

Dring Behaviour and Explosion Resistance of No-Cement Refractory Castables

H. Peng, B. Myhre

For cement bonded refractory castables explosive spalling due to removal of free water and/or dehydration of cement hydrate have always been challenging. Naturally, cement free castables are very interesting due to fast dry-out and excellent hot properties. However, their green strength is often so low that even the removal of free water becomes a challenge, particularly in larger pieces. Drying industrial-scale specimens are not straight forward and always more complicated than lab-scale samples. In this paper, the dry-out behaviour and explosion resistance of microsilica-gel bonded No-Cement Refractories (NCCs) have been evaluated based on testing of large industrial-scale specimens. The mechanism of fast dry-out behaviour of microsilica-gel bonded NCC with and without drying agents was evaluated by TGA analysis and SEM characterisation. Replacing cement bond with microsilica-gel bond results in true fast dry-out and improved explosion resistance. The explosion resistance can further be significantly improved by using a specialty drying agent (EMSIL-DRY™); as demonstrated by the problem free production of a perfect 400 kg block of microsilica-gel bonded NCC using a fast firing schedule (20–850 °C at a heating rate of 50 °C/h).

1 Introduction

Cement free castables such as colloidal silica bonded refractory castables are very interesting due to their fast dry-out and excellent hot properties. However, their green strength is often so low that demoulding and handling after curing become a challenge, particularly for larger pieces as opposed to small laboratory test specimens [1–3]. Recent work by Elkem demonstrates that microsilica-gel bonded NCCs show improved green strength compared to colloidal silica bonded, excellent hot properties and exhibit fast dry-out performance compared to LCCs [4–9]. In microsilica-gel bonded no-cement castables, only a

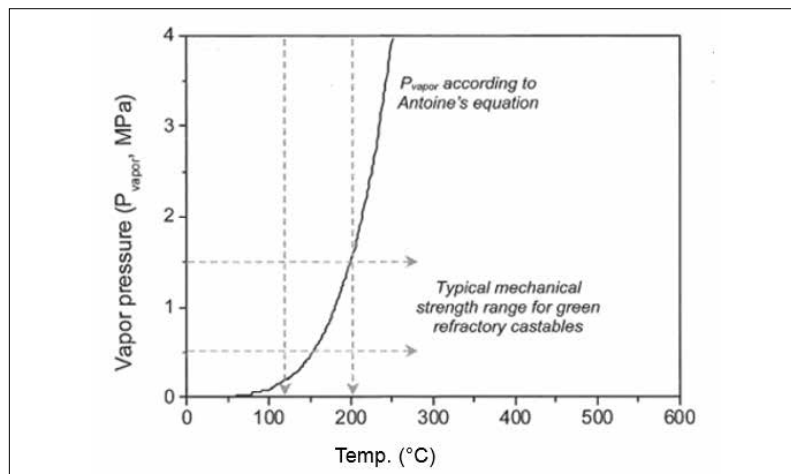


Fig.1 Vapour pressure (P_v) increases exponentially with the temperature according to Antoine's equation (11)

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very small amount of the mixing water is retained after drying at 110 °C, hence, most of the free water can be removed by simple drying. In LCC, a high fraction of the water is chemically bound and must be fired at temperatures up to 600 °C to remove it.

The vapour pressure increases potentially with the temperature in a closed liquid/vapour aqueous system, as described by Antoine's equation [10].

$$\log_{10} p = A - \frac{B}{C + T} \quad (0-374 \text{ } ^\circ\text{C})$$

Fig. 1 [11] shows the evolution of vapour pressure (P_v) as a function of temperature according to Antoine's equations and the typical green tensile strength for refractory castables are indicated. The dry-out process of cement bonded castables involves 3 stages:

- evaporation from room temperature to 100 °C,

- ebullition from 100 to ~300 °C,
- hydrate decomposition at a temperature above 250–350 °C.

When the temperature in the sample reaches 100 °C, the ebullition starts and leads to massive water loss, and the water removal is ruled by vapour pressure. This is the most critical dewatering step and spalling and/or explosion most likely takes place in this stage. Vapour pressure is dependent on the heating profile and the permeability and thickness of the refractory body. It has always been challenging to remove the water in the centre of refractory LCCs.

