

COLLOIDAL SILICA AS A NANOSTRUCTURED BINDER FOR REFRACTORY CASTABLES

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ABSTRACT

Great efforts have been carried out in order to replace calcium aluminate cement (CAC) by other types of binders in refractory castables. CAC contents higher than 2-3 wt% can impose difficulties for the drying step and for the system's refractoriness when microsilica is present. The present work applies a nanostructured colloidal suspension as a binder for refractory castable compositions. Colloidal silica's (CS) are stable water based suspensions that, when combined with castable particles, provide, among other advantages, a higher drying speed and sinterability for the product. In this work, the performance of CAC, HA (Hydratable Alumina) and CS as binder agents in refractory castables was compared and analyzed.

INTRODUCTION

The reasons for the growing market of monolithic refractories, at the expense of traditional bricks, are their easy production, cheap installation and similar performance shaped products [1]. A significant advance in monolithics technology is the current supply of designed aggregates and dispersant additives, as well as in placing techniques. The use of a refractory binder less susceptible to curing conditions than the traditionally employed calcium aluminate cement (CAC) is a subject under constant investigation [2].

Calcium aluminate cement is the most used hydraulic binder in refractory castables compositions. Nevertheless, CAC amounts higher than 2-3 wt% in Al_2O_3 -CaO-SiO₂ systems may induce liquid formation at lower temperatures [1, 3]. Other important concerns for the high CAC content castables are the curing and dewatering steps, which must be carefully conducted in order to reduce explosive spalling [1].

Among the different binding systems for cement free castables, hydratable aluminas (HA) have attracted great attention [4-6]. HA are low crystalline mesophase transition aluminas (e.g. κ , θ , ρ), which, similar to cement, harden after reacting with water [7]. During heating, the hydrated phases lose their chemically bound water, giving rise to the stable form of alumina (α -Al₂O₃), which at higher temperatures will help to develop a strong ceramic bond [1, 7]. However, the use of hydratable aluminas also present limitations, such as the high likelihood of explosive spalling during drying, because of its less permeable structure when compared with a cement based composition [1, 4].

Concerning all these hydraulic binders' drawbacks, the present work applies a nanostructured colloidal suspension as a binder for refractory castable compositions. Colloidal silica sols are stable water-based suspensions, containing up to 50 wt% of nanometric spherical amorphous silica particles (8-15 nm diameter). These materials have been broadly used in the formulations of coatings, catalysts, papers, and anti-soil treatments as well as high temperature binders for fibrous isolating and investment castings [8, 9]. Although the application of col-

loidal silica as a refractory bonding system has been known for a while in the refractory industry, little systematic research has been found in the open literature.

When combined with other solid particles, colloidal silica can be linked together in branched chains, in a process known as gelation [2, 10], which can be induced by water removal. During the drying step, the hydroxyl groups (Si-OH) on the surface of the particles generate siloxane bonds (Si-O-Si), which results in a three-dimensional network (Figure 1) [10].

Gelation can also be induced by pH changes and a salt or water-miscible organic solvent addition, named gelling agents. With the proper selection of these agents or the pH variation, the colloid is gelled around the solid particles providing mechanical strength to the system after drying [2, 10-11]. The resulting structure is highly permeable and allows the composition to be easily dried, reducing cracks and explosive spalling. During sintering, its high surface area (typically close to 200 m²/g) may induce the formation of mullite in alumina-based sys-

