Improvements in Drying Behaviour and Explosion Resistance of Microsilica-Gel Bonded No-Cement Castables

H. Peng, B. Myhre

Microsilica-gel bonded no-cement refractory castables (NCCs) have drawn lots of interest lately, because of their easier handling, storage and transportation compared to silica-sol NCCs.
This paper mainly focuses on dry-out and explosion resistance of microsilica-gel bonded NCCs. The effects on water loss and explosion resistance of microsilica-gel bonded NCCs using different heat-up profiles, sample dimensions and types of drying agents have been studied in detail. The results confirm that the explosion resistance of microsilica-gel bonded NCCs can been further significantly improved by using a specialty drying agent (EMSIL-DRY™); a perfect 400 kg block was produced with no problems using a fast firing program (20–850 °C at a heating rate of 50 °C/h).

1 Introduction

Silica-sol bonded no-cement castables (NCCs) have been used in the refractory industry for many years. Compared to low-cement castables, they exhibit fast dry-out and excellent high temperature properties. However, the use has been limited due to long set-time/complex set-behaviour and inadequate development of green strength. Handling, storage and use of liquid silica-sol are logistic factors that must be dealt with, especially at lower temperatures [1–5].

Recently, microsilica-gel bonded no-cement castables (NCCs) have drawn increasing attention, not only because of easier handling, storage and transportation thanks to the "all-in-the-bag" solution, but also because of improved setting behaviour and higher green strength compared to silica-sol bonded NCC [6, 7]. Microsilica powder is introduced as a "dry-version" silica binder to replace silica-sol. Recent reports disclose that a genuine bond based on microsilica coagulation is created, and that the setting of microsilica-gel bonded castables is caused by cations, a similar set mechanism to colloidal silica [8–10]. The cations not only contribute to the reduction of the net repulsion effect of microsilica, but also bridge with the negatively charged microsilica particles. If, e.g. calcium aluminate cement is used as coagulating agent, Ca^{2+} (and/or other polyvalent cations) released during dissolution of the cement will react at the negative sites on the microsilica surface to form a three-dimensional network of linked microsilica particles. Therefore, the number of cations controls the set-time.

Based on our long experience and understanding of the characteristics of microsilica and its performance in refractory castables, a speciality product (SioxX®-Zero) was developed for microsilica-gel bonded NCCs [11]. By using SioxX-Zero in combination with polyvalent cations, microsilica-gel bonded NCCs attain improved green strength and controllable set-behaviour [11]. It not only provides similar advantages as silica-sol NCCs but also eliminates some of the drawbacks of a two-component system (e.g. frost sensitivity resulting in storage and transportation challenges). The bond system of microsilica-gel bonded NCCs contains only small amounts of bound water. Once the free water is removed, the castables can be fired at very high heating rates. Furthermore, it contains only a minor amount of cement as coagulating agent; hence, the hot properties are better than that of ULCCs and LCCs [12].

In this paper, bauxite based NCCs with microsilica-gel bond have been chosen to explore the drying behaviour and explosion resistance. The following aspects are covered: i) effects of drying agent/anti-explosion agent on flowability, ii) effects of drying agent/anti-explosion agent and sample dimensions on water loss and explosion resistance, and iii) improvement of explosion resistance by anti-explosion agent, EMSIL-DRY.

2 Experimental

2.1 Mix design

To understand the drying behaviour, two series of bauxite based NCCs were designed. Tab. 1 shows the mix designs. SioxX-Zero (Elkem/NO) is tailored for microsilica-gel bonded NCCs. The NCC-1 series was used to investigate the effect of sample dimensions and heat-up profiles on drying behaviour of industrial-scale samples. A modified

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

	NCC-1			NCC-2		
	A	B	C	D	E	F
Bauxite [0–6 mm]	65,5	65,5	65,5	52	52	52
Kyanite [0–0,16 mm]	2,5	2,5	2,5			
Sintered alumina [0–0,5 mm]	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		

