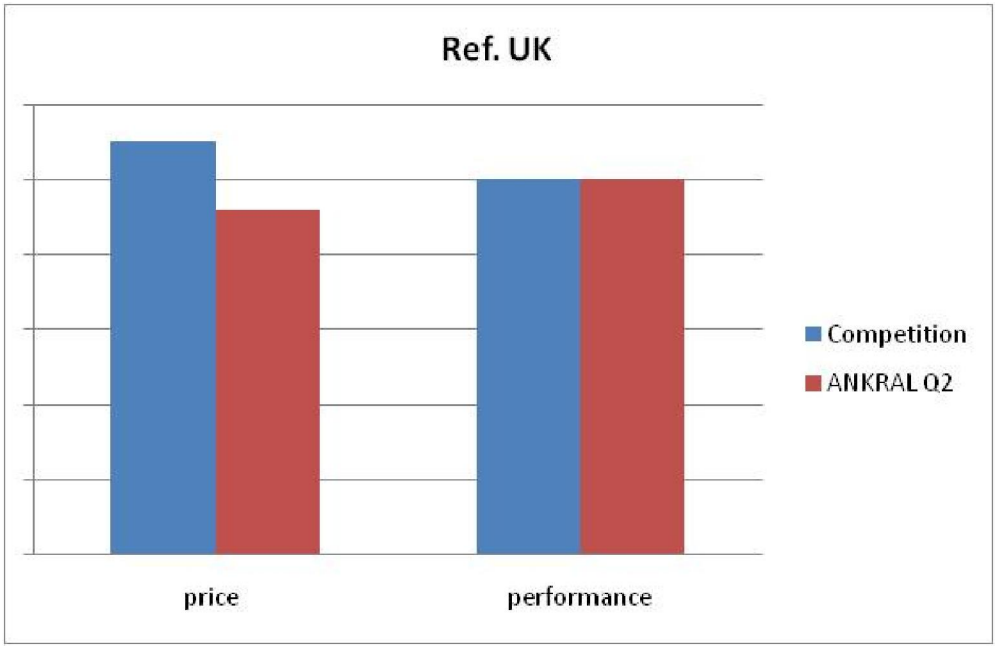


ANKRAL Q2 after a full campaign in operation. The cut section shows severe infiltration by alkaline salts. The cold face shows also magnetic properties due to corrosion of the kiln shell. This outlines the strong chemo-thermal load within the lining area.

ANKRAL Q2: UK

General information			
Customer	Lafarge		
Plant	Cauldon, UK		
Aggregate	Cement rotary kiln		
Position	Upper transition zone		
Brand	ANKRAL Q2		ANKRAL Q2
Sampling	5-20 mm from the hot face	145-165mm from the hot face	Technical data sheet
Chemical analyses			
	Wt.%	**Wt.%**	**Wt.%**
Loss on ignition (1050 °C) (DIN 51081)	0.59	3.77	
Determination by XRF[1] (ISO 12677)			
MgO	86.51	80.58	86.3
Al_2O_3	8.47	8.59	9.0
SiO_2	0.89	0.84	0.8
CaO	0.26	2.00	1.6
MnO	0.02	0.04	
Fe_2O_3	2.24	2.37	2.3
Determination by titration[2]			
Chloride	0.24	1.62	
Determination by C-S elemental analysis[2] (DIN 51085)			
Sulfur	0.24	0.87	
SO_3	0.61	2.17	
Determination by ICP-OES[2][3] (ISO 26845)			
K_2O	0.74	1.68	
Na_2O	0.03	0.11	
Alkali-sulfate ratio, molar[4]			
$\frac{(K_2O/94)+(Na_2O/62)-(Cl/71)}{(SO_3/80)}$	0.66	-0.12	

ANKRAL Q2: UK



The trial was only 1 running meter but was in the worst area and gives positive indications. The photo below shows the Q2 in position and spalls can be seen in the brickwork either side (competitor high grade brick). The brick top missing from the lower part was removed by the author to check for infiltrating salts. In comparison to the competitive high cost product ANKRAL Q2 shows an excellent price performance ratio.