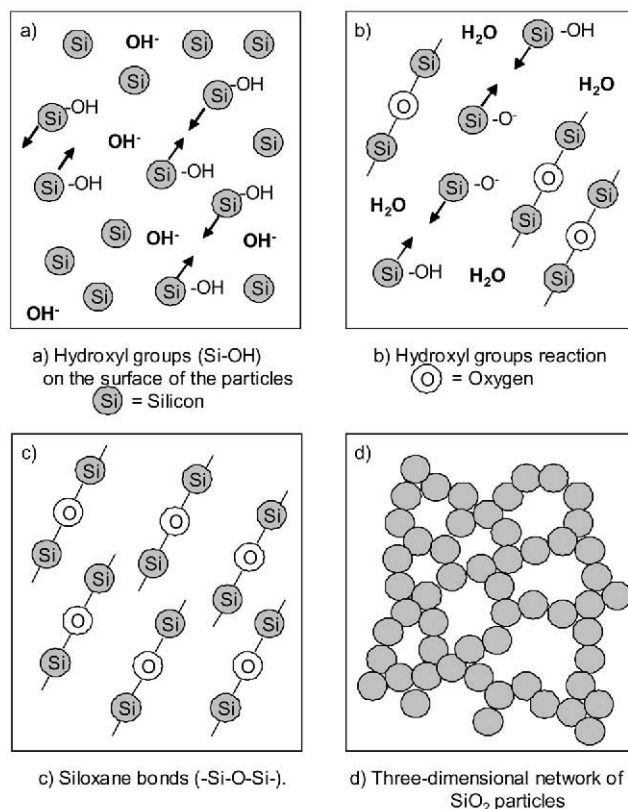


Figure 1. Colloidal silica gelling mechanism.

tem, which improves the chemical resistance and the hot-strength properties [11].

As the use of colloidal silica in refractory castables may reduce the problems presented by the current hydraulic binders [2, 11-12], in this work the performance of calcium aluminate cement and hydratable alumina as binder agents in refractory castables was compared to this nanostructured binder. Their rheological behavior, mechanical strength, permeability, apparent porosity, drying profile, refractoriness under load and creep were compared and analyzed.

EXPERIMENTAL PROCEDURE

High-alumina self-flow castable compositions were formulated using the software PSDesigner [13]. A particle-size distribution adjusted to theoretical curves based on Andreasen's packing model [14], with a distribution coefficient (q) equal to 0.21, was used. The mixtures were composed of calcined alumina (A1000 and A17NE – Almatris U.S.), white fused alumina (grades 4/10, 8/20, 20/40, TP 40 and TP 200 – Elfusa Brazil) and 3.0 wt% of a hydraulic binder: calcium aluminate cement (CA14M – Almatris U.S.) or hydratable alumina (Alphabond 300–Almatris U.S.) or colloidal silica (Bindzil 40 wt% SiO₂ – Nalco). The composition with the hydratable alumina (HAB) was dispersed with a polyethyleneglycol based additive (SKW Polymers) and the other systems (CAC and CS) with citric acid (Labsynth Brazil). For the CS compositions, MgO sinter (d_{50} = 15 μ m; 98 wt% MgO) was used as a gelling agent (0.6 wt% of the colloidal silica) [12]. A 4.5 wt% water content was added to the compositions for mixing and binder hydration. Mixing was carried out under constant rotation (44 rpm) in a castable rheometer developed in the authors' research group [15].

Compositions of castables were cast into 40 mm x 40 mm cylindrical molds for the drying tests, mechanical strength and apparent porosity measurements. For the permeability, 75 mm diameter by 22 mm thick disks were prepared, whereas for refractoriness under load and creep measurements, 50 mm external diameter and height and 12.4 mm central hollowed cylinders were cast. Samples were cured at 50°C in an acclimatized chamber (Vötsch 2020) for 24, 72, 96 and 168 h.

Cement containing compositions were cured in a moisture-saturated environment (~ 100% RH), in order to favor the hydration mechanism. The other compositions were cured without moisture (in open air), inside the acclimatized chamber. For those bonded with hydratable alumina, there was no need for moisture for strength development; in fact, its presence may inhibit full strength development, particularly at the surface of the castable [16]. Those bonded with colloidal silica required water removal so that the gelling mechanism could take place. The water removal decreases the inter-particle separation distance, increasing the particle collision and siloxane bond formation [10]. After the curing time, the samples subjected to permeability and apparent porosity tests were first dried in silica gel for 96 hours, at the curing temperature.

RESULTS AND DISCUSSION

Mixing Process

The literature reports colloidal silica bonded castables as self-dispersing systems due to the nanometric size and spherical shape of silica particles [2, 12]. For the composition studied, however, this effect was not observed, as the dispersant-free colloidal silica containing formulation could not be properly mixed and homogenized. This could be attributed to the differences between the amounts of col-

loidal silica employed in each case (8-14% by weight in literature, and 7.5 wt % of a 40 wt% SiO₂ solution, in the present study) [12].

In order to destabilize the colloidal silica suspension and then increase the probability for bond forming collisions, MgO sinter was added. MgO favors anionic reaction mechanisms on its surface, by the withdrawal of hydrogen ions from Si-OH groups, which, as a result, provides a higher siloxane bond formation, increasing the colloidal silica gelation rate [10].

Mixing was carried out by a two-stage water addition method [17]. During the processing step, the torque (N.m) required was computer recorded. The results are presented in **Figure 2**.