Hence, optimisation of dry-out schedules and improvement in permeability of hydraulic bonded refractories have been given special attention to reduce the risk of spalling and/or explosion.

The permeability of hydraulic bonded refractory castables can be increased by

- adding polymeric fibres or Al-metal powders [11], and
- replacing cement by colloidal silica to inhibit hydrate formation [12]. The first alternatives have been investigated for many decades. The latter, cement-free binder, has been the state-of-the-art for fast dry-out castables.

However, drying industrial-scale specimens are not easy and always more complicated than lab-scale samples. In this paper, tabular alumina based refractory castables have been chosen to investigate the dry-out behaviour and explosion resistance based on both lab-scale and industrial-scale trials. The following aspects are covered:

- effects of drying agent/anti-explosion agent on flowability and mechanical strength,
- improvement in explosion resistance of microsilica-gel bonded NCC by introducing anti-explosion agent, EMSIL-DRY™,
- investigation of the fast dry-out mechanism using Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) characterisation of NCCs.

2 Experimental

2.1 Mix design

Tab. 1 shows the overall compositions of microsilica-gel bonded NCCs. Different fractions of tabular alumina (Almatis/DE) were used as aggregate, and microsilica (Elkem Microsilica® 971U, Elkem) and SioxX®-Zero (Elkem) were used as binder. SioxX®-Zero

Tab. 1 Mix design of tabular alumina based NCCs [mass-%]

	REF	P1	P2	P3	EMSIL-DRY™
Elkem Microsilica® 971U	5	5	5	5	5
Cement (70 % Al ₂ O ₃)	0,5	0,5	0,5	0,5	0,5
Tabular alumina 0–6 mm	82,5	82,5	82,5	82,5	82,5
Al ₂ O ₃ fines	9	9	9	9	9
SioxX®-Zero	3	3	3	3	3
Fibre-P1		0,05			
Fibre-P2			0,1		
Fibre-P3				0,1	
EMSIL-DRY™					0,1

is a tailor-made product for microsilica-gel bonded NCCs. Four types of drying agent/anti-explosion agent were used in the tests:

- three commercially available fibres, labelled Fibre-P1, -P2, -P3,
- one specialty fibre (EMSIL-DRY™ Elkem). EMSIL-DRY™ is a special polymeric fibre for refractory castables to speed up the drying and reduce the risk of spalling and explosion during heat-up.

The main features of EMSIL-DRY™ can be summarized as:

- marginally impairs flow of fresh castable,
- no negative effect on the high green-strength of microsilica-gel bonded NCC,
- low melting point: 100–120 °C.

The water addition was 4,35 % for all mixes.

2.2 Experimental procedures

Self-flow and vibration-flow were measured after 4 min wet-mixing using the flow-cone described in ASTM C230 (height 50 mm, not the 80 mm self-flow cone described in EN 1402-4:2003). The self-flow value is the percentage increase of the diameter measured 90 s after removing the cone.

Lab-scale explosion resistance testing per Chinese Standard YB/T4117-2003 were carried out for all mixes. 50 mm cubes are placed into a hot furnace at a pre-set temperature. The cubes are inspected after 30 min exposure. The temperature at which cracks start to form or explosive spalling occurs is reported as the explosion resistance. For industrial-scale explosion resistance tests, the castables were cast into larger moulds with dimensions of:

- 300 x 300 x 300 mm (~80 kg), and
- 600 x 600 x 350 mm (~400 kg).

The castables were de-moulded after one day and placed in the oven for further dry-

ing behaviour studies and/or explosion resistance tests. The heating schedule for the explosion test was 20–850 °C at 50 °C/h; cooling from 850–20 °C at 50 °C/h.

