FAST DRY-OUT OF NO-CEMENT CASTABLE BY USING A SPECIALTY DRYING AGENT

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ABSTRACT

The effect of drying agents on flowability, mechanical strength and lab- and industrial- scale explosion resistance of microsilica-gel bonded no-cement refractories (NCCs) was first investigated. The type of drying agent had a profound impact on flow/workability of the fresh castables and the speciality drying agent, EMSIL-DRY™, ensured the best workability. Then, drying behaviour of industrial-scale large samples (300mm cubes, approximately 80kg) was studied using a unique macro-thermo-balance (macro-TGA). The results confirmed that EMSIL-DRY™ reduced the temperature level for maximum dewatering rate and effectively helped prevent explosions during heat-up, compared to the other polymer fibres. The NCC with EMSIL-DRY™ showed excellent explosion resistance, as demonstrated by the production of a perfect 400kg block that was fired to 850°C at a rate 50°C/hr.

Keywords: Drying behaviour, fast heat-up, no-cement castable, microsilica, macro-TGA

1. INTRODUCTION

Energy saving and extension of service life of refractories have been essential for developing future sustainable refractories. Naturally, no-cement refractory castables (NCC) has been drawn great attention due to fast dry-out and excellent hot properties compared to low cement bonded refractory castables (LCC). Refractory castables are normally cement bonded and require special attention during the first heat-up. When vapour pressure generated inside the refractory exceeds its mechanical strength, the result could be significant damage due to explosion and/or spalling. Vapour pressure increases potentially with the temperature in a closed liquid/vapour aqueous system, as described by Antoine's equation [(1)].

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

Fig.1 [(2)] 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 three stages: i) evaporation from room temperature to 100°C, ii) ebullition from 100 to ~300°C, iii) 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. A high fraction of the water in cement bonded refractories is chemically bound which need to be fired at temperatures up to 600°C to remove it. Therefore, the heating profile for a refractory lining is normally divided into steps for safe removal of free water at lower temperatures and decomposition of cement hydrates at higher temperatures[3-4]. It has always been challenging to remove water from the centre of LCCs. Hence, optimisation of dry-out schedules and improvement in permeability of cement bonded refractories need special attention to reduce the risk of spalling and/or explosion.

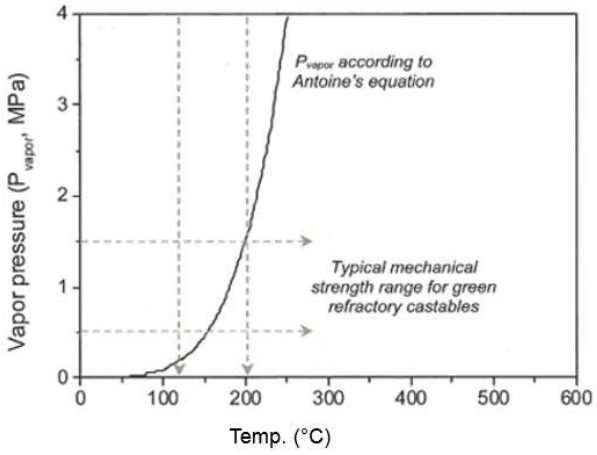

Fig.1: Vapour pressure (P_v) increases exponentially with the temperature according to Antoine's equation (2).

NCC, such as colloidal silica bonded refractory castables are very interesting due to their fast dry-out and excellent hot properties. Yet, 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[5-6]. 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[7-11]. In microsilica-gel bonded no-cement castables, only a very small amount of the mixing water is retained after drying at 110°C, hence, most of the free water are removed by simple drying.

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: i) effects of drying agent/anti-explosion agent on flowability and mechanical strength, ii) improvement in explosion resistance of microsilica-gel bonded NCC by introducing anti-explosion agents, and iii) investigation of the fast dry-out mechanism using a unique macro-thermo-balance (macro-TGA).