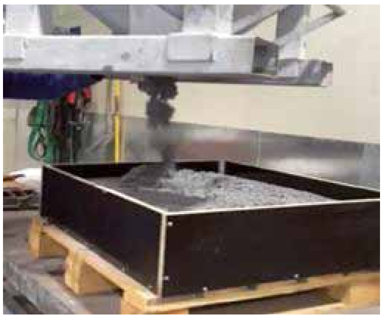

Fig. 1 Casting a 300 kg microsilica-gel bonded NCC block

recipe NCC-2 (modified due to availability of raw materials in the lab) was used for further explosion resistance tests. Since the SioxX-Zero contain both some alumina and microsilica as carrier material, the compositions were adjusted accordingly. Three types of drying agent/anti-explosion agent were used in the tests, i) commercial available fibres, P1 and P2, and ii) EMSIL-DRY from Elkem, Norway.

2.2 Experimental procedure

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 blocks, the castables were cast into larger moulds with dimensions of: i) 300 mm × 300 mm × 300 mm (~75 kg), ii) 800 mm × 600 mm × 200 mm (~300 kg) and iii) 600 mm × 600 mm × 350 mm (~400 kg). Fig. 1 shows the casting of a 300 kg microsilica-gel bonded NCC block. Blocks were demoulded after one day and put into the oven for further drying behaviour studies and/or explosion resistance tests. For industrial-scale explosion resistance tests, both 75 kg and 400 kg blocks were used.

3 Results and discussion

3.1 Flowability and green strength

Self- and vibration-flow measurements are summarised in Fig. 2. The addition of Fiber-P1 has a strong negative impact on the self-flow value. When the dosage increases from 0,05 % to 0,1 %, the self-flow value drops from 60 % to below 20 % at a water content of 5,0 %. When 0,1 % EMSIL-DRY and Fiber-P2 were introduced, the flowability was still fine, approximately 40 % at a water content of 4,4 %. At 5 % water, the self-flow was around 88 %. This indicates that the type of drying agent has a strong impact on flowability. Fig. 3 shows the green crushing strength (CCS) and modulus of rupture (CMOR) (24 h at >90 % RH and 20 °C). The microsilica-gel bonded NCCs have adequate green strengths, with CMOR around 3 to 4 MPa. The type of drying agent mainly influences the self-flow value, and does not interfere with the strength development.

