Microsilica-Gel Bonded Refractory Castables with Improved Set-Behaviour and Mechanical Properties

H. Peng, B. Myhre

Silica-sol bonded no-cement refractory castables are attractive to the industry due to their high temperature performance and fast dry-out in comparison to low cement castables. However, these castables are not widely used, due to inadequate green strength and long set-time/complex set-behaviour. In this paper, dry silica-gel bonded no-cement castables were developed using microsilica-gel as binder and the novel SioxX-Zero as a speciality additive package. SioxX-Zero has been purposely developed for use in microsilica-gel bonded no-cement castable systems and the main functions are to control flow properties and set characteristics. When SioxX-Zero replaces other dispersants, the set behaviour and green mechanical strength of the NCCs are substantially improved. Furthermore, the performance of various high alumina aggregates was evaluated and the results confirm that in comparison with silica-sol, the microsilica-gel bonded refractory NCCs exhibit improved set-behaviour and green strength.

1 Introduction

No-cement refractory castables have been of great interest in the last two decades. Different no-cement systems such as microsilica, colloidal silica, hydratable alumina, and colloidal alumina have been developed [1–4]. Silica-sol bonded refractory castables have been comprehensively studied; while hydratable alumina bonded systems have been less explored due to its application limitation such as low green strength and difficulties in mixing [5–8]. The main advantages of silica-sol in no-cement refractory castables are fast drying, volumetric stability, good mechanical strength at intermediate temperatures and better thermomechanical properties at high temperatures due to mullite formation in alumina-silica-based systems and no liquid formation from cement and silica.

Since the hydration of cement is not involved in the bond phase, it is essential to understand the set mechanism of the silica-sol bond to develop no-cement castables. By controlling the pH, silica-sol is stabilised through electrostatic repulsion. Therefore, efficient methods to destabilise the system would be pH changes; adding gelling agent, drying and freezing to remove water and so on. In silica-sol bonded castables, dead burned magnesium oxide and calcium aluminates seem to be the most frequent used gelling agents [9–11]. Although the silica-sol bonded no-cement castable is considered the state-of-the-art, its use has been limited due to the following challenges:

- Inadequate green strength leading to handling problems.
- Frost sensitivity under installation, storage and transportation due to liquid binder.
- Complex logistics due to two-component system.

Naturally, a “dry-version” of a silica binder, microsilica powder, is of great interest in order to develop no-cement castables. Recent reports disclose that genuine bond based on microsilica coagulation is created, a similar set mechanism to colloidal silica [12–14]. As illustrated in Fig. 1, the set of microsilica-gel bond castables is caused by cations. The cations not only contribute to the reduction of overall net repulsion effect of microsilica, but also react with the negatively charged microsilica. For instance, when calcium aluminate cement is used as coagulating agent, Ca²⁺ (and/or other polyvalent cations) released during cement dissolution will react at the negative sites on the microsilica surface to form a three-dimensional network of linked microsilica particles. Therefore, the set-time will be affected by the amount of cations.

Keywords: no-cement castable, silica-sol, microsilica, gel-bond, additive
Microsilica is a dry powder (SiO₂) consisting of spherical particles of amorphous silicon dioxide (SiO₂) with an average particle size of 150 nm. Microsilica-gel bond not only provides similar advantages as silica-sol but also overcomes some of the drawbacks such as two-component system and frost sensitivity. Furthermore, due to the spherical shape of microsilica, closer packing and consequently enhanced flowability/reduction in water demand are important factors [15].

Despite this, no-cement refractories using microsilica-gel as binder are not widely used either, even though the potentials have been investigated for nearly 20 years. One of the major challenges may lie in the lack of a suitable additive package to overcome its intrinsic weakness such as moderate/low green strength after demoulding and a long set time. It is well known that parameters such as dispersants, accelerators and super-fines play an essential role in the design of no-cement refractory castables. Based on ELKEM’s experience and understanding of the characteristics of microsilica and its performance in refractory castables during the last thirty years, a new specialty product (SioxX-Zero) has been developed for microsilica-gel bonded no-cement castables (NCCs). For ease of application and improved functionality, high-grade microsilica is used as carrier in the product; the recommended dosage is approximately 3 mass-%. The addition of SioxX-Zero will enhance green strength and control the set and hardening process. By using SioxX-Zero in combination with polyvalent cations, for example, up to 0.5 % calcium aluminate cement, the set time can be controlled.

