

# High-alumina refractory castables bonded with novel alumina-silica-based powdered binders

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## ABSTRACT

In recent years, nano-binders (mainly colloidal suspensions) have been proposed as alternative materials for applications that require CaO-free refractory lining or improved mechanical behavior at intermediate temperatures ( $700\text{ }^{\circ}\text{C} < T < 1200\text{ }^{\circ}\text{C}$ ). Despite the benefits of these suspensions, nano-bonded castables usually present limited green mechanical strength and different on site logistics to handle the liquid. Considering the availability of novel alumina-silica-based powdered binders, this work investigated the role of submicron alumina and SioxX<sup>®</sup>-Zero (both supplied by Elkem company) on rheological and mechanical properties of vibratable high-alumina castables, aiming to identify whether they can be suitable options to replace colloidal silica suspensions. Cold and hot mechanical strength and apparent porosity in the range of 110–1400 °C, cyclic thermal shock resistance, creep tests and hot elastic modulus of the designed formulations were evaluated. According to the results, SioxX<sup>®</sup>-Zero-bonded compositions presented good flowability levels and their sintering process started around 800 °C. Adding boron carbide to the same formulations resulted in transient liquid sintering of the silica-containing refractories, which allowed the development of compositions with improved thermo-mechanical performance in the 600–1400 °C temperature range. Furthermore, the submicron alumina-bonded samples presented fast sintering, resulting in E values close to 200 GPa (the highest value so far registered in our lab for a coarse grain size formulation) after one heating-cooling thermal-cycle up to 1400 °C.

## 1. Introduction

Throughout the years many efforts have been made to develop calcium-free binders [such as hydratable alumina (HA), colloidal silica (CS) and colloidal alumina (CA)] for monolithic refractories as one of the main drawbacks related to the presence of CaO in formulations containing  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  is the generation of low melting-temperature phases, which affect the overall thermo-mechanical behavior of these products [1–3].

In order to overcome this issue, colloidal silica suspensions have been introduced as alternative binders for monolithic compositions. The setting of these nano-bonded castables is commonly induced by CS gelation (with no generation of hydrated phases), which can be triggered by water withdrawal, pH changes or adding a salt [2,4,5]. As pointed out by Nouri-Khezrabad et al. [2], the hydroxyl groups (Si-OH) contained on the surface of the silica particles give rise to siloxane bonds (Si-O-Si), forming a three-dimensional network during setting. However, the addition of gelling agents are still required to adjust the workability and setting time of CS-bonded compositions. Other well

known disadvantages (i.e., low green mechanical strength, frost sensitivity of the suspension under installation, storage and transportation, etc.) of these colloidal suspensions are also highlighted in many studies presented in the literature [1,3,5–10].

A “dry-version” of this silica binder is of great interest to refractory producers, considering their aim to develop cement-free castables. Recently, Elkem company has introduced a novel microsilica-alumina-based binder (SioxX<sup>®</sup> -Zero) for  $\text{SiO}_2$ -gel bonded no-cement refractories into the market. According to this producer, by adding SioxX<sup>®</sup>-Zero to castable mixtures, an improved green mechanical strength and better setting and hardening control can be obtained when compared to colloidal silica-bonded systems [3,11,12]. Nevertheless, it is recommended to incorporate small contents of a basic compound (i.e., 0.5 wt% of calcium aluminate cement) into the dry-mix while preparing the composition as the binding effect of SioxX<sup>®</sup>-Zero is triggered by the presence of cations. In fact, this species ( $\text{Ca}^{2+}$  or other polyvalent cations) should act reducing the overall net repulsion of  $\text{SiO}_2$  particles and also react with the negative sites contained on the microsilica surface, giving rise to the link or binding effect among the coarse and fine components

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of the compositions [3,12].

Submicron alumina is another interesting material due to its high reactivity ( $d < 8 \mu\text{m}$  and specific surface area  $\sim 8.6 \text{ m}^2/\text{g}$ ) and spherical morphology, leading to the development of refractories with: (i) enhanced particle packing, (ii) lower water consumption during mixing, (iii) faster sintering and densification at high temperatures, etc [13]. However, further analyses are still required to investigate the potential of using sub-micron alumina as a likely alternative binder for castables.