The dry mixing (up to 60 s of mixing, **Figure 2**-segment a) is characterized by the disruption of the dry powder agglomerates and the subsequent particles' homogenization. When part of the water amount (\cong 75.0 wt %) is added to the system (at 60 s), strong capillary forces start to actuate, increasing the torque values required. This effect is commonly known as the castable turning point (**Figure 2**-segment b) [17]. After the remaining water has been added (after the turning point), the material was mixed for another couple of minutes (**Figure 2**-segment c) [17].

The mixing curves attained for the different systems studied showed that the colloidal silica containing composition (after proper dispersion) required lower torque values and a shorter mixing time to complete the process than those containing CAC or HAB. It can be associated with two main effects: 1) the greater viscosity of colloidal silica (about 10 mPa.s) when compared to water, which keeps the particles apart, and makes the mixing process easier, and, 2) colloidal silica does not promote chemical reactions during the mixing step such as calcium aluminate hydrates (CAC bonded) and alumina gel formation (HAB bonded), that can disturb the ionic force and the viscosity of the suspension.

Mechanical Strength, Permeability and Porosity Measurements

The mechanical strength was measured according to the ASTM C496-90 standard (Splitting Tensile Strength of Cylindrical Concrete Specimens) in a MTS Systems, Model 810 using five samples of each castable composition, immediately after curing.

Permeability was measured at room temperature using two samples of each composition. The Darcyan (k_1) and the non-Darcyan (k_2) permeability constant were obtained by a polynomial fitting

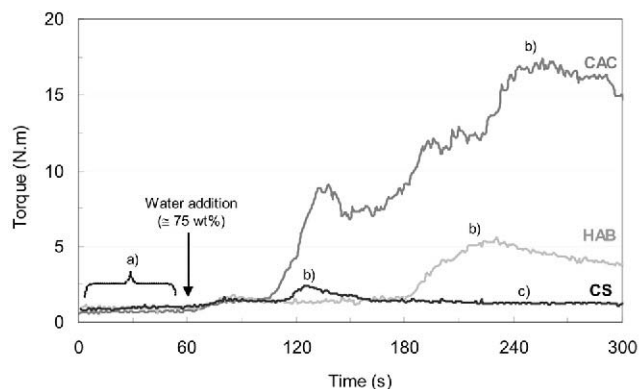


Figure 2. Mixing behavior for castables containing different hydraulic binders: a) dry mixing; b) castable turning point and c) addition of the total water remaining and castable homogenization.

between the airflow and air pressure values using Forchheimer's equation (Equation A) [18].

$$\frac{P_i^2 - P_o^2}{2PL} = \frac{\mu V_s}{k_1} + \frac{\rho V_s^2}{k_2} \quad (\text{A})$$

where P_i and P_o are the absolute inlet and outlet air pressures, respectively; V_s is the air velocity; L is the sample thickness; μ is the air viscosity and ρ its density.

Apparent porosity was obtained according to the ASTM C 20-87 (immersion test), using kerosene as the immersion liquid.

Figure 3 compares CS bonded castables cured in two conditions: open air and a moisture-saturated environment. The results indicate that the CS system requires water removal to develop mechanical strength. In addition, **Figure 3** also shows two distinct mechanical strength behaviors. Whereas HAB and CS containing compositions developed their maximum mechanical strength after the first 24 hours at 50°C, the CAC containing ones needed at least 72 more hours to achieve its highest value. For the CAC bonded castable, this gradual increase in mechanical strength is well reported in the literature and associated with the time required for the dissolution/precipitation processes involved in the hydraulic bonding mechanism [19]. The HAB and CS bonded systems, on the other hand, have their mechanical strength development related to the drying: during the water removal, the sol is converted to dried gel, increasing the mechanical strength [10]. Therefore, as drying is promoted, mechanical strength is developed. An important consequence of this mechanism is the reduction of the full processing time, since the curing step and the mechanical strength development can occur simultaneously.

The binders tested display distinct permeability levels (**Figure 4**) and these differences can be related to each consolidation mechanism and sub-products. The CAC cured below 20°C and the HA, during their hydration process, generate low-density products (calcium aluminate hydrates and alumina gel, respectively) that pores and reduce permeability [4, 20]. CS, on the other hand, does not generate hydrates [2], which, after gelation, favors the formation of an open and highly permeable structure.