3 Results and discussion

3.1 Flowability

Self- and vibration-flow measurements are summarised in Fig. 2. The addition of Fibre-P2, -P3 and EMSIL-DRY™ is 0,1 % while Fibre-P1 had to be reduced to 0,05 % to achieve similar flow. The self-flow and vibration-flow values with fibres at a water addition of 4,35 % are approximately 40 % and 100–120 %, respectively. When 0,1 % Fibre-P1 was used, the self-flow value dropped to a mere 12 % and caused problems to cast samples. Tab. 2 shows the green crushing strength (CCS) and modulus of rupture (CMOR) (24 h at >90 % RH and 20 °C). The microsilica-gel bonded NCCs with EMSIL-DRY™ has adequate green strength, with CCS of 11,2 MPa, slightly higher than the others. The results show that the type of fibres have some impact on strength development.

3.2 Lab-scale explosion resistance

Microsilica-gel bonded NCCs with different drying agents were used to further investigate the drying behaviour. Tab. 2 shows the lab-scale explosion test results of both “wet” and “dried” samples tested according to Chinese Standard YB/T4117-2003. The samples were cured for 24 h at room temperature and 100 % relative humidity before de-moulding. The freshly de-moulded samples are labelled “wet” and samples further dried for 24 h at 110 °C are called “dried”. All “dried” samples show excellent explosion resistance and pass the

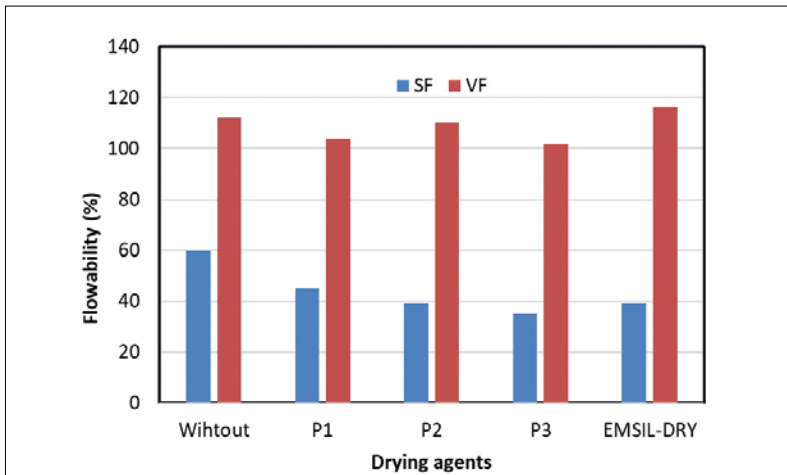


Fig. 2 Flowability of microsilica-gel bonded NCCs with different drying agents

Tab. 2 Mechanical strength after demoulding and drying of tabular based NCCs with various fibres [MPa]

		REF	P1	P2	P3	EMSIL-DRY™
20 °C/24 h	CMOR	2,6	2,0	2,9	3,4	3,1
	CCS	8,9	9,7	8,6	8,5	11,2
110 °C/24 h	CMOR	6,4	6,3	7,4	5,7	7,1
	CCS	44,6	32,5	30,4	41,6	42,8

Tab. 3 Explosion resistance of microsilica-gel bonded NCCs

		Wet [20 °C/24 h]				
Temp. [°C]	Ref	P1	P2	P3	EMSIL-DRY™	
300	√	√	√			
350	x	x	√			
400		x	x	√	√	
450				x	√	
500				x	√	
550					x	
		Dried [110 °C/24 h]				
1000	√	√	√	√	√	
1200	√	√	√	√	√	

√: passed; x: failed



Fig. 3 ~80 kg block (A) before and (B) after explosion resistance test (from 20–850 °C at 50 °C/h)

test at 1200 °C. The good performance is attributed to a stable bond phase and the low amount of residual water in the bond phase. When the “wet” samples were tested, good explosion resistance was achieved for the microsilica-gel bonded NCC containing anti-explosion agents. For the REF mix and the mix with low dosage Fibre-P1, the specimens only survived the test at 300 °C, and exploded at 350 °C. The mix with EMSIL-DRY™ had the best explosion resistance. This indicates that EMSIL-DRY™ causes the fastest dewatering of the NCC samples.

3.3 Industrial-scale explosion resistance

To further improve and understand the explosion resistance, two types of larger blocks with and without fibre addition were produced, ~80 kg (300 mm cubes) and ~400 kg (600 mm x 600 mm x 350 mm). All blocks were cured at room temperature for 24 h, then de-moulded and put directly into the furnace. The heating schedule was 20–850 °C at 50 °C/h; cooling from 850–20 °C at 50 °C/h.