2. EXPERIMENTAL

2.1 Mix design

Table 1 shows the overall compositions of microsilica-gel bonded NCCs. Different fractions of tabular alumina (Almatis, Germany) were used as aggregate, and microsilica (Elkem Microsilica® 971U, Elkem, Norway) and SioxX®-Zero (Elkem, Norway) were used as binder. SioxX®-Zero is a tailor-made product for microsilica-gel bonded NCCs. Four types of drying agent/anti-explosion agent were used in the tests: i) three commercially available fibres, labelled Fibre-P1, -P2, -P3, and ii) one specialty fibre (EMSIL-DRY™ Elkem, Norway). 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 water addition was 4.35% for all mixes.

Table 1: Mix design of tabular alumina based NCCs (wt%)

	REF	P1	P2	P3	EMSIL-DRY™
Elkem Microsilica® 971U	5	5	5	5	5
Cement (70% Al_2O_3)	0.5	0.5	0.5	0.5	0.5
Tabular alumina 0-6mm	82.5	82.5	82.5	82.5	82.5
Al_2O_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

2.2 Experimental procedures and characterisations

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

Lab-scale explosion resistance testing per Chinese Standard YB/T4117-2003 were carried out for all mixes. 50mm cubes are placed into a hot furnace at a pre-set temperature. The cubes are inspected after 30-minute 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 i) 300x300x300mm (~80kg), and ii) 600mmx600mmx350mm (~400kg). The castables were de-moulded after one day and placed in the oven for further drying behaviour studies and/or explosion resistance tests. The heating schedule for the explosion test was 20 to 850°C at 50°C/hr; cooling from 850 to 20°C at 50°C/hr.

To understand the thermal behaviour during dry-out, a specially designed industrial-scale macro-thermo-balance (Macro-TGA, Elkem, Norway) was applied. During testing the mass change, sample temperature, and furnace temperature were recorded. For Macro-TGA, 300mm cubes (approximately 80kg) were used.

The heating schedule was 20 to 450°C at a rate of 50°C/hr and cooling at the same rate. Fig. 2 shows a schematic drawing of the Macro-TGA. A specialty balance capable of measuring industrial-scale samples is installed on the top of the furnace. A steel net cage holds the 80kg cube during heating (to prevent damage to the furnace wall if explosion occurs) and the mass loss of the specimen is recorded. A thermocouple is embedded in the centre of the cube to monitor the temperature during the heat-up process, as shown in Fig. 3.

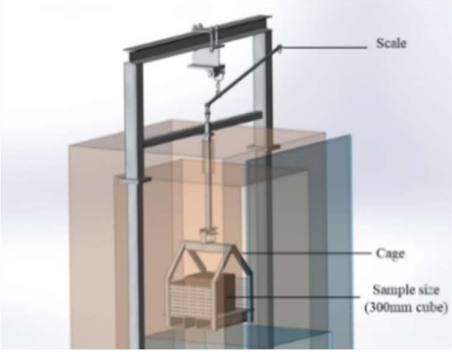

Fig. 2: Illustration of the industrial-scale thermo-balance (Macro-TGA)

Fig.3 and 300mm cube with embedded thermocouple in the centre

The mass loss, temperature in the centre of the cube and in the furnace are/were recorded. The drying rate at time t_i was calculated using the derivative of the *W* (dW/dt) parameter, which represents the cumulative fraction of water released during the heat-up, according to the expressions:

$$W=100\%\times(M_0-M)/(M_0-M_F) \qquad (1)$$

$$(dW/dt)_i=(W_{i0}-W_{i-10})/(t_i-t_{i-10}) \qquad (2)$$

Where *M* is the instantaneous mass recorded at time t_i during the heating stages of the samples, M_0 is the initial mass and M_F is the final (dry) mass of the sample.

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.

