IMPROVED DRYOUT BEHAVIOUR OF REFRACTORY CASTABLES

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THE DESIGN OF MONOLITHIC LININGS
WEDNESDAY 8TH NOVEMBER

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Why do industrial-sized monolithics sometimes explode during heat-up?

Is there a remedy to ensure safe and fast heat-up of castables?

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Outline

- Challenge: Risk of explosive damage
- Why will some materials increase the risk compared to others? How to minimise risk of damage during dryout?
- A novel methodology to improve dryout behaviour of monolithics
  - Example 1: Fast dryout of cement-free of NCC
  - Example 2: Further improvement in explosion resistance of NCCs by adding a speciality drying agent
- Application areas of NCCs

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Challenge: Risk of explosive damage

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80 kg block of NCC without fiber

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Explosion under fast heat-up

80kg block fired at 50°C/hr from room temperature

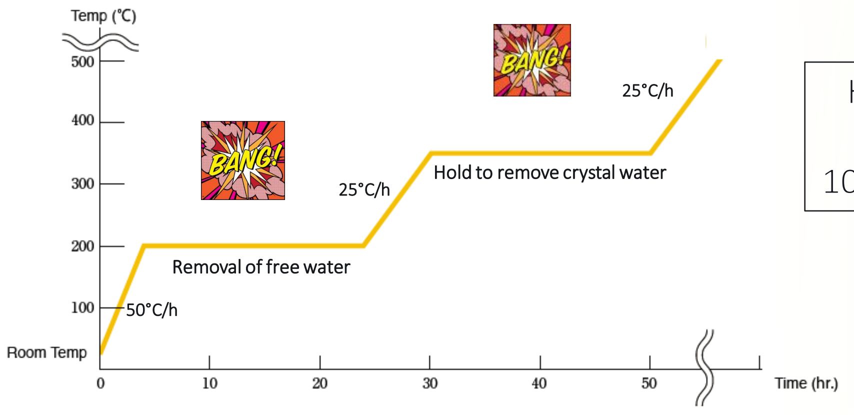
After opening ….

Why?

- Wrong dryout schedule?
- Low green strength?

- Low permeability
- Steam generation
- High vapor pressure inside the samples
- Dimension/size, thickness and shape

Typical dryout of LCC for aluminium industry (lining thickness 200mm)



Holding time:
1 hour per
10 mm thickness

Source: http://www.agcc.jp/Portals/0/images/en/core/alumi/about/methodDrying.pdf

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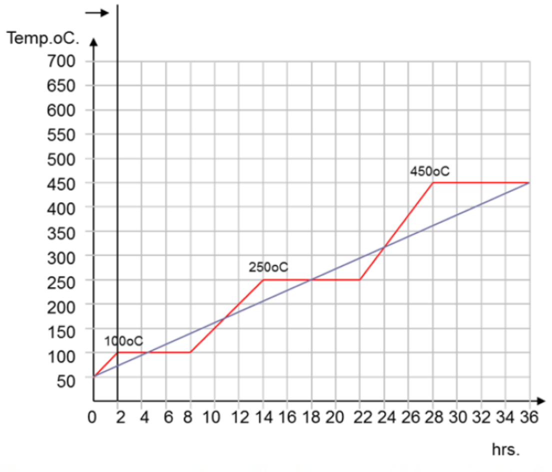
Thermal Dryout graph, ramp and hold vs. Strainght line



- The ramp and hold schedule is showing ramp rates of 25°C/hr, where the straight line curve calcualtes to a continuous 12.5°C.
- The internal steam pressure at vaiour points through this overlaid schedule shows reduced peak steam pressure at all points for the straigth line.

"Hotwork Services for the Hydrocarbon Processing Industry" Power Point Presentation (2008) by Hotwork Combustion Services in Lexington, Kentucky (www.Hotwork.com).

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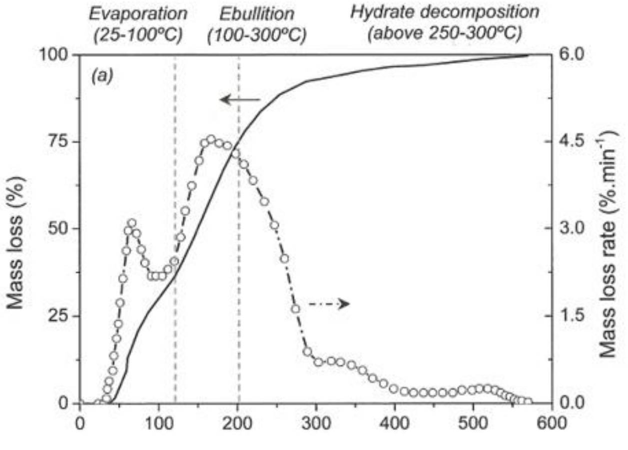
Why will some materials increase the risk compared to others?
How to minimise risk of damage during dryout?

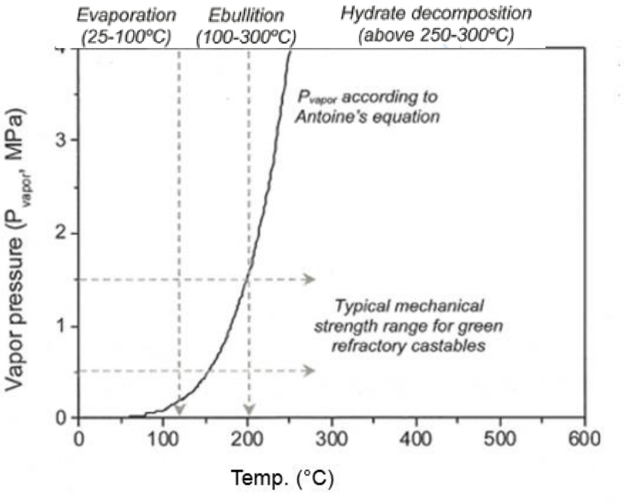
Drying behavior evaluation by TGA



Source: R.Salomao and P.C Pandofelli, Ceramics, 54(2008) 259-267

- Three stages: evaporation, Ebuliition and hydrate decomposition

Vapour pressure under heat-up

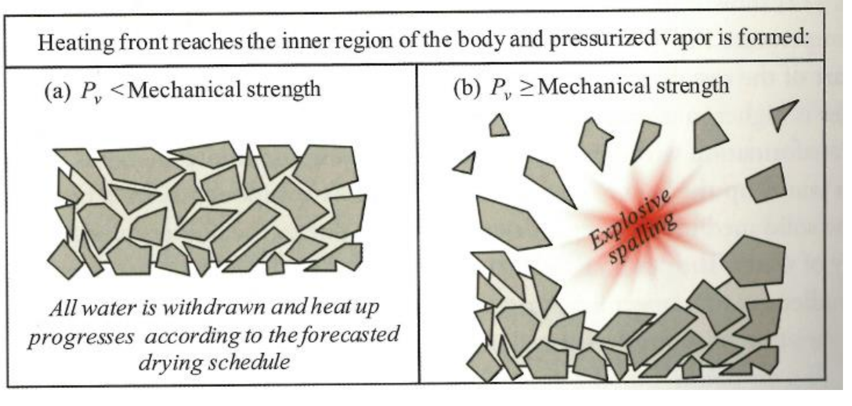


- Vapour pressure inside the sample exponential increase with the temperature

$$\log_{10} p = A - \frac{B}{C+T}.$$ (0 to 374°C)

- Typical green tensile strength: 0.5-1.5 MPa (160 - 200°C)
- In an actual lining, even a little water highly restricted can develop pressures that exceed the strength of refractory resulting in significant damage from spalling.