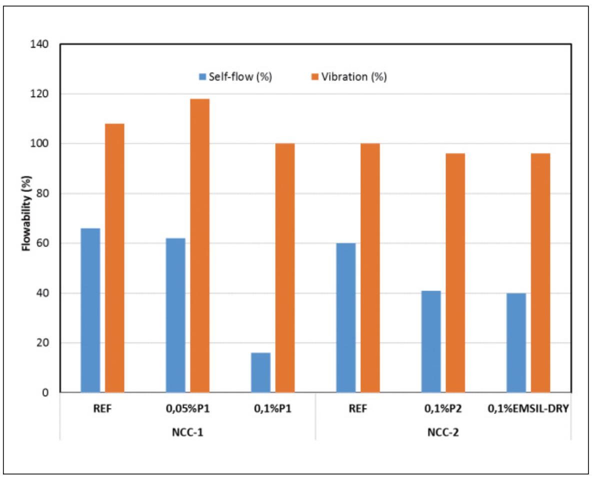

Fig. 2 Flowability of microsilica-gel bonded NCCs with different drying agents

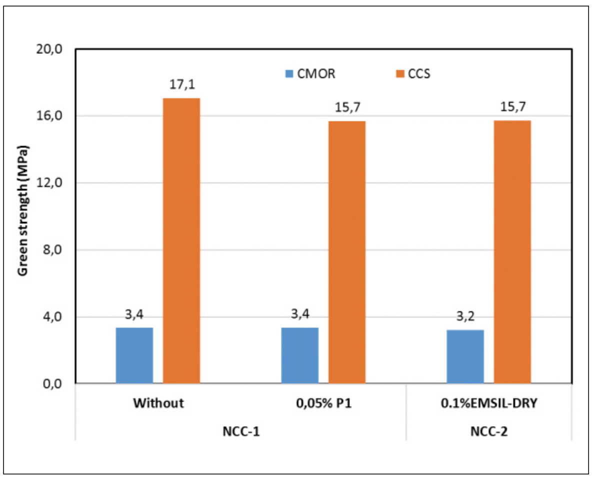

Fig. 3 Green strength of microsilica-gel bonded NCCs with different drying agents

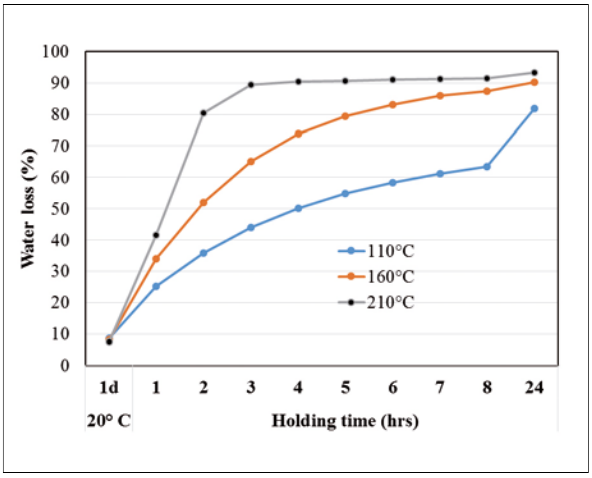

Fig. 4 Water loss of 100 mm cubes dried at different temperatures [6]

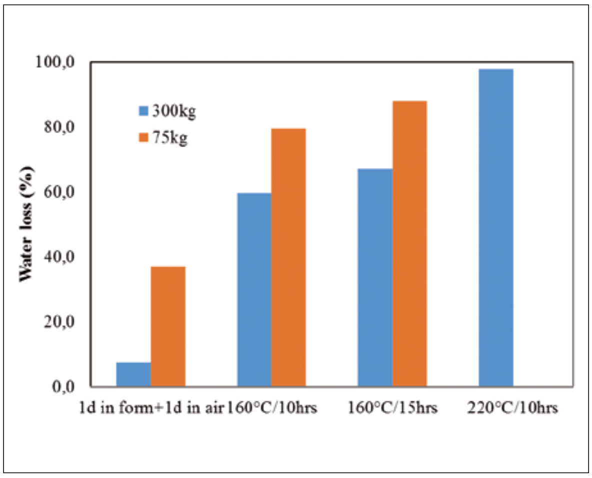

Fig. 5 Effect of samples size and holding temperature on removal of free water [6]

3.2 Drying behaviour and heat-up profiles

To understand the drying behaviour of microsilica-gel bonded bauxite NCC, lab-scale specimens (100 mm cubes) of NCC-1C were first tested at various temperatures. The water loss as a function of holding time is shown in Fig. 4. After 8 h at 110 °C, only about 62 % of the total water was released, whereas at 160 °C the water loss was some 88 %. When the temperature was increased to 210 °C, about 90 % of the total water was removed after 3 h drying.

Larger specimens, 300 mm cubes (~75 kg) and 800 mm × 600 mm × 200 mm blocks (~300 kg), were produced and dried at 160 °C and 220 °C. They were all intact after drying. The 300 kg blocks released water much slower than the 75 kg cubes as seen in Fig. 5. When the holding time at 160 °C was 10 h, the 300 kg block still contained more than 40 % of the water. However, when keeping the block at 220 °C for 10 h, as much as 97 % of the total water was removed.