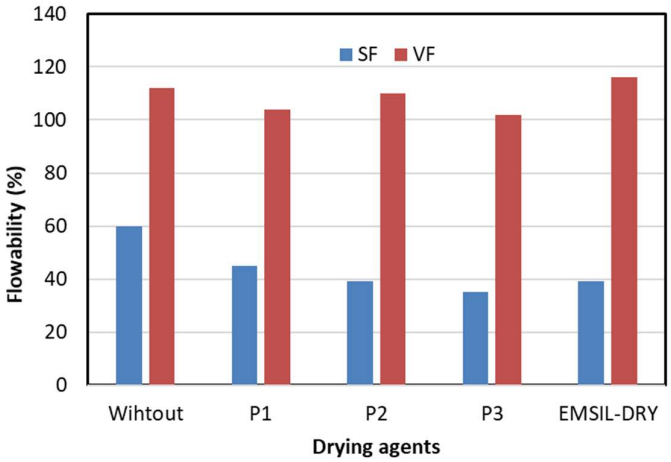

Fig.4: Flowability of microsilica-gel bonded NCCs with different drying agents.

Table 2 shows the green crushing strength (CCS) and modulus of rupture (CMOR) (24hrs 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.

Table 2: Mechanical strength after demoulding and drying of tabular based NCCs with various fibres (MPa)

		REF	P1	P2	P3	EMSIL-DRY™
20 °C/24 hrs	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 hrs	CMOR	6.4	6.3	7.4	5.7	7.1
	CCS	44.6	32.5	30.4	41.6	42.8

3.2 **Lab-scale explosion resistance**

Microsilica-gel bonded NCCs with different drying agents were used to further investigate the drying behaviour. Table 3 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 24hrs at room temperature and 100% relative humidity before de-moulding. The freshly de-moulded samples are labelled “wet”, and samples further dried for 24 hrs 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. 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.

Table 3: Explosion resistance of microsilica-gel bonded NCCs

	Wet (20°C/24hr)				
Temp. (°C)	**REF**	**P1**	P2	P3	**EMSIL-DRY™**
300	√	√	√		
350	x	x	√		
400		x	×	√	√
450				√	√
500				×	√
	Dried (110°C/24hr)				
1000	√	√	√	√	√
1200	√	√	√	√	√

√: passed; x: failed

3.3 **Industrial-scale explosion resistance**

All blocks were cured at room temperature for 24hrs, then de-moulded and put directly into the furnace. The heating schedule was 20 to 850°C at 50°C/hr; cooling from 850 to 20°C at 50°C/hr.

Fig.5 shows ~80kg (300mm) microsilica-gel bonded NCC cubes without drying agent before and after the explosion resistance test. With no addition of drying agent, the 80kg block disintegrated during the test and parts of the block were completely pulverised.

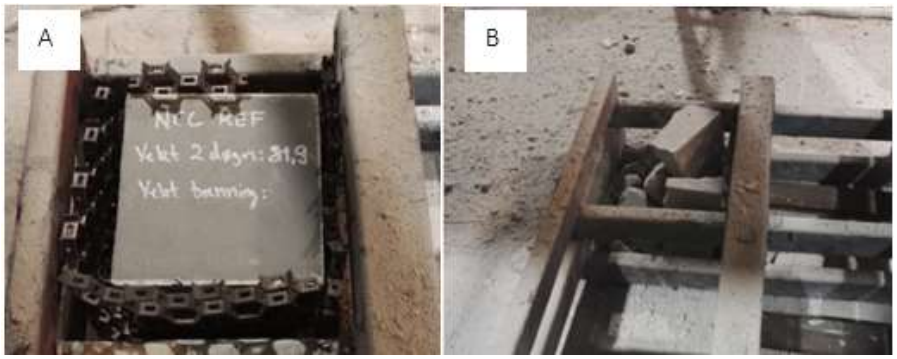

Fig.5: ~80kg block (A) before and (B) after explosion resistance test (from 20 to 850°C at 50°C/hr).