Fig. 3 shows ~80 kg (300 mm) microsilica-gel bonded NCC cubes without drying agent before and after the explosion resistance test. With no addition of drying agent, the 80 kg block disintegrated during the test and parts of the block was completely pulverised.

Fig. 4 shows ~80 kg (300 mm) cubes containing Fibre-P1, -P3 and EMSIL-DRY™ after explosion resistance test at 850 °C. The NCC with Fibre-P2 exploded and looked like the cube with Fibre-P1. Further an NCC with 0,1 % Fibre-P1 was also tested and this exploded. The castables with EMSIL-DRY™ and Fibre-P3 show good explosion resistance and the ~80 kg blocks were perfect after the test, whereas the blocks with Fiber-P1 and -P2 disintegrated completely. This confirms that the type of fibres has strong impact on explosion resistance and that the risk of explosion could be high when an improper fibre is used.

It is difficult to differentiate the effect of EMSIL-DRY™ and Fibre-P3 on the explosion resistance since both blocks were perfect after the test (Fig. 4). Hence, the authors carried out further explosion resistance testing on ~400 kg blocks (600 mm x 600 mm x 350 mm) containing both

EMSIL-DRY™ or Fibre-P3. Fig. 5 shows the blocks after the tests. The block containing EMSIL-DRY™ performed perfectly at a heating rate of 50 °C/h while the one with Fibre-P3 disintegrated into several pieces.

The explosion resistance tests show that both lab-scale and industrial-scale NCC with EMSIL-DRY™ exhibit the best explosion resistance. A good correlation between the lab-scale and industrial-scale test results has also been observed. In other words, lab-scale explosion resistance tests may provide good guidance for industrial installation. Not surprisingly, the higher the temperature at which the lab-scale specimens survive, the better the explosion resistance becomes for large blocks.

3.4 Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) characterisation

To understand the mechanism of fast dry-out behaviour, a tabular alumina based microsilica-gel bonded NCCs with and without EMSIL-DRY™ (Tab. 1), were produced for TGA analysis and SEM characterisation. For the TGA measurement the specimen size was 40 mm x 40 mm cylindrical and the heating rate was 20 °C/min.

Fig. 6 illustrates the dry-out behaviour of microsilica-gel bonded NCCs. The drying rate of both specimens was about similar up to ~125 °C after which the drying rate (weight loss in % per min) of the NCC specimen with EMSIL-DRY™ was much higher than the reference specimen. At 185 °C, the specimen with EMSIL-DRY™ reached its maximum drying rate of 0,19 % per min, whereas the reference specimen exploded. The drying rate before the explosion was merely 0,08 % per min indicating that much more free water remained in the NCC specimen without fibre in the temperature range from 125–185 °C. The vapour pressure in the centre of the specimen without fibre was much higher than in the one with EMSIL-DRY™. This explains why the one without drying agent exploded while the one with EMSIL-DRY™ survived the TGA measurement.

When the temperature exceeds the melting point of EMSIL-DRY™ numerous channels are produced, facilitating water removal during the ebullition stage, as exemplified