To look at various heat-up schedules, more of the industrial-scale blocks (300 kg) were produced and dried using two different heat-up schedules, as shown in Fig. 6. Schedule-A is holding at 160 °C for 6 h before continuing to 850 °C at a rate of 75 °C/h. In schedule-B the block is kept at 220 °C for 10 h before continuing to 850 °C at the rapid rate of 100 °C/h.

When the block was heated from 160 °C to 850 °C at a heating rate of 75 °C/h, an increasing vapour pressure in the core of the block eventually exceeded the mechanical strength of the castable resulting in a complete disintegration of the block. Fig. 7 A shows the remainder of 300 kg NCC block. Unfortunately, the temperature inside this block was not monitored so we are unable to determine the exact temperature when it exploded. When a block was kept in the furnace at 220 °C for 10 h ~97 % water was removed (Fig. 5). The heating from 220 to 850 °C at a rate of 100 °C/h caused no problem at all, and a perfect block was produced (Fig. 7 B).

Fig. 8 shows the record of the temperature as a function of time for both the centre of the furnace and the core of the block. Surprisingly, a temperature plateau at ~180 °C

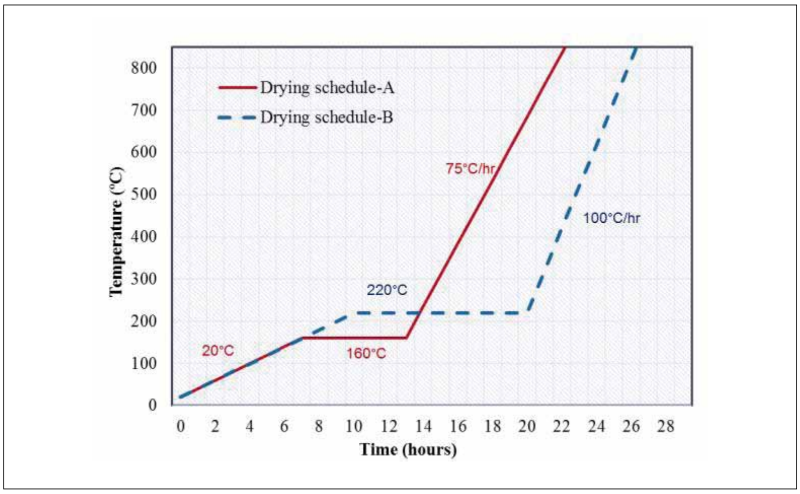

Fig. 6 Heat-up schedules

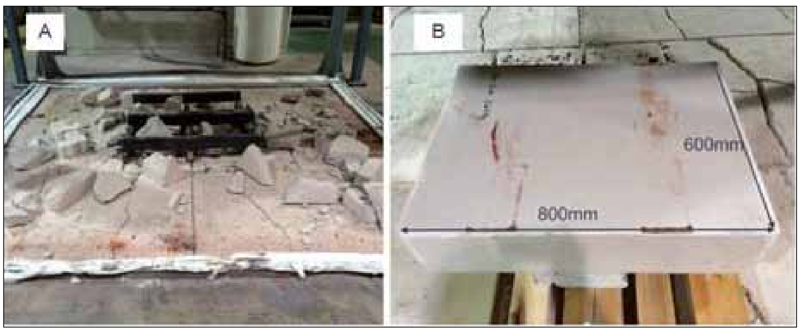

Fig. 7 300 kg blocks after rapid heat-up: A) drying schedule-A, and B) drying schedule-B6