Fig.6 shows ~80kg (300mm) 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 showed good explosion resistance and the ~80kg blocks were perfect after the test, whereas the blocks with Fibre-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 if an improper fibre is used.

Fig.6: ~80kg (300mm) cubes *with different fibres after explosion resistance test (from 20 to 850°C at 50°C/hr). A) Fibre P3, B) EMSIL-DRY™ and C) Fibre-P1. The NCC with Fibre-P2 looked like cube C) Fibre-P1.*

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.6). Hence, we carried out further explosion resistance testing on ~400kg blocks (600x600x350mm) containing EMSIL-DRY™ or Fibre-P3. Fig.7 shows the blocks after the tests. The block containing EMSIL-DRY™ performed perfectly at a heating rate of 50ºC/hr while the one with Fibre-P3 disintegrated into several pieces.

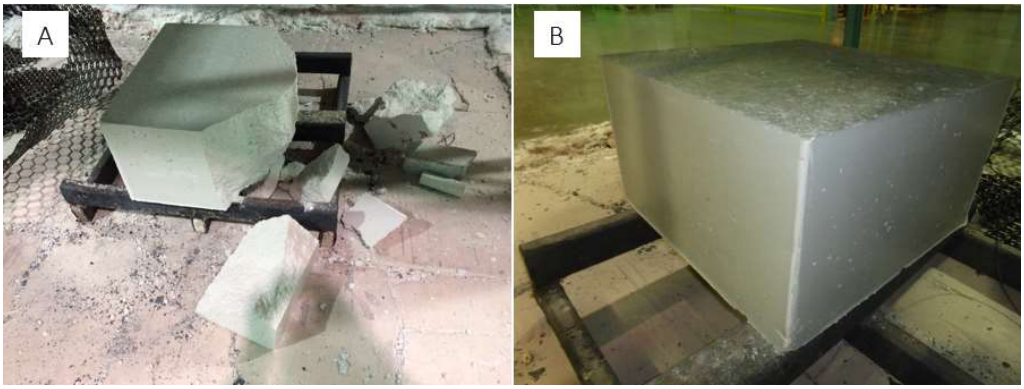

Fig.7: ~400kg blocks after explosion testing at 850°C. A) Fibre-P3 and B) EMSIL-DRY™

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 Differential Scanning Calorimetry (DSC), Scanning Electron Microscope (SEM) characterization

So, what is the reason that EMSIL-DRY™ can improve the explosion resistance of refractory castables? EMSIL-DRY™ and Fibre-P1 are chosen for further investigation using Differential Scanning Calorimetry (DSC) and Scanning Electron Microscope (SEM). Under DSC characterization, samples were heated to 600°C in oxidizing environment with air flow of 50 ml/min at a heating rate of 5°C/min. Fig. 8 and 9 present the mass loss (%) and DSC (mW/mg) as a function of firing temperature for EMSIL-DRY™ and Fibre-P1, respectively.

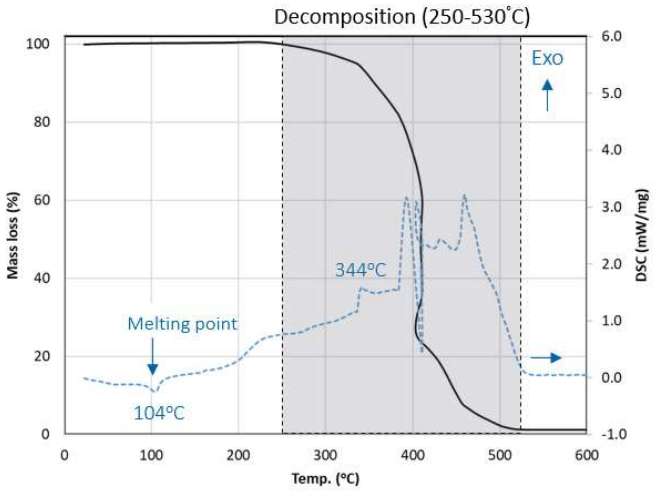

Fig. 8 Mass loss (%) and DSC (mW/mg) of EMSIL-DRY™ during heat up.