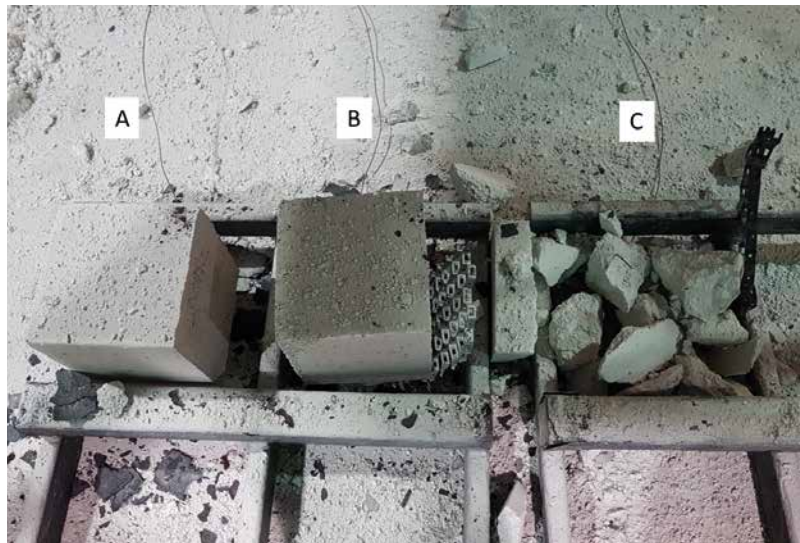


Fig. 4 ~80 kg (300 mm) cubes with different fibres after explosion resistance test (from 20–850 °C at 50 °C/h): A) Fibre P3, B) EMSIL-DRY™, and C) Fibre-P1. The NCC with Fibre-P2 looked like cube C) Fibre-P1

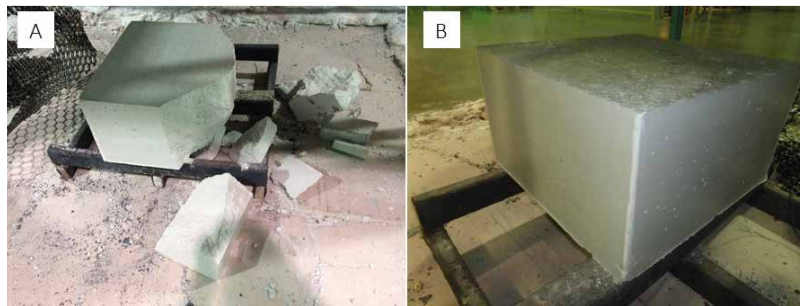


Fig. 5 ~400 kg blocks after explosion testing at 850 °C: A) Fibre-P3, and B) EMSIL-DRY™

in Fig. 7. The NCC with EMSIL-DRY™ sample contains needle-like channels, indicating that the vapour pressure inside the NCC

specimen with EMSIL-DRY™ should be much lower than the reference. Therefore, at a heating rate of 20 °C/min during the

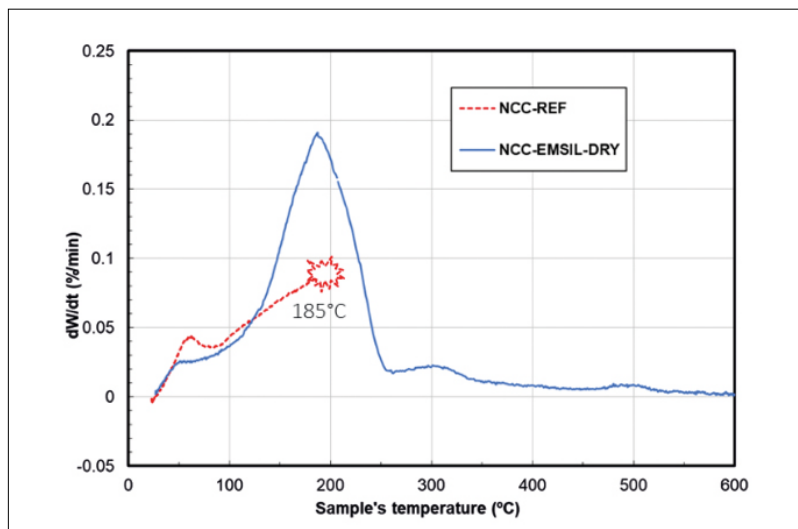


Fig. 6 Drying rate as a function of sample temperature

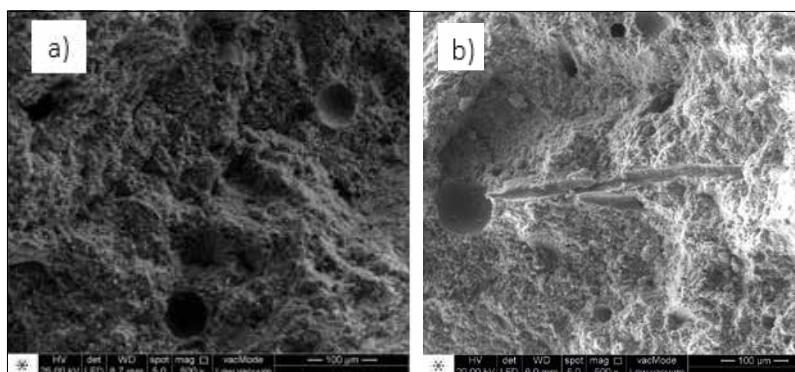


Fig. 7 SEM of fractured surface of samples heated at 200 °C for 12 h: a) NCC REF, and b) NCC with EMSIL-DRY™