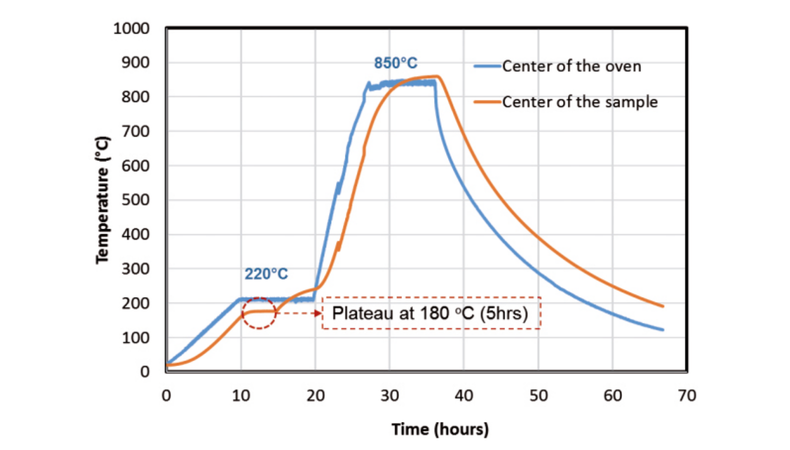

Fig. 8 Temperature development as a function of time

Tab. 2 Explosion resistance of microsilica-gel bonded NCC-2 with and without EMSIL-DRY

	Wet [20 °C/24 h]			Dried [110 °C/24 h]		
Temp. [°C]	Without	EMSIL-DRY	Fiber-P2	Without	EMSIL-DRY	Fiber-P2
300	√	√	√			
350	x	√	√			
400		√	√			
500		√	x			
600	x					
1000				√	√	√
1200				√	√	√

√: passed; x: failed

was observed in the core of the block. This indicates that an endothermic process is ongoing, e.g. boiling of water, decomposition of some hydrate or some other endothermic process. After approximately 5 h the source of the endothermic process is depleted and the temperature increases again and eventually attains the furnace temperature. Another 300 kg block was produced using a modified heat-up schedule-B where the holding time at 220 °C was reduced to only 6 h. After drying, the block was perfect. This confirms that the microsilica-gel bond system contains only small amounts of bound water, and that castables can be fired at very high heating rates as soon as the free water is removed, e.g. 100 °C/h as demonstrated, without problems.

3.3 Explosion resistance

Microsilica-gel bonded NCCs (castable NCC-2 in Tab. 1) were used for further investigations to better understand the drying behaviour. Both lab-scale and industrial-scale explosion resistance tests were conducted.

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 % RH 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 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. Without anti-explosion agent, the specimens only survived the test at 300 °C, and exploded at 350 °C. The one with EMSIL-DRY exhibited the best explosion resistance. It passed the test at 500 °C, whereas the one with Fiber-P2 exploded. This indicates that EMSIL-DRY causes the fastest dewatering of the NCC samples.

To further improve and understand the drying behaviour, a series of ~75 kg (300 mm) cubes were made.

The cubes were cured at room temperature for 24 h, 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/h; cooling from 850 to 20 °C at 50 °C/h.

Fig. 9 shows microsilica-gel bonded NCC without anti-explosion agent before and after the explosion resistance test. With no addition of drying agent, the 75 kg block disintegrated during the test and part of the block was completely pulverised.

Fig. 10 shows blocks containing EMSIL-DRY and Fiber-P2. The NCC-2 castable with EMSIL-DRY shows excellent explosion resistance and the ~75 kg block was perfect after the explosion resistance test. The block with Fiber-P2 fibre was divided into two large parts and a ball-like crater was observed in the core. This indicates that high vapour pressure was generated in the centre while the outer surface was hard, like an "autoclave".

When the vapour pressure in the centre exceeded the mechanical strength, the block disintegrated. Certainly, the explosion

Fig. 9 ~80 kg block before (A), and after (B) explosion resistance test

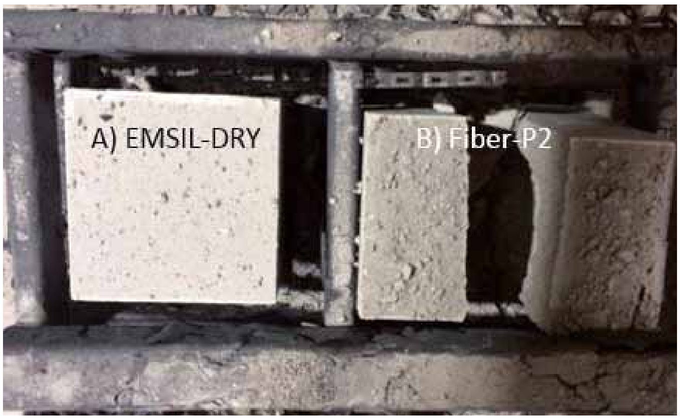

Fig. 10 **~75 kg blocks after explosion resistance test: A) 0,1% EMSIL-DRY™, and B) 0,1% Fiber-P2**