Fig. 8 shows that the melting point of EMSIL-DRY™ is 104°C and that decomposition takes place from 250°C-530°C. Some 80% decomposes between 350-450°C. In contrast, the melting point of Fibre-P1 (Fig. 9) is about 160°C, decomposition temperature range is 230-460°C, and approximately 80% of Fibre-P1 disappeared between 250-350°C. Both mass loss and DSC results confirm that EMSIL-DRY™ melts at a much lower temperature and degrades at a higher temperature in oxidizing environment compared to Fibre-P1 Consequently, as seen in our experiments, explosion/spalling resistance of NCCs has been significantly improved when EMSIL-DRY™ is added as a drying agent.

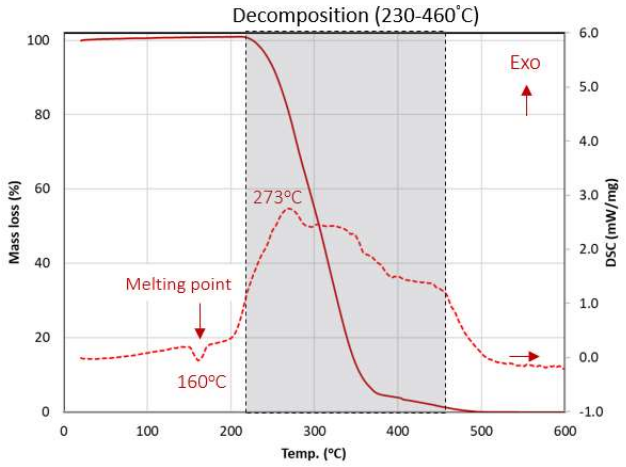

Fig. 9 Mass loss (%) and DSC (mW/mg) of Fibre-P1 during heat up.

EMSIL-DRY™ and Fibre-P1 are examined by SEM, as presented in Fig. 10. The former appears to be flexible and easy to disperse in both dry state and in water. Yet, the latter one is more rigid and difficult to redisperse in refractory castable. As results, the addition of Fiber-P1 would impair the flowability of refractory castable as demonstrated in §3.1.

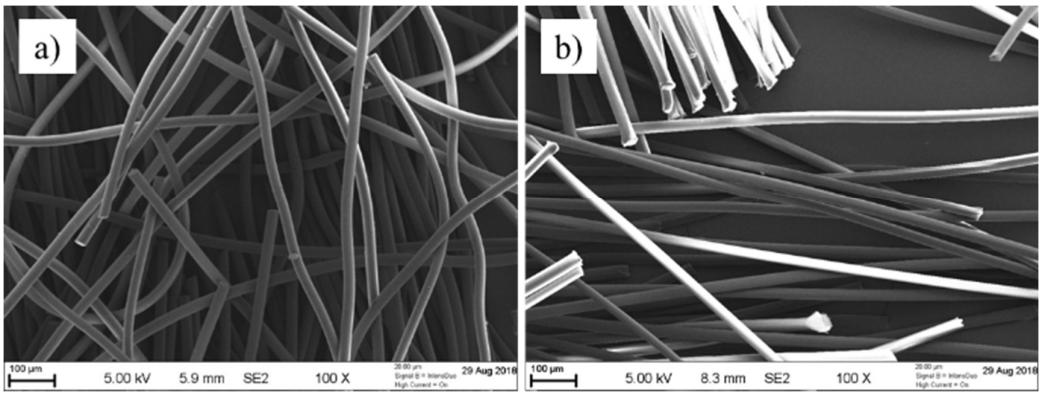

Fig. 10 SEM image of drying agents. a) EMSIL-DRY™ and b) Fibre-P1.