In this paper, the effects of dispersants on green strength and set-behaviour of microsilica-gel bonded castables were first explored. For comparison, a silica-sol bonded castable was included as reference. Later, microsilica-gel bonded NCCs with various alumina aggregates were further evaluated. The results demonstrate that microsilica-gel bonded NCCs with SioxX-Zero perform excellent in terms of green strength and set-behaviour.

2 Experimental

2.1 Mix design

The particle size distributions (PSDs) of microsilica-gel bonded NCCs were calculated using the EMMA program [16]. EMMA uses the Andreassen model and is widely used to evaluate and optimize particle packing in castables. In the present study, the q-value was 0.25 for all mixes. Tab. 1 shows the compositions of bauxite based NCCs with different dispersants; the water addition was 5 mass-%. The optimized dosage of SioxX-Zero, Dispersant-B and -C were 3 mass-%, 0.05 mass-% and 0.23 mass-%, respectively. Since SioxX-Zero both contain alumina and microsilica carrier the compositions have been adjusted accordingly. A silica-sol bonded castable was included for reference.

Tab. 1 Composition of bauxite based NCCs with different types of alumina aggregates [mass-%]

<table>
<thead>
<tr>
<th>Bauxite</th>
<th>WFA</th>
<th>BSA</th>
<th>T60</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>80</td>
<td>83</td>
<td>84.5</td>
</tr>
<tr>
<td>12.5</td>
<td>10.5</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>4.5</td>
<td>4.15</td>
<td>4.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Tab. 2 Composition of microsilica-gel bonded refractory NCCs with different types of alumina aggregates [mass-%]

<table>
<thead>
<tr>
<th>Microsilica-Gel Bonded</th>
<th>Silica-Sol Bonded</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Bauxite, 0–5 mm</td>
<td>78</td>
</tr>
<tr>
<td>Calcined alumina fines</td>
<td>12.5</td>
</tr>
<tr>
<td>Elkem 971U</td>
<td>6</td>
</tr>
<tr>
<td>Silica-sol, 40/130 *</td>
<td></td>
</tr>
<tr>
<td>SioxX-Zero</td>
<td>3</td>
</tr>
<tr>
<td>Dispersant-B</td>
<td>0.05</td>
</tr>
<tr>
<td>Dispersant-C</td>
<td></td>
</tr>
<tr>
<td>Hydratable alumina</td>
<td>0.5</td>
</tr>
<tr>
<td>70 % CAC</td>
<td>0.5</td>
</tr>
<tr>
<td>Gelling agent</td>
<td></td>
</tr>
<tr>
<td>Water content</td>
<td></td>
</tr>
</tbody>
</table>

*) The solid loading of silica-sol is 40 mass-%, with a surface area of 130 m²/g, 4.8 mass-% water was introduced by the silica-sol and 0.2 mass-% additional water was added.
Gouda Refractories’ products and services are based on a tradition that goes back more than one hundred years to 1901. Gouda Refractories supplies customer specific refractory linings in several industries such as the aluminium industry, the petrochemical industry and special high demanding applications in steel, energy, environmental and raw material processing industries. For these industries bricks, monolithics and prefab shapes are designed and manufactured using advanced production technology and applying the highest standards. Through professional cooperation with local partners, Gouda Refractories can offer a complete package, from design and production to supply, installation, aftersales and maintenance. Gouda Refractories is the worldwide reference for refractory linings for extremely critical equipment. For the primary aluminium industry for example, Gouda Refractories has set the standards with its LP50S brick offering a longer service life, better anode quality and lower energy consumption compared with other bricks for anode baking furnaces. This technology for brick manufacturing has resulted in a complete product line of (ultra) low porosity bricks that are nowadays applied in temperature equipment in petrochemical, energy and environmental industries. Being front runner in the development of new refractory materials, Gouda Refractories is able to provide a high quality fit for purpose refractory lining for almost any application and at lowest possible costs of ownership.
Propagation of ultrasonic waves through the castable containing castables. On the contrary, castable B, C, and D have much slower set-behaviour. Even though the time to final set of castable B and D seems to be fine, approximately 10 h, it does not have the same quick and well-defined set behaviour and never reaches the strength level of the SioxX-Zero containing mix. The castable with Dispersant-C did not fully set even after curing for two days as illustrated in Fig. 5.