Explosion risk vs. mechanical strength



Optimising the dryout schedule for refractories

- Evaporation period (20 - 100°C) - to remove free water
  - Curing time and curing temperature
  - Less water
- Ebullition (100 - 300°C) is the most critical drying stage
  - Minimise the steam entrapment within the microstructure
  - Maximise water removal during evaporation period
- Hydrates decompose – removal of crystal water (typically range above 250-300°C)
  - Cement content
  - Binder types (cement-free)

NCCs (silica-sol, alumina-sol and microslilca-gel bonded)

CCs, LCCs, ULCCs

Permeability and heating rate are the primary factors controlling whether monolithics will explode during initial dryout

Possible solutions

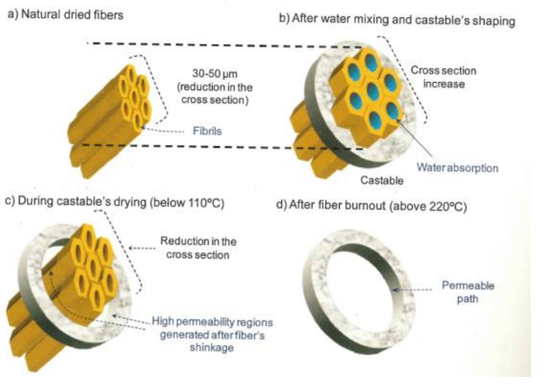
- Optimise the dryout schedule - water removal as required
  - Holding time and heating rate
- Engineer the microstructure of the castable
  - Improve permeability to remove water faster
  - Improve the mechanical strength to withstand higher vapour pressure
  - Replace hydraulic bond with cement-free bond to eliminate dehydration process at late dryout stage
- Use less water

Importance of permeability

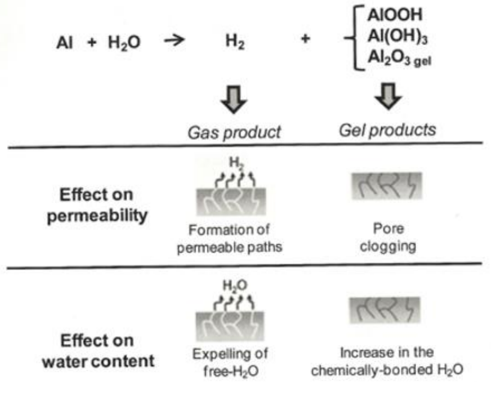
Type Materal	Low Cement	Dense Conventional	Medium Weight	Insulating	Ultra-light Insulating
	Type of Refractory Castable				
Density (lb/ft^3)	140-180	130-170	100-130	30-100	20-30
Water Content %	4-8	8-12	15-18	20-40	40+
Permeability (after air cure)	Least →				Most
Water release issues	More difficult →				Less difficult

- Permeability of the lining is therefor a significant key to the criticality of the dryout.

Improve permeability by adding drying agent



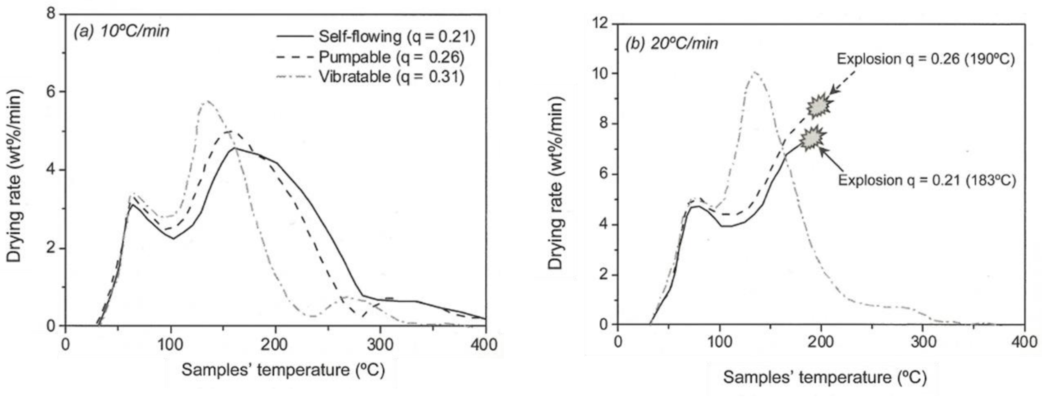
Fibers



Aluminium powder

Introducing PP fiber and/or adding Al fines have become two of the most common methods to improve permeability of monolithics in order to prevent/avoid explosive spalling during dryout.

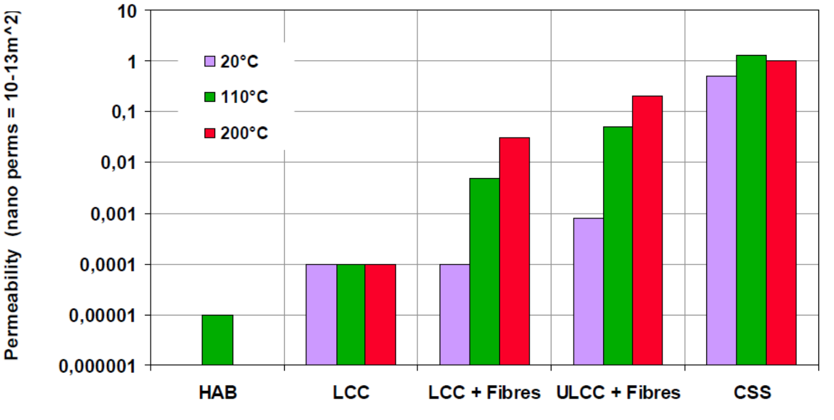
Effect of PSD on drying rate of castables (4.5% water)



Higher q-value leads to a lower amount of fine particles, an increase in permeability and consequently better explosion resistance.

Source: R. Salomao, VC, Pandolfelli: "The particle size distribution effect on drying efficiency of polymeric fibers containing cstables", Ceramics International, 34 (2008) 31-36

Effect of binder on permeability



Permeability has been significantly improved when the hydraulic binder (CA) is replaced by colloidal Silica binder.

Source: C. Parr, Ch. Wöhrmeyer, «The advantage of calcium aluminate cement as a castable bonding system». St. Lois Section meeting, USA, 2006

Summary; guide to minimize the explosion risk

- Optimise the dryout schedule (hold and ramp)
  - Maximise water removal during evaporation period (20-100 °C)
  - Minimise the steam entrapment within the microstructure during Ebullition (100 - 300°C)
- Improvement of permeability in monolithics
  - Adding drying-agent, e.g. polymeric fibres or aluminium powder, which generate permeable paths for water towards the surface
  - Adjusting the particle size distribution (PSD) of monolithics to create a matrix with higher permeability, higher q-value, less fines
- Replacing hydraulic binders by colloidal binders, inhibiting formation of hydrates.
- Adding metal fibres to enhance mechanical strength and fracture energy

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A novel methodology to improve dryout behaviour of monolithics

- Replacing hydraulic binder by microsilica binder

Advantage of drying out process of cement-free castables

- Evaporation period (20 - 100°C) - to remove free water
  - Curing time and curing temperature
  - Less water
- Ebullition is the most critical drying stage
  - Minimise the steam entrapment within the microstructure
  - Maximise water removal during evaporation period
- Hydrates decompose – removal of crystal water (typically range 180 - 600°C)
  - Cement content
  - Binder types (cement-free)

NCCs (silica-sol, alumina-sol and microslilca-gel bonded)

CCs, LCCs, ULCCs

Development of NCCs

- Compared to low-cement castables, silica-sol bonded no-cement castables (NCCs) are very attractive due to their rapid dryout and excellent high temperature performance

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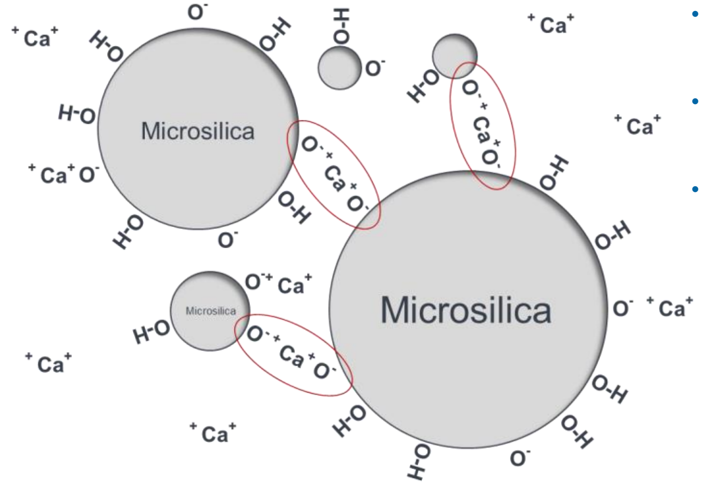
Drawbacks

- Frost sensitivity under installation, storage and transportation
- Inadequate green strength leading to handling problems
- Long set-time/complex set-behaviour

- A “dry-version” of a silica binder, based on gelling of microsilica powder, has drawn great interest in developing NCCs.
- The features and benefits of microsilica and its performance in refractory castables have been studied at Elkem for more than fifty years. Recent work confirm that microsilica acts as a binder in NCCs, with a similar gelling mechanism to silica-sol binder.