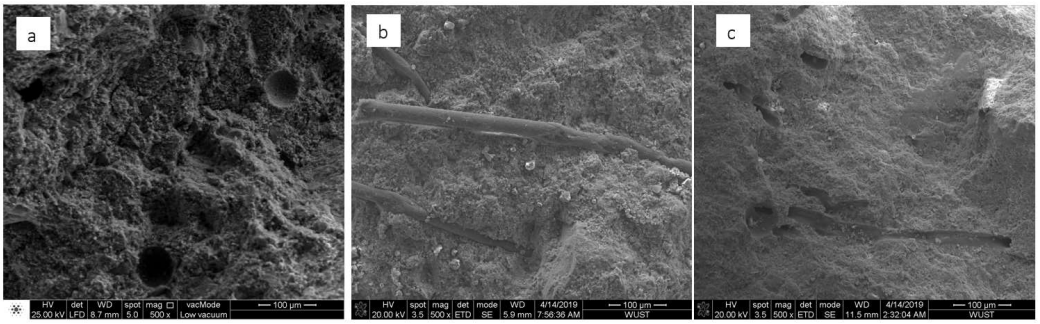

Fig.11: SEM of fractured surface of NCC samples heated at 120ºC for 12hrs. a) NCC REF, b) NCC with Fibre-P1, and c) NCC with EMSIL-DRY™.

Finally, the NCC specimens containing EMSIL-DRY™ and Fibre-P1 were fired at 120ºC for 12hrs, and their fractured surfaces were used for SEM characterisation, as presented in Fig. 11. When the temperature exceeds the melting point of EMSIL-DRY™ numerous needle-like channels are produced, facilitating water removal during the ebullition stage. As seen, Fibre-P1 still remains intact at 120ºC with no channels formed. This indicates that the vapour pressure inside the NCC specimen with EMSIL-DRY™ should be much lower than the reference and the one containing Fibre-P1.

All this demonstrates that the explosion resistance/drying behaviour of microsilica-gel bonded NCC is significantly improved. EMSIL-DRY™ contributes to faster dewatering in the early stage of the firing process (ebullition stage at 110-300°C, as illustrated in Fig.1), mainly due to lower melting point and lower extra pressure from fibre decomposition. It indicates that true rapid firing is possible for NCCs.

3.5 Mass loss and drying rate evaluation by industrial-scale Macro-TGA

To better understand the thermal behaviour of NCC, a large specimen containing EMSIL-DRY™ (300mm cube, ~80kg) was produced. A unique macro-thermo-balance (Macro-TGA) was applied to evaluate the water loss (%) and drying rate (dW/dt, %/min) during heat-up. The heating rate was 40°C/hr from 20 to 400°C.