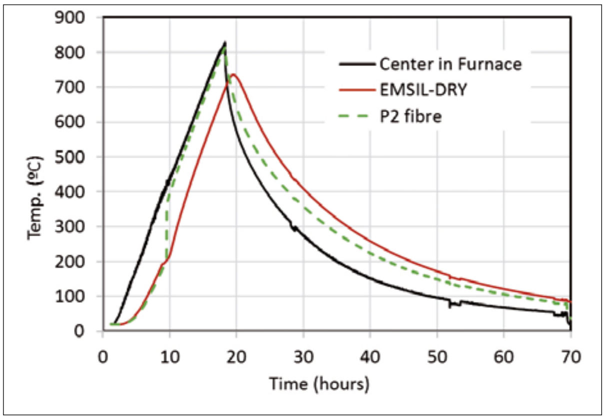

Fig. 11 **Temperature as a function of time**

resistance of NCC with Fiber-P2 has been improved compared to the NCC without drying agent (Fig. 9), but unfortunately not sufficiently to avoid damage.

The temperature in the furnace and in the cores in the NCC-2 blocks were recorded as a function of time, as shown in Fig. 11. Under the rapid heat-up, the temperature in the cores of the blocks was lower than that in the furnace.

For example, the block with Fiber-P2 disintegrated at a core temperature of about 200 °C while the temperature in the furnace was 400 °C. At disintegration, the thermocouple was exposed to the furnace air, thus soon attaining the furnace temperature.

For the sample containing EMSIL-DRY, there was a small "break" around 200 °C even though no plateau as appeared in Fig. 8 was observed. Prior to the "break" the rate of the temperature increase in the core is slower than in the furnace air. After the "break", a similar rate is observed even though the actual temperature in the core is lower. This indicates that an endothermic reaction is taking place at the "break" point, such as a massive evaporation. Obviously, the type of drying agent has strong influence on the rapid heat-up, which is related to the permeability and pore structure. By introducing EMSIL-DRY, the permeability and strength of the block seems suitable for removing the vapour and prevent an explosion even at a rapid heating rate of 50 °C/h.

Finally, an even larger block, 600 mm × 600 mm × 350 mm (~400 kg), of microsilica-gel bonded based NCC-2 containing EMSIL-DRY was produced for explosion resistance test. The block performed perfectly at a heating rate of 50 °C/h. Fig. 12 shows the block after the test.

All this demonstrates that the explosion resistance/drying behaviour of microsilica-gel bonded NCCs was significantly improved by the introduction of EMSIL-DRY that contributes to fast dewatering during firing and consequently improved explosion resistance. It indicates that a true rapid heating is possible. The mechanism is still not fully understood yet, and more work focusing on

Fig. 12 ~400 kg block with EMSIL-DRY after explosion testing at 850 °C

permeability, pore structure and strength development of microsilica-gel bonded NCCs will be carried out and reported in the future.

4 Conclusions

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

- The type of drying agent not only have a strong influence on flowability but also on the drying behaviour.
- The heat-up schedule and the physical dimensions of castables play essential roles during the dry-out process of the 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 very high heating rates.
- The microsilica-gel bonded NCC with EMSIL-DRY has excellent explosion resistance. A perfect 400 kg block was produced with no problems heating from 20 °C to 850 °C at a heating rate of 50 °C/h without any holding time at the "break" point.

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