ANKRAL Q2: UK 2

FLS, PC kiln, 2450 tpd
3,950 x 58 m

50% alternative fuels: pelletized sewage sludge
tyre chips
recycled liquid fuel with coal.

ANKRAL Q2 installed in Jan. 2012 in LTZ area of unstable coating

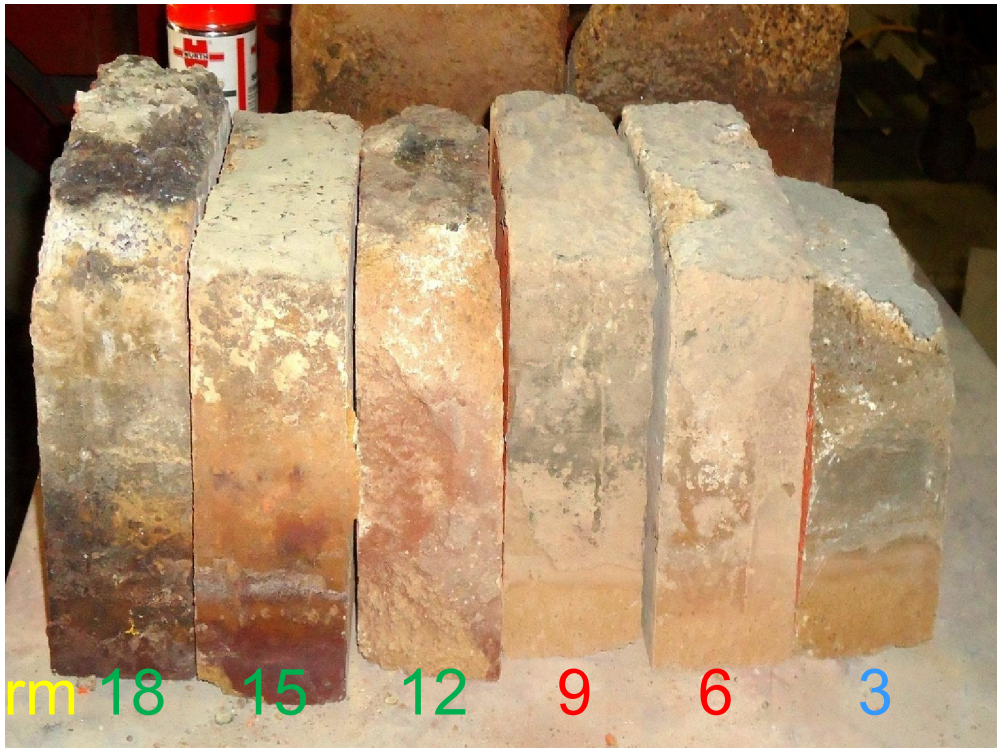
Residual thickness after a full campaign about 150mm.
Some spalling in the key area. Removed for safety reasons.

ANKRAL Q2: UK 2

4 m of ANKRAL Q2 were fitted last year from 5.8 to 9.8 metres between competitor MA spinel brick at the front and competitor MA spinel brick at the back. The interface of LTZ and CBZ is considered to be 8 metres from nose.

There was no visible difference in thickness or condition.

All bricks were removed after the campaign.



ANKRAL Q2: UK 2

Competition / ANKRAL Q2 (5.8 to 9.8) / Competition

outlet

ANKRAL Q2: Austria

Kiln details: Pol – PC kiln, Ø= 3,4 x 48m, 900 tpd (tyres 4,2/20,5/39,4)

ANKRAL Q2 installed in UTZ between rm 27,4 and 29,2 results after one full campaign in UTZ (see pic). Competitive magnesia spinel brick, installed together with Q2 and adjacent to Q2 (rm 25,4 to 27,4), showed partly only 3 cm res. thickness and strong spalling.

Thank you for your attention!

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