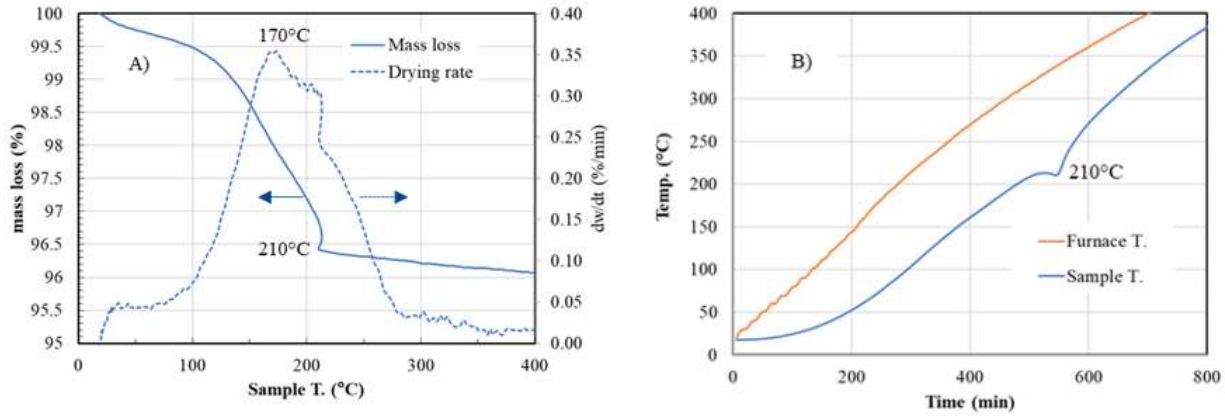

Fig. 12: Drying behaviour of NCC containing EMSIL-DRY™ using Macro-TGA. a) Mass loss (%) and Drying rate (dW/dt), and b) Furnace temperature and sample temperature.

Fig. 12A illustrates the water loss (%) and drying rate (%/min) plotted as a core temperature of the sample. At the core temperature range of the specimen from 100 to 210°C, the mass loss was 3.0%, i.e. ~68.9% free water was removed. Additionally, the maximum dewatering rate of ~0.34%/min was detected at sample temperature of ~170°C. The results confirm that massive free water is removed at the beginning of ebullition period (100-300°C, as indicated in Fig. 1). Therefore, the risk for spalling and/or explosion during the ebullition stage can be reduced significantly.

As shown in Fig. 12B, a small “break” point in development of the sample temperature was seen at ~210°C, where a total mass loss was 3.5%, corresponding to a free water removal of ~82%. At this point it seems the evaporation (endothermic reaction) is taking place. The sample temperature won’t rise until it is completed. After this “break” point, the core temperature inside sample increases at the same speed as the furnace temperature.

The macro-TGA results demonstrate that EMSIL-DRY™ contributes to fast dewatering in the early stage of the firing process. When the temperature exceeds the melting point of EMSIL-DRY™, numerous channels are formed. The vapour pressure inside large specimens of NCC during the later stage of ebullition, will be significantly lowered with EMSIL-DRY™. This will contribute to reduce the risk of explosion/spalling during the heat-up process and indicate that rapid firing is possible for NCC with EMSIL-DRY™. As demonstrated (Fig. 7B), a perfect 400kg block with EMSIL-DRY™ was produced after firing

from 20 to 850°C at a heating rate of 50°C/hr. Furthermore, it is possible to design a close-to-reality heat-up profile based on the input from this Macro-TGA characterisation to prevent industrial failures.

4 CONCLUSIONS

The paper highlights the optimisation of drying behaviour of NCCs using different drying agents. Based on our studies of DSC and SEM characterisation of the drying agents, flowability, lab- and industrial- scale explosion resistance, macro-TGA characterization of NCCs with and without drying/anti-explosion agents, the following conclusions can be drawn.

- The types of drying agent have significant impact on flowability and drying out behaviour of refractory castables.
- Good correlation between lab- and industrial-scale explosion resistance tests has been observed. But dewatering behaviour is strongly affected by the dimensions of the cast piece and industrial-scale tests always provide more accurate guidance than testing at lab-scale.
- The ebullition stage is the most critical dewatering step at which spalling and/or explosion most likely takes place. The Macro-TGA results show that EMSIL-DRY™ facilitates faster water removal at the beginning of the ebullition stage, hence minimises the risks of explosive spalling.
- The microsilica-gel bonded NCC with EMSIL-DRY™ has excellent explosion resistance.

Finally, true fast drying of no-cement refractory castables has become possible by introducing the drying agent and by designing the close-to-reality heat-up profile based on the input from Macro-TGA. A perfect 400kg block with EMSIL-DRY™ was produced after fired to 850°C at a rate 50°C/hr with no problem. Nevertheless, drying industrial-scale specimens are not easy and always more complicated than lab-scale samples. To better understand the drying mechanism, more research such as permeability and pore size distribution, microstructure development of NCCs with different drying agents are necessary to carry out.

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