Microsilica-gel bond mechanism in alumina castables



- Microsilica-gel bond acts by gelling of the microsilica slurry and not primarily by hydration of cement
- The 0.5% cement serves as a “retarded gelling agent” supplying Ca^{2+} that makes the microsilica-gel
- The microsilica surface with negative charges are linked (gelled) by Ca^{2+}

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Microsilica-gel bond NCC

	[weight %]
Elkem Microsilica 971U	5,5
CAC cement, Secar 71	0,5
SioxX-Zero-P*	3
White Fused Alumina 3-5mm	10
White Fused Alumina 0,5-3 mm	32
White Fused Alumina 0-0,5mm	16
White Fused Alumina -74 mic	20
Calcined alumina,CT 9FG	13

+ 4.15% water = «matrix slurry»

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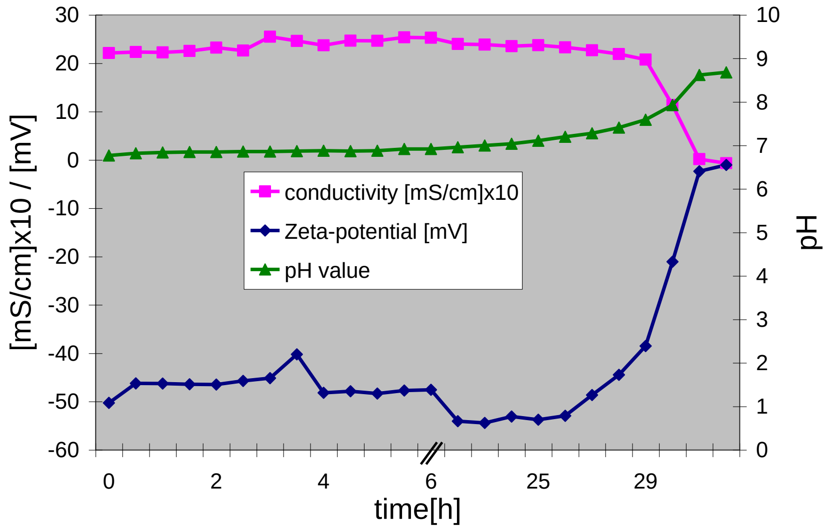
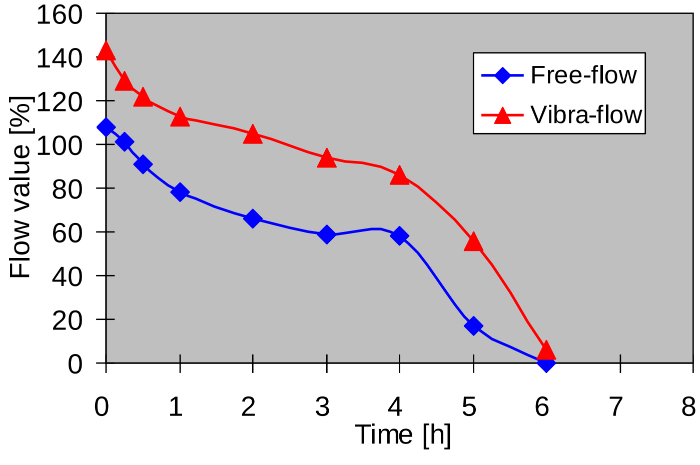
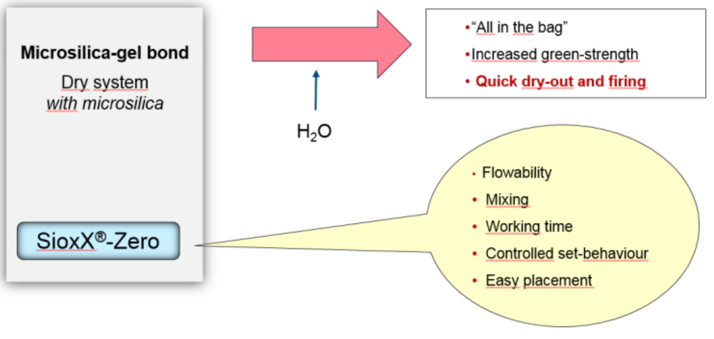
Zeta-potential, conductivity and pH of «matrix slurry»



Flow development of castable with 0.5wt% cement and SioxX-Zero-P



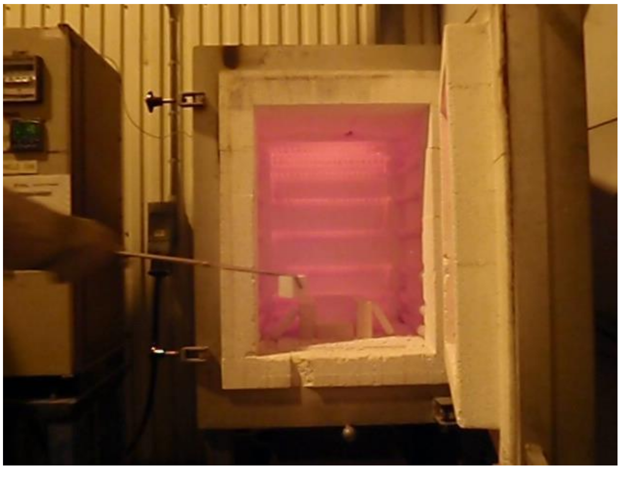
Advantages of microsilica-gel bond vs. silica-sol system



"Add water only" NCC with excellent flow, controllable setting, increased green strength and quick dry-out and firing.

Source: H. Peng and B. Mhyre, "Development of self-flowing no-cement refractory castables with improved properties", Aachen, Germany, 2016.

Lab-scale explosion testing



Explosion resistance testing according to Chinese standard YB/T 4117-2003

50mm un-dried (green) cubes are placed into a furnace at test temperature for 30 minutes.

Explosion testing microsilica-gel bonded NCC

- 450°C, green sample

Explosion testing microsilica-gel bonded NCC

- 800°C, dried at 110°C

Explosion resistance of microsilica-gel bonded NCC vs LCC

Test temperature [°C]	"Green"		Dried at 110°C	
	LCC	NCC	LCC	NCC
200		☺		
250		☺		
300		☺		
350		x		
400	☺	x	☺	☺
500	☺	x		
550	☺			
600	x		x	☺
800				☺
1000				☺
1200				☺

☺ - passed x - failed

- WFA LCC with 6% cement
- 50mm cubes placed into furnace at temperature – without and with drying prior to testing.
- The apparent lower explosion resistance of "green" NCC is attributed to the lower green-strength compared to the LCC.
- After drying at 110°C the gel-bonded NCC has gained strength and contains less water than the LCC resulting in superior explosion-resistance compared to LCC.