Regarding alumina-silica containing castables (i.e., compositions bonded with colloidal silica or SioxX®-Zero), the interaction of these two oxides above  $1100 \text{ }^\circ\text{C}$  should lead to mullite generation in the structure of the refractories. This phase is one of the most important compounds for technical ceramic materials as it presents high thermal stability (melting point at  $1890 \text{ }^\circ\text{C}$  [14]), low thermal expansion coefficient ( $\sim 4.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ), low thermal conductivity, high creep resistance and corrosion stability and improved mechanical strength and fracture toughness [14–17]. Besides that, mullite is also able to form solid solutions in a wide  $\text{Al}_2\text{O}_3/\text{SiO}_2$  range ( $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$ , where  $x = 0.2\text{--}0.9$ ), incorporating a large variety of foreign cations (i.e. boron, which may replace silicon, as indicated in Eq. (1)) [14,17–19].



Werdning and Schreyer [20] introduced the term “boron mullite” for compounds in the  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--B}_2\text{O}_3$  system within a compositional range between 3:2 and 2:1 mullite and two silicon-free borates:  $\text{Al}_5\text{BO}_9$  with a mullite-type structure and  $\text{AlBO}_3$  of calcite-type structure (Fig. 1). More recent studies [17,18] showed that there is no complete solid solution between mullites and aluminum borates, resulting in significant changes of B-mullite lattice parameters. Nevertheless, the combination of these compounds is pointed out as an important route for developing high-performance materials.  $\text{Al}_{18}\text{B}_4\text{O}_{33}$  presents very close features to  $\text{Al}_5\text{BO}_9$ , and the former has gained industrial interest due to its properties, such as high strength, low thermal expansion and conductivity, etc [18–21].

Another important aspect is associated with the faster reaction rate and earlier generation of mullite in boron-containing alumina-silica compositions [16–20,22]. Lühns et al. [17] highlighted that long-term thermal stability at  $800 \text{ }^\circ\text{C}$  was obtained for B-mullite, whereas complete decomposition of this compound (into boron-free mullite and corundum) was observed at  $1400 \text{ }^\circ\text{C}$  after 90 h thermal treatment. Furthermore, the incorporation of B-mullite into the alumino-silicate crystal structure reduced its thermal expansion coefficient by 15% in comparison to the boron-free phase [18].

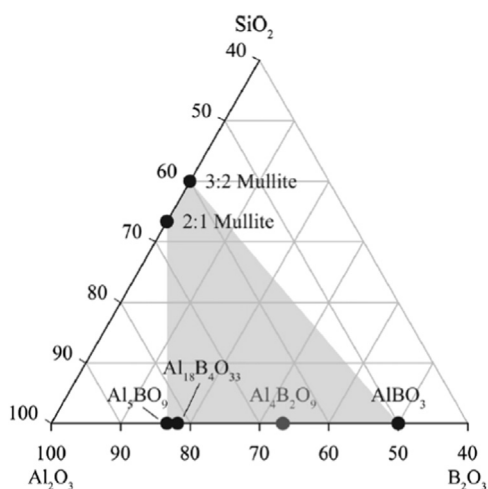


Fig. 1.  $\text{Al}_2\text{O}_3$ -rich section (% mol) of the  $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--B}_2\text{O}_3$  ternary phase diagram, pointing out the boron-mullite stability field (gray area) according to Werdning and Schreyer [20].

Despite the great potential of B-mullite to be used to develop advanced refractory compositions, its formation and influence on the performance of castables at intermediate and high temperatures have still not been well explored. Therefore, this work addresses the investigation of high-alumina (with in situ mullite formation) refractory castables bonded with colloidal silica or SioxX®-Zero and containing 0 or 1 wt% of boron carbide in order to induce transient liquid sintering. Additionally, a silica-free composition (containing submicron alumina as a binder) was also evaluated and compared to the other designed materials.

## 2. Experimental

Eight vibratable castable compositions consisting of tabular alumina aggregates (Almatis, USA) and reactive aluminas (Almatis, USA) were designed according to Alfred's particle packing model ( $q = 0.26$  [1], Table 1). The binding behavior of three different raw materials [colloidal silica (00BZLO21, Nalco, Brazil), SioxX®-Zero (SZ) and submicron alumina (SMA) with  $d_{\text{max}} < 8 \mu\text{m}$  (both supplied by Elkem, Norway)] were investigated, considering a fixed  $\text{SiO}_2$  content (total = 3 wt%) in the castables containing this oxide (compositions SC, SZ and SZ + SMA in Table 1).