TGA, the NCC with EMSIL-DRY™ remains intact, while the reference exploded at 185 °C. All this demonstrates that the explosion resistance/drying behaviour of microsilica-gel bonded NCCs is significantly improved using EMSIL-DRY™ that contributes to fast dewatering during heating/firing. It indicates that true rapid heating is possible.

4 Conclusions

Based on these studies of flowability, drying behaviour, explosion resistance, TGA and SEM characterisation of microsilica-gel bonded NCCs with and without drying/anti-explosion agents, the following conclusions can be drawn.

- The type of drying agent has a strong influence on flow.
- The microsilica-gel bond system contains only small amounts of bound water. Once the free water is removed, the castables can be fired at very high heating rates.

- With introduction of EMSIL-DRY™, the drying rate has been significantly improved.
- Explosion resistance of lab-scale samples and of large industrial-scale blocks show good correlation.
- The microsilica-gel bonded NCC with EMSIL-DRY™ has excellent explosion resistance. A ~400 kg block was heated, with no holding times, from 20–850 °C at a heating rate of 50 °C/h – it came out perfect!

References

- [1] Connors, C.W.; Anderson, M.W.: Colloidal silica refractory system for an electric arc furnace. US Patent 6528011, 4 March 2003
- [2] Ismael, M.R.; Anjos, R.D.; Salomão, R.; Pandolfelli, V.C.: Colloidal silica as a nano-structured binder for refractory castables. *Refract. Appl. News* **11** (2006) [4] 16–20
- [3] Peng, H.; Myhre, B.: Comparison of Setting Behaviour and Mechanical Properties of Various

Silica-Bonded No-cement Castables. *China's Refractories* **26** (2017) [1] 8–12

- [4] Myhre, B.; Sunde, K.: Alumina based castables with very low contents of hydraulic compound. Part II. Strength and High-Temperature Reactions of No-cement Castables with Hydraulic Alumina and Microsilica. *Proc. UNITECR'95*, Kyoto, Japan, 19–22 Nov. 1995, II/317–24
- [5] Myhre, B.; Peng, H.: Microsilica-gel bonded castables – a bond with potential. *Proc. 53rd Symp. on Ref. Am. Ceram. Soc* (2015) 43–56
- [6] Myhre, B.; Peng, H.: 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. 53rd Symp. on Ref. Am. Ceram. Soc* (2017) 43–56
- [7] Myhre, B.; Peng, H.: Microsilica-gel bond castables with potentials. *Proc. 49th Symp. on Ref. Am. Ceram. Soc* (2015) 112–121
- [8] Myhre, B.; Peng, H.: Microsilica-Gel Bonded Refractory Castable with Improved Setting Behaviour and Mechanical Properties. *refractories WORLDFORUM* **7** (2015) [3] 69–75
- [9] Myhre, B.; Peng, H.: Improvements in Drying Behavior and Explosion Resistance of Microsilica-Gel Bonded No-Cement Castables. *refractories WORLDFORUM* **9** (2017) [3] 61–65
- [10] Reid, R.G.; Prausnitz, J.M.; Poling, B.E.: *The properties of gases and liquids*. McGraw-Hill International (1989) 208–209
- [11] Saloao, R.; Bittencourt, L.R.M.; Pandolfelli, V.C.: Drying behaviour for refractory castables: aluminium powder and polymeric fibers. *Ceramica* **54** (2008) 259–267
- [12] Parr, Chr.; Wöhrmeyer, Chr.: The advantage of calcium aluminate cement as a castable bonding system. *St. Louis Section Meeting, USA*, 2006

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