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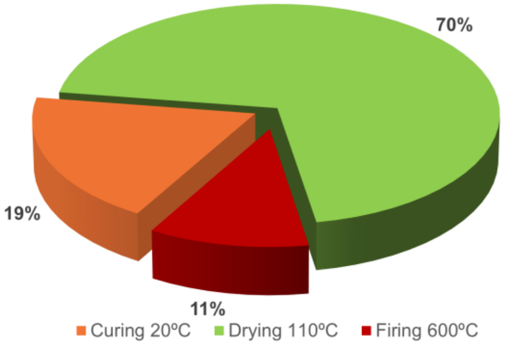
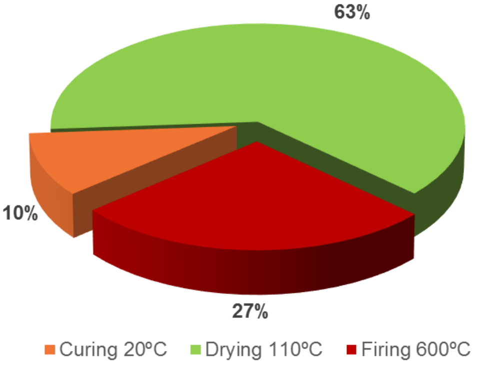
Weight loss, NCC vs. LCC

Gel-bonded WFA NCC - 4.15% water



LCC - 6% cement



Microsilica-gel bonded NCC with a higher permeability than LCC after drying at 110°C, makes faster heat-up without spalling problems possible.

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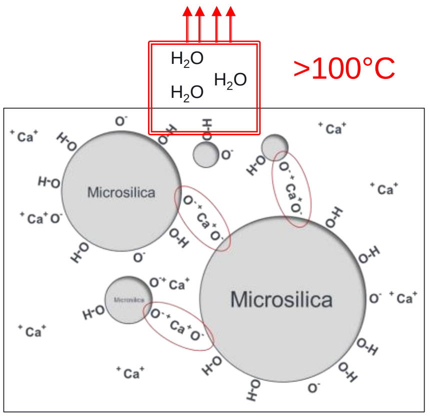
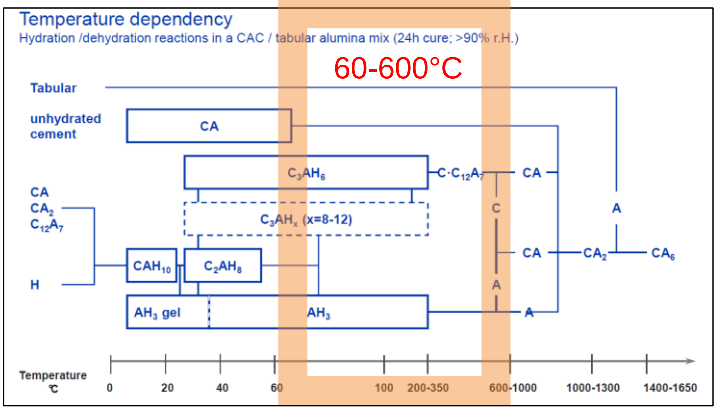
Microsilica-gel bonded binder performance



Microsilica-gel bond

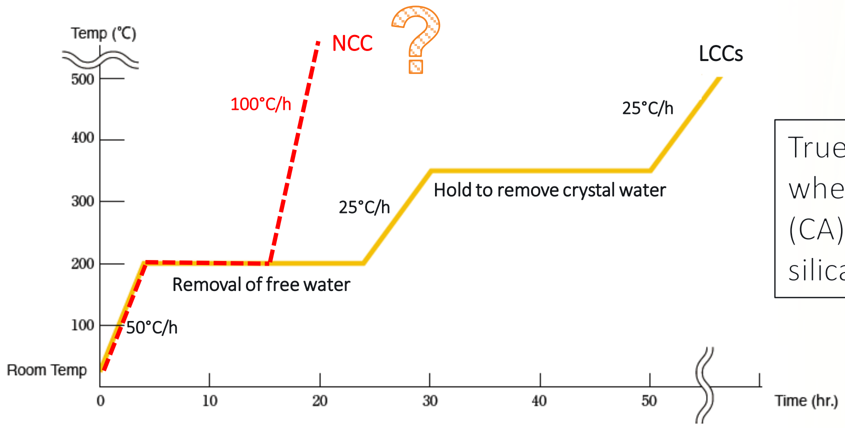


Hydraulic bond (CA)

Summary; novel technology to improve explosion resistance

- The apparent lower explosion resistance of “green” NCC is attributed to the lower green-strength compared to the LCC
- After drying at 110°C the gel-bonded NCC has gained strength and contains less water than the LCC, resulting in superior explosion-resistance compared to LCC.
- Faster dryout is possible when the hydraulic bond (CA) is replace by cement-free bond (microsilica), as no cement hydrates are produced during the curing process
- As a results, the explosion risk in the temperature range 180 - 600°C is minimised for cement-free monolithics

Dryout of LCC vs. NCC for aluminium industry (lining thickness 200mm)



True fast heat-up when hydraulic bond (CA) is replaced by silica-gel bond?

Source: http://www.agcc.jp/Portals/0/images/en/core/alumi/about/methodDrying.pdf

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Example 1:
Fast-dryout of microsilica-gel bonded NCC
(industrial scale specimens)

Castable composition with SioxX-Zero and PP fiber

		Bauxite NCC (%)
Bauxite	3.15-6.15mm	10
	1-3mm	32
	0-0.5mm	16
	0-0.2mm	7.5
Kyanite	0-0.16mm	2.5
Tabular alumina	0-0.2mm	10
Calcined alumina		12.5
Cement	70%CAC	0.5
Microsilica	971U	6
PP-fiber		0.05
SioxX-Zero		3
Total		100.05
Water addition		5

Self-flow [%]		62	
Vibra-flow[%]		118	
	Green-strength:	Dried at 110 °C (24h)	Fired at 850 °C (12h)
C-MOR [MPa]	3.4	7.3	7.8
CCS [MPa]	15.7	42.5	74.5

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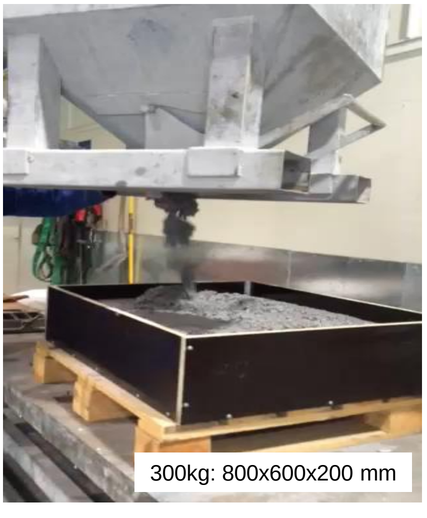
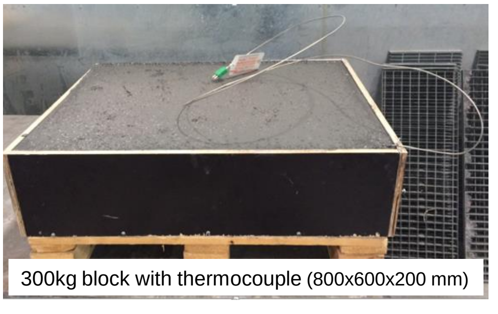
Specimens for drying tests



300kg: 800x600x200 mm

~75kg (300x300x300 mm)



300kg block with thermocouple (800x600x200 mm)

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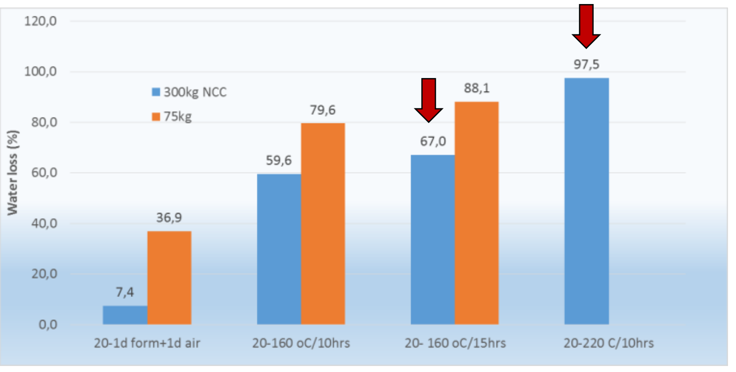
Drying schedule vs. water loss



75kg: 300x300x300 mm (one specimen);
300kg: 800x600x200 mm (two specimens)

In the large specimens 97,5% of the water was removed after 10hrs at 220°C, while only 67,0% water was released after drying at 160°C for 15hrs.