Four formulations (SC + B, SZ + B, SMA + B and SZ + SMA + B) containing 1 wt% of boron carbide ( $\text{B}_4\text{C}$ ,  $d < 45 \mu\text{m}$ , China Refractories, China) were also analyzed as this additive may induce faster mullite phase generation and densification (due to transient liquid sintering) during the samples' heating treatments and improve their mechanical performance.

The compositions were dry-homogenized for 1 min and mixed for an additional 3 min in a rheometer [23]. The required water amount and attained vibratable flow (ASTM C860) are presented in Table 1. After that, prismatic samples ( $150 \text{ mm} \times 25 \text{ mm} \times 25 \text{ mm}$ ) were cast under vibration, cured at  $50 \text{ }^\circ\text{C}$  for 24 h, dried at  $110 \text{ }^\circ\text{C}$  for another 24 h and fired in the range of  $600\text{--}1550 \text{ }^\circ\text{C}$  for 5 h.

Aiming to understand the elastic modulus (E) evolution with temperature, dried and pre-fired ( $1400 \text{ }^\circ\text{C}/5 \text{ h}$ ) samples of the designed refractories were analyzed according to the ASTM C 1198-91 standard using the bar resonance technique (Scanelastic equipment, ATCP, Brazil). More details of this method can be found elsewhere [24,25]. The tests were conducted in the  $30\text{--}1400 \text{ }^\circ\text{C}$  temperature range in air ( $p\text{O}_2 = 0.21 \text{ atm}$ ) with heating and cooling rates of  $2 \text{ }^\circ\text{C}/\text{min}$ . Additionally, the same procedure was also used to follow (at room temperature) the E decay of the castable samples as a function of thermal shock cycles (ASTM C1171-91) at  $815 \text{ }^\circ\text{C}$  or  $1025 \text{ }^\circ\text{C}$  (10 cycles,  $\Delta T \sim 790 \text{ }^\circ\text{C}$  or  $\sim 1000 \text{ }^\circ\text{C}$ , respectively) and using pre-fired bars ( $815 \text{ }^\circ\text{C}$  or  $1400 \text{ }^\circ\text{C}/5 \text{ h}$ ).

Cold flexural strength (ASTM C133-97), apparent porosity (ASTM C380-00, using kerosene as the immersion liquid) and hot modulus of rupture (HMOR) measurements were selected to evaluate the refractories' thermo-mechanical performance. The latter test was carried out at  $600 \text{ }^\circ\text{C}$ ,  $815 \text{ }^\circ\text{C}$ ,  $1000 \text{ }^\circ\text{C}$ ,  $1200 \text{ }^\circ\text{C}$  and  $1400 \text{ }^\circ\text{C}$  (using samples pre-fired for 5 h at the same testing temperature) in HBTS 422 equipment (3-point bending device, Netzsch, Germany). Additional tests of SZ and SZ + B compositions were also performed at  $1400 \text{ }^\circ\text{C}$  with specimens pre-fired at  $1400 \text{ }^\circ\text{C}$  for 10 h and 20 h or  $1450 \text{ }^\circ\text{C}$ ,  $1500 \text{ }^\circ\text{C}$  and  $1550 \text{ }^\circ\text{C}$  for 5 h.

In order to identify the phases generated in the castables after firing at high temperatures ( $600\text{--}1550 \text{ }^\circ\text{C}$  for 5 h), X ray diffraction analyses of the compositions' matrix (fine components of the formulations,  $d < 100 \mu\text{m}$ ) were carried out in Bruker equipment (model D8 Focus,  $\text{CuK}\alpha$  radiation [ $\lambda = 1.5418 \text{ \AA}$ ] and with a nickel filter, using 40 mA, 40 mV and scanning step = 0.02).

Creep measurements were accomplished to find out the thermal stability of the samples at  $1450 \text{ }^\circ\text{C}$  for 24 h. Cylindrical specimens (height and external diameter = 50 mm and central inner diameter = 12.5 mm) were prepared according to the 51053 DIN standard

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