Dring Behaviour and Explosion Resistance of No-Cement Refractory Castables

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For cement bonded refractory castables explosive spalling due to removal of free water and/or dehydra-
tion of cement hydrate have always been challenging. Naturally, cement free castables are very interest-
ing 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 us-
ing 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 interest-
ing due to their fast dry-out and ex-
cellent hot properties. However, their green
strength is often so low that demoulding
and handling after curing become a chal-
lenge, particularly for larger pieces as op-
posed to small laboratory test specimens
[1–3]. Recent work by Elkem demonstrates
that microsilica-gel bonded NCCs show
improved green strength compared to col-
loidal silica bonded, excellent hot proper-
ties and exhibit fast dry-out performance
compared to LCCs [4–9]. 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 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].

\[
\log_{10}p = A - \frac{B}{C + T} \quad (0–374 \, ^{\circ}C)
\]

Fig. 1 Vapour pressure (Pv) increases exponentially with the temperature according to
Antoine’s equation (11)
• 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 dewetting 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

Table 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 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 summarised 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. The 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.

#### 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.

#### 3.2 Lab-scale explosion resistance

Microsilica-gel bonded NCCs with different drying agents were used to further investigate the drying behaviour. Table 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...
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 ºC/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 ºC/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 ºC 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 ºC, 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 ºC. 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 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 ºC/min during the
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
[12] Part, Chr.; Wöhlmeyer, Chr.: The advantage of calcium aluminate cement as a castable bonding system. St. Louis Section Meeting, USA, 2006