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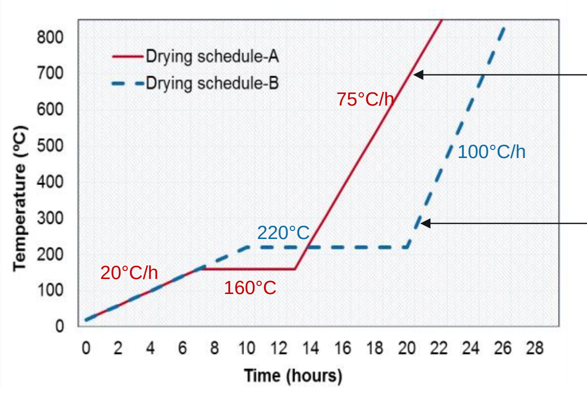
Drying schedule vs. explosive spalling



- The microsilica-gel bond system contains only small amounts of bound water. Once the free water is removed, the castables can be fired at a very high heating rate.
- The dimension of the samples and the drying schedule have strong impact on the drying behaviour.

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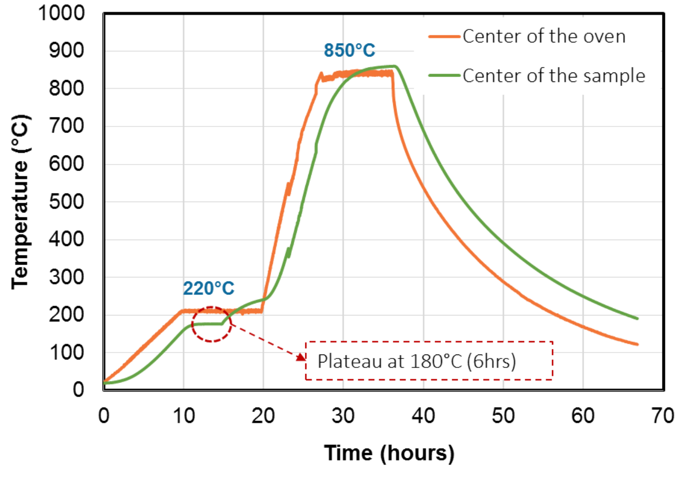
Temperature development in the specimen



The temperature in the specimen stabilises at 180°C for 6hrs although the temperature in the oven is kept at 220°C.

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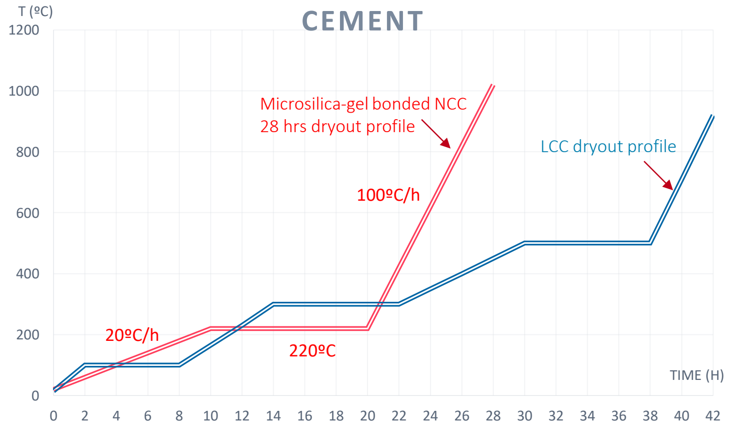
Example of heat-up program for a rotary kiln



For microsilica-gel bonded castable nearly all the water will evaporate during drying at low temperature. After drying at 220°C for 10hrs, about 97% of the water is removed and the castable can be heated to 850°C at a heating rate of 100°C/hr.

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Summary: faster dryout of microsilica-gel bonded NCCs

- The microsilica-gel bond system contains only small amounts of bound water. Once the free water is removed, the castables can be fired at a very high heating rate.

But …

- Extra care is needed during dryout on site; otherwise, explosion or spalling may occur
- Fast drying is slightly challenging in microsilica-gel bonded NCC

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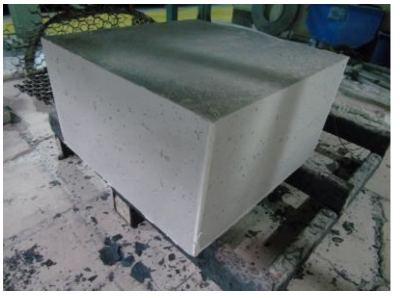
Example 2:
Improved explosion resistance
by using drying agent (EMSIL-DRY™)

Industrial-scale explosion resistance testing

- **Sample sizes:**
  - 300mm cubes(75-80kg)
  - 600 x 600 x 350mm (~400kg)

- **Preparation and test procedure**
  - Cured at room temperature for 24hrs, then demoulded and put directly into the furnace.
  - The heating schedule for this explosion test was heating from 20 to 850°C at 50°C/hr; cooling from 850 to 20°C at 50°C/hr.
  - All samples were monitored with a thermocouple embedded in the center of the block

- **Objective:**
  - To investigate the effect of drying agent/fibers on explosion resistance



Microsilica-gel bonded NCC without PP fiber

- Microsilica-gel bonded tabular alumina based NCCs containing SioxX-Zero without EMSIL-DRY™, was chosen for industrial-scale explosion resistance testing
- Weight of the block: 80 kg
- The block was demoulded after 24hrs at room temperature, then put into the oven for explosion testing
- A rapid heating schedule from 20 to 850°C at a constant rate of 50°C/hr was used

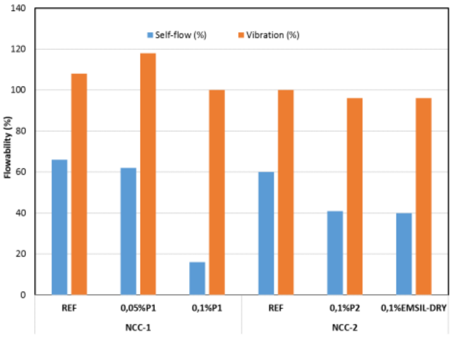
It may explode even without hydrates ….
80kg block fired at 50°C/hr from room temperature

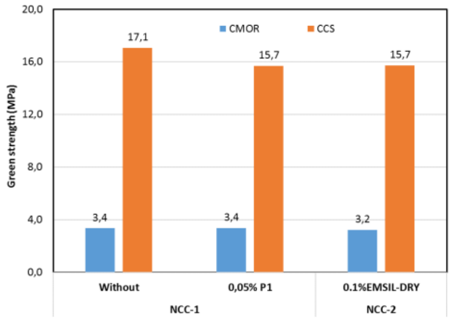
After opening…. ☹

EMSIL-DRY™ in gel bond system

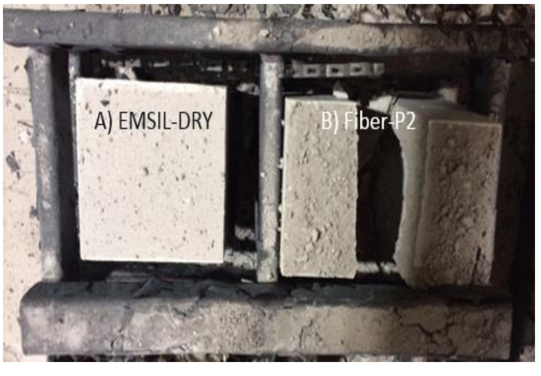
	NCC-1			NCC-2		
	A	B	C	D	E	F
Bauxite, 0-6mm	65,5	65,5	65,5	52	52	52
Kyanite, 0-0,16mm	2,5	2,5	2,5			
Sintered alumina, 0-0,5mm	10	10	10	30,5	30,5	30,5
Alumina Fines	12,5	12,5	12,5	10	10	10
Elkem 971U	6	6	6	6	6	6
SioxX-Zero	3	3	3	3	3	3
70% CAC	0,5	0,5	0,5	0,5	0,5	0,5
Fiber-P1		0,05	0,1			
Fiber-P2					0,1	
EMSIL-DRY						0,1
Water content	4,5	5		4,4		