The results demonstrate that the type of dispersant and the binder system have strong impact on the set and hardening process of NCCs. The mechanism of how the dispersants influence the set-behaviour is not well understood yet and further research is ongoing and will be published in the future.

3.2 Green strength/strength after drying

Fig. 6 shows the green compressive strength (24 h at >90 % RH at 20 °C) and the strength after drying (24 h at 110 °C) of the bauxite NCCs. The green strength of the castable with SioxX-Zero is much higher, up to 10 MPa, than the other castables. One could argue that the low strength of the mixes at least partly is a consequence of the slow set but even with prolonged curing time, the results of the sonic velocity measurements indicate that the silica-sol containing composition will never reach the same level as "pure" microsilica-gel bond with SioxX-Zero. After drying, the difference in strength is smaller. The castable with Dispersant-C also set and hardened after drying and strength was fine, although it did not set after two-day curing in the curing chamber. Nevertheless, the castable
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The green compressive strength of the microsilica-gel bonded NCCs with different types of alumina aggregates in combination with SioxX-Zero (as given in Tab. 2) are summarised in Fig. 7.

The water addition for this series was 4,0–4,5 mass-%; there are some variations with the different aggregates. For comparison, the bauxite castable with silica-sol bond at 5,0 mass-% water (mix D in Tab. 1) was included.

As shown in Fig. 7, the green strength of the microsilica-gel bonded NCCs containing SioxX-Zero is substantially higher than that of silica-sol bonded NCC. It is also noticed that when the water addition was reduced from 5 mass-% (castable A in Tab. 1) to 4,5 mass-%, the green strength of the bauxite NCC with SioxX-Zero increased from 10 MPa to 17 MPa.

3.3 Mechanical strength at intermediate temperatures

Cold modulus of rupture (CMOR) of the microsilica-gel bonded NCCs with various alumina aggregates as a function of pre-firing temperatures are given in Fig. 8. For comparison, silica-sol bonded NCC is included as well.

A similar trend for all NCCs is observed, irrelevant of the type of high alumina aggregate used. After drying at 110 °C, the CMOR of microsilica-gel bonded NCCs are above 7,0 MPa. At 300 °C, the CMOR slightly increases and at 600 °C it drops. With further increase of pre-firing temperature to 800 °C, the strength increases again.

The variation in strength between the NCCs is probably attributed to the impurity level of the aggregates. Bauxite and BSA based NCCs give relatively higher strength than those using WFA and T60 as aggregates, even though the binder systems are more or less the same (as shown in Tab. 2). It is also interesting to notice that the microsilica-gel bonded bauxite NCC shows much higher...
strength at 110 °C compared to the silica-sol bonded one (mix D in Tab. 1).

4 Conclusions
These studies on the set behaviour, mechanical- and hot- properties of NCCs using either microsilica-gel or silica-sol as binders, provide us with valuable information on developing high performance microsilica-gel bonded NCCs.

• The microsilica-gel bonded NCCs seem to have better workability, higher green strength and improved mechanical properties compared to the silica-sol bond system.
• The types of dispersants have strong impact on set-behaviour and green mechanical properties of microsilica-gel bonded NCCs. The use of SioxX-Zero not only provide “well-defined” set and short time to “final” strength, but also give high self-flow and improved mechanical properties.
• The microsilica-gel bonded NCCs with various aggregates (bauxite, WFA, BSA and T60) have been developed in combination with SioxX-Zero, exhibiting improved green mechanical strength.
• 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.

References
[16] EMMA (Elkem Materials – Mixture Analyzer) software, free download at: www.materials.elkem.com/
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