H. Peng, B. Myhre, "Improvements in drying behaviour and explosion resistance of microsilica-gel bonded no-cement castables", Refractories Worldforum, 9(2017) (3), 61-65



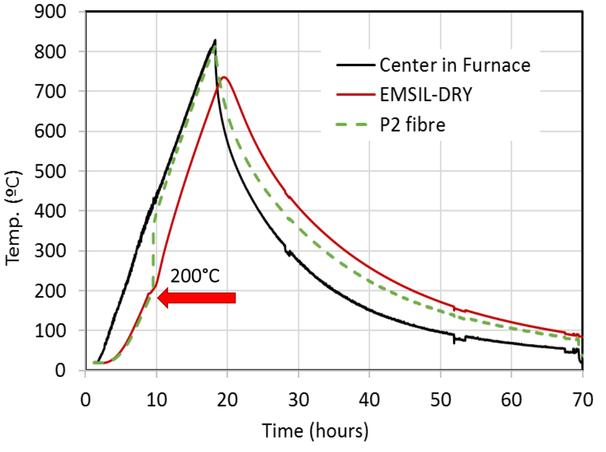


Microsilica-gel bonded NCC with different drying agent



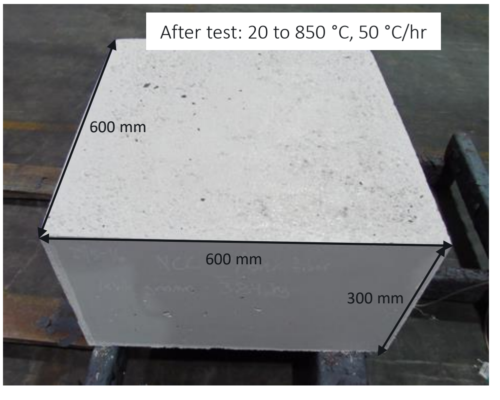
- The NCC castable with EMSIL-DRY shows excellent explosion resistance
- The exploded photo clearly indicates the explosion process: i)the dried thickness from the surface inwards the center, ii) a big explosion from the center to the surface, and iii) the undried part in the center exploded gradually and left a hole-like surface

Temperature inside the blocks versus furnace temperature



- The block with Fiber-P2 disintegrated at a core temperature of about 200ºC while the temperature in the furnace was 400ºC.
- For the sample containing EMSIL-DRY, there was a small "break" around 200ºC even though no plateau as appeared
- This indicates that an endothermic reaction is taking place at the "break" point, such as a massive evaporation.

Block (400kg) with 0.1% EMSIL-DRY™

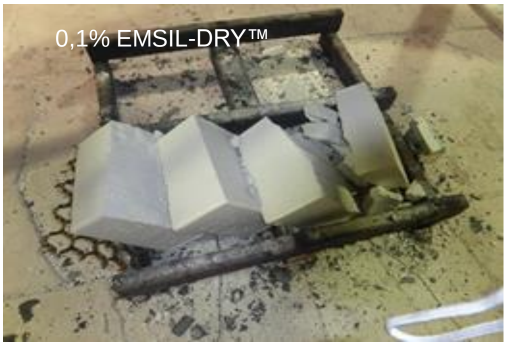


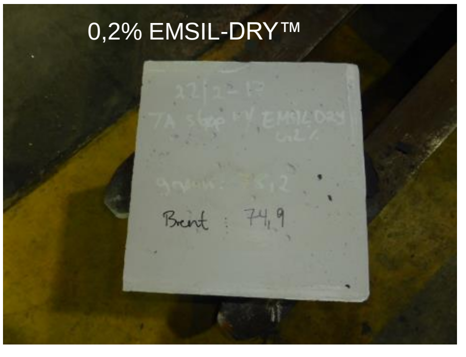
- A perfect 400kg block was produced with no problems using a fast firing schedule

What about fast-firing?

75°C/hr – is that attainable?

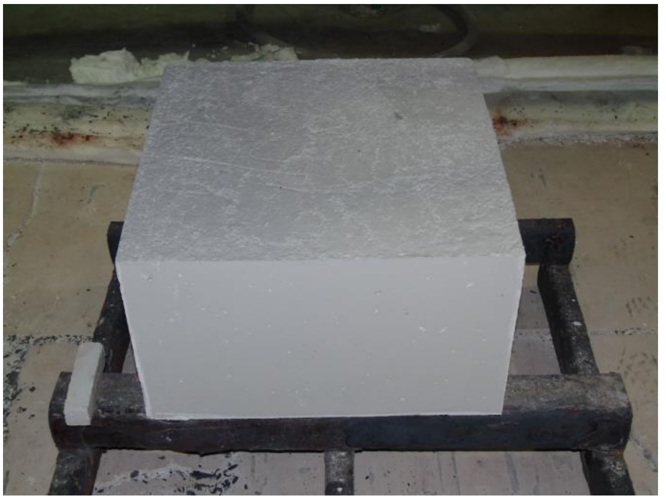
75kg NCC green block fired at 75°C/hr



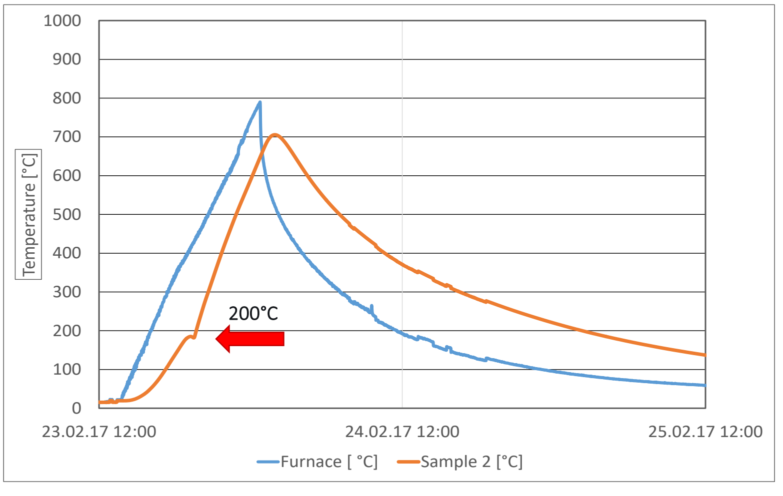


- The block was demoulded after 24hrs at room temperature, then put into the oven for explosion testing
- A rapid heating schedule from 20 to 850°C at a constant rate of 75°C/hr was used

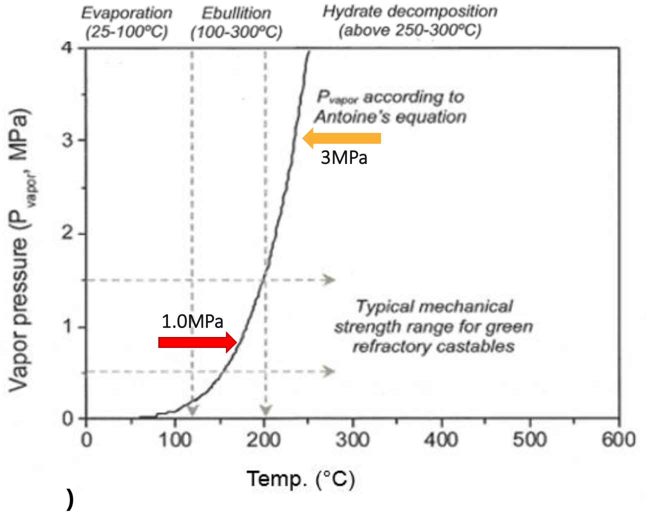
400kg block after test



400kg green block fired at 75°C/hr (0,2% EMSIL-DRY™)



Vapour pressure under heat-up



)

- Removing the free water as much as possible at lower temperature is crucial for fast dryout.
- Adding EMSIL-DRY seems to be a powerful tool to minimise the steam entrapment within the microstructure during **Ebullition (100 - 300°C)**

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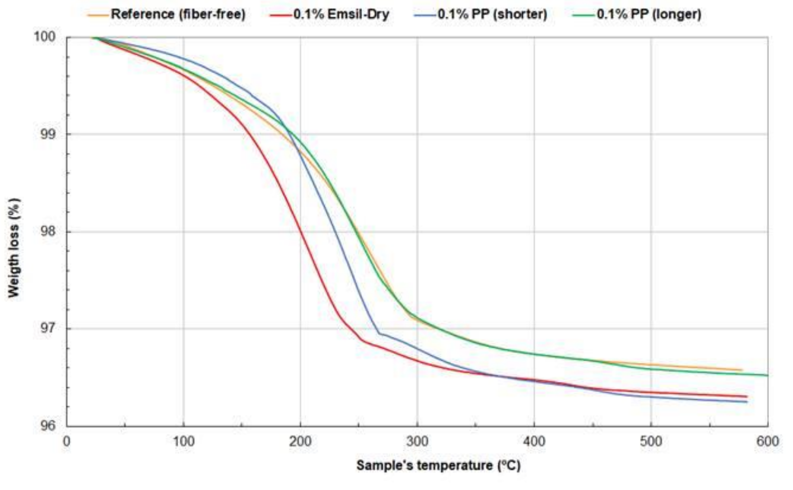
Weight loss of NCC with various fibers



- 0.1 % fiber dosage
- TGA tests after 1 day curing at 25°C and heating rate of 20°C/min.
- EMSIL-DRY had the best drying behavior compared to the two PP fibers.

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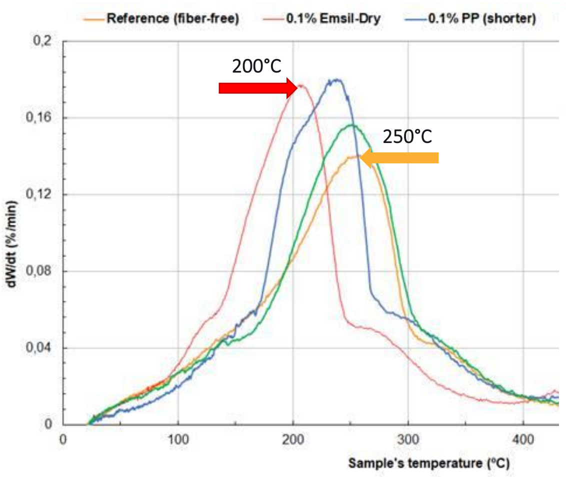
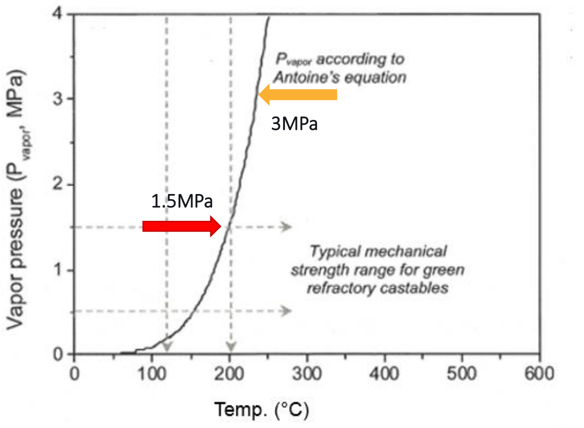
Drying rate of NCC with various fibers





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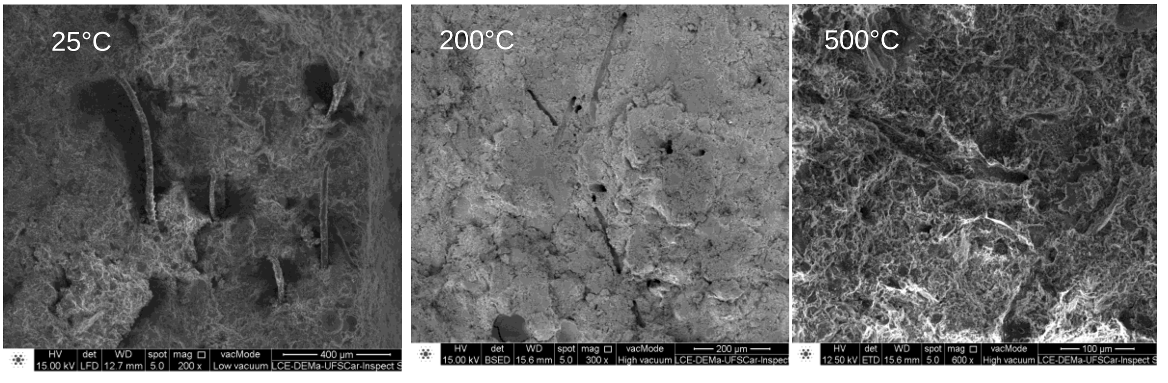
SEM of NCCs with EMSIL-DRY after firing at different Temp.



- At 200°C, the EMSIL-DRY have already melt and leave very nice channels for dewatering
- To combine good green-strength and fast-firing properties seems a difficult task – almost impossible, but finally, a solution has been gradually crystallized

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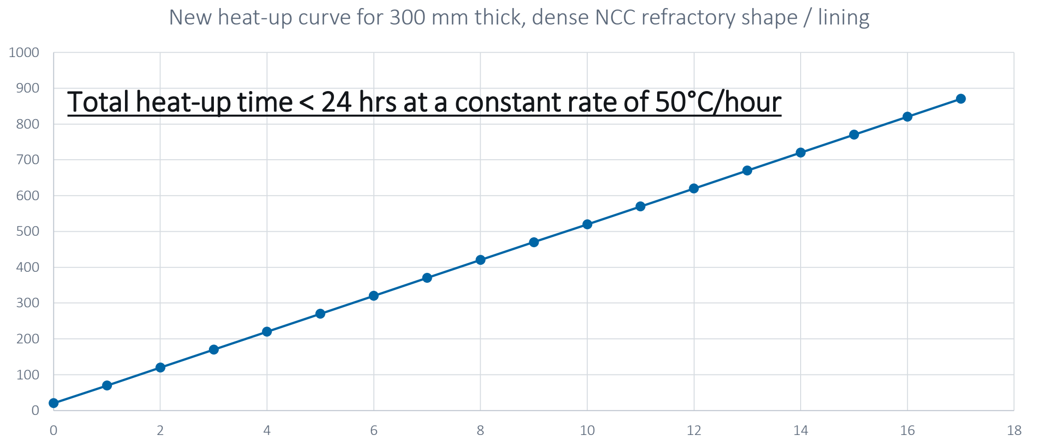
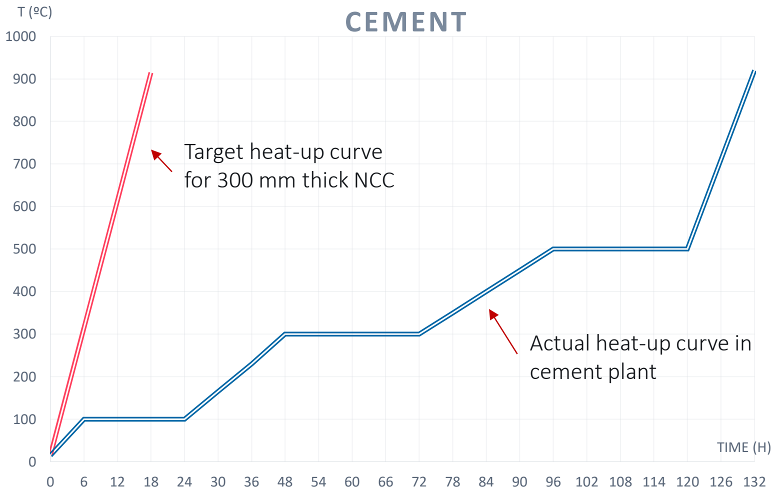
Change the way we heat-up monolithic refractories …

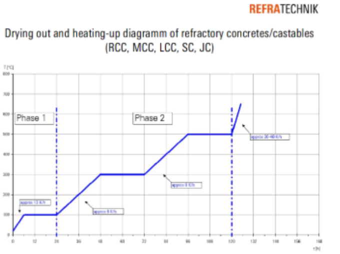


Summary: improved explosion resistance by using drying agent

- Microsilica-gel is a promising bond system, but could be challenging to fire very fast
- With EMSIL-DRY™ addition fast-firing becomes attainable. It turns out that EMSIL-DRY seems to be an efficient alternative for optimising the dryout schedule of monolithics by
  - Maximising water removal during evaporation period (20-100 **°C**)
  - Minimising the steam entrapment within the microstructure during **Ebullition (100 - 300°C)**
- For 400kg green blocks:
  - With 0.1% EMSIL-DRY™ at firing rate of 50°C/h was possible
  - With 0.2% addition, even 75°C/h was successful

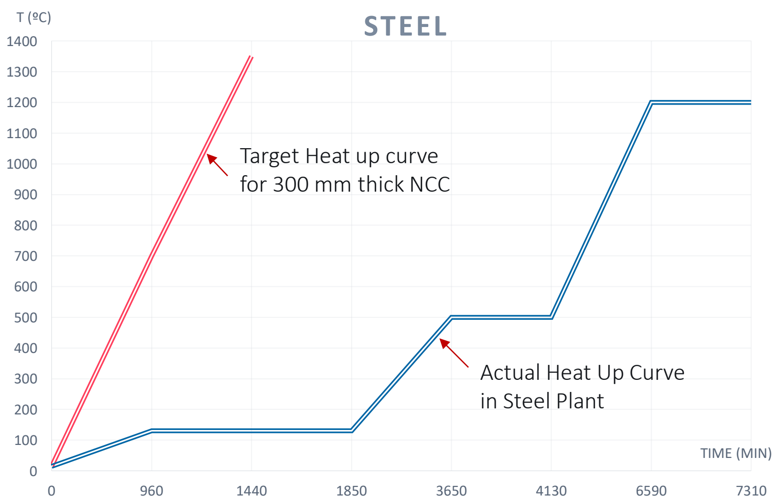
The heat-up challenge (explosion resistance)

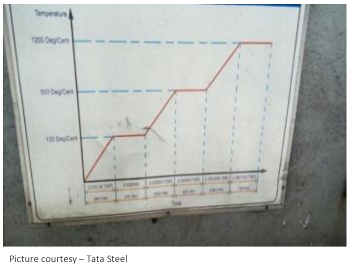




Picture courtesy – Refratechnik

The heat-up challenge (explosion resistance)





Picture courtesy – Tata Steel

EMSIL-DRY™
The way to make monolithics. No cracks… No explosions…

Before and after explosion resistance test (400kg LCC with EMSIL-DRY)

Video

Industrial-scale applications of NCCs with EMSIL-DRY

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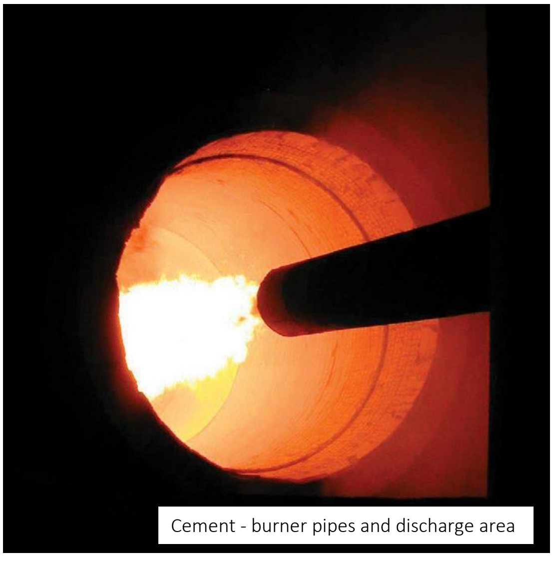
Application areas

Microsilica-gel bond castables/ pumpables give benefits both in terms of ease of application and technical properties in a variety of industries:

- **Cement industry** - high temperature rotary kiln burning zone, rotary kiln incinerator lining, nose ring, bull nose, burner tilt, TAD off-take, raiser duct, coolers….
- **Glass industry** - outside the glass melting tank furnace, sidewalls and roofs
- **Iron & Steel**
  - In **blast furnace troughs** – a better lining can be installed by pumping a highly workable NCC thus reducing installation time
  - In **torpedo ca**rs and other transfer ladles, tundish back-up lining, electric arc furnace (EAF) deltas and runners
  - In **secondary operations** - reheating furnace hearth, roof.
    - Gel-bond castables/pumpables have shown significant improvements especially in reheating furnace roof areas, both during installation and drying (which only takes about 60% of the time compared to conventional ramming mixes & plastics)

Applications of microsilica-gel bond castables


Cupola furnace castable


Cement - burner pipes and discharge area

Applications of microsilica-gel bond castables

Elkem
A Bluestar Company

Why do industrial-sized monolithics sometimes explode during heat-up?

Is there a remedy to ensure safe and fast heat-up of castables?

Elkem
A Bluestar Company

Acknowledgement

• Mr. Andrea Alfano and Mr. Roy Hagen for lab-work

More technical papers from Elkem:
https://www.elkem.com/silicon-materials/refractories/

Contact info: Hong.peng@elkem.no

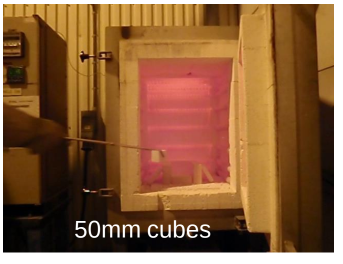
Papers

- B. Myhre and H. Peng, "Why do industrial-sized no-cement castables sometimes explode during heat-up? A remedy to ensure safe and fast heat-up of microsilica-gel bond castables." *Proc. 53th Symp. On Ref. Am. Ceram. Soc* (2017) pp 43-56
- H. Peng, B. Myhre, "Improvements in drying behaviour and explosion resistance of microsilica-gel bonded no-cement castables", Refractories Worldforum, 9(2017) (3), 61-65
- H. Peng and B. Myhre, "Further development of microsilica-gel bonded non-cement castables." *Refractories Engineer*, January 2016, p. 22-25
- H. Peng, B. Myhre, "Comparison of Setting Behaviour and Mechanical Properties of Various Silica- Bonded No-cement Castables", China's Refractories, vol 26. No.1 (2017), 8-12

DELIVERING YOUR POTENTIAL

Lab-scale explosion resistance test of NCC (green samples)

20°C/24hr	NCC-2-Ref	NCC-2-EMSIL-DRY	NCC-2-P1	S-NCC-2-P2
300	OK	OK	OK	OK
350	Exploded	OK	OK	OK
400		OK	OK	OK
500		OK	Exploded	Exploded
600		Exploded		
110°C/24hr				
1000	OK	OK	OK	OK



- Explosion resistance has been significantly improved by adding fibres.
- The drying agent EMSIL-DRY seems to provide best explosion resistance performance.

- After drying at 110°C for 24hrs, about 83-86% water was removed and all specimens survived at the explosion test temperature of 1000°C.

Video of microsilica-gel bonded NCC with SioxX-Zero

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Precast at customer site with SioxX-Zero and Emsil-DRY

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