As all formulations were mixed with the same water amount (4.5 wt %) it would be reasonable to expect similar values of apparent porosity (**Figure 5**). Nevertheless, due to its nanometer size, colloidal silica particles could behave as a liquid increasing the apparent volu-

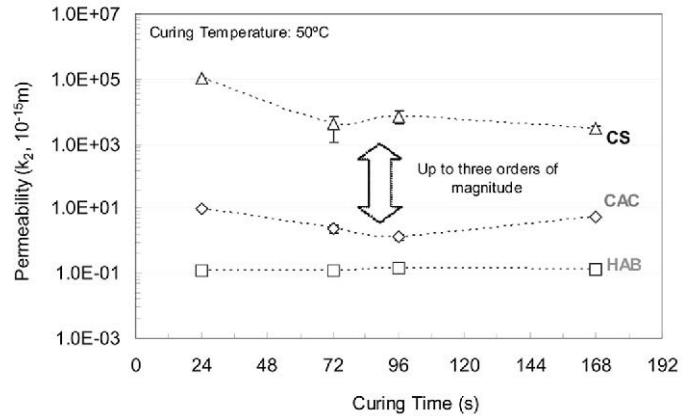


Figure 4. Permeability measurements (k_2) as a function of curing time for different binders containing compositions, cured at 50°C.

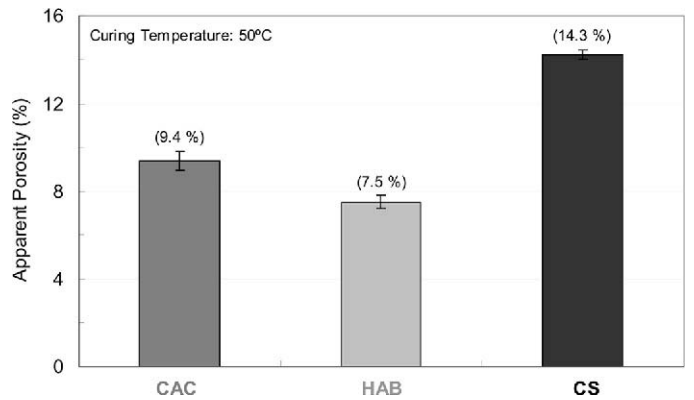


Figure 5. Apparent porosity (AP) for castables based on different binders, cured at 50°C.

metric amount. A superior liquid content promotes the separation of the matrix particles and an inter-particle force reduction, resulting in a more porous structure [21].

Drying Behavior

Dewatering tests were conducted in a thermo gravimetric device composed by an electric furnace coupled to a digital scale [22]. Results correlating the samples' temperature with their mass loss rate were obtained applying continuous heating (5°C/min) from room temperature up to 600°C. Mass loss was analyzed using the W parameter and dW/dt (drying rate), calculated following equations B and C, respectively:

$$W(\%) = 100 \times \left(\frac{M_o - M}{M_o - M_f} \right) \quad (\text{B})$$

$$\frac{dW}{dt} (\% / \text{min}) = \frac{d}{dt} \left(\frac{M_o - M}{M_o - M_f} \right) \quad (\text{C})$$

where, W represents the cumulative fraction of water expelled during the heat-up per total amount of water initially present in the body; M is the instantaneous mass during the heating stage, M_o is the initial mass and M_f is the final mass of the tested sample. **Figure 6** shows the drying behavior for the different systems analyzed, for samples cured for 24 hours at 50°C.

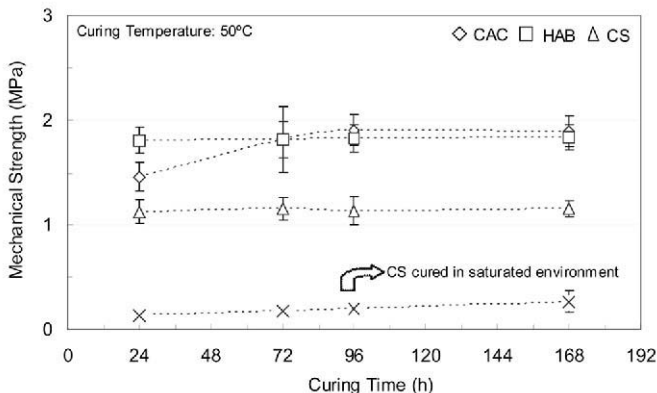


Figure 3. Mechanical strength as a function of curing time for castables prepared with different binders, cured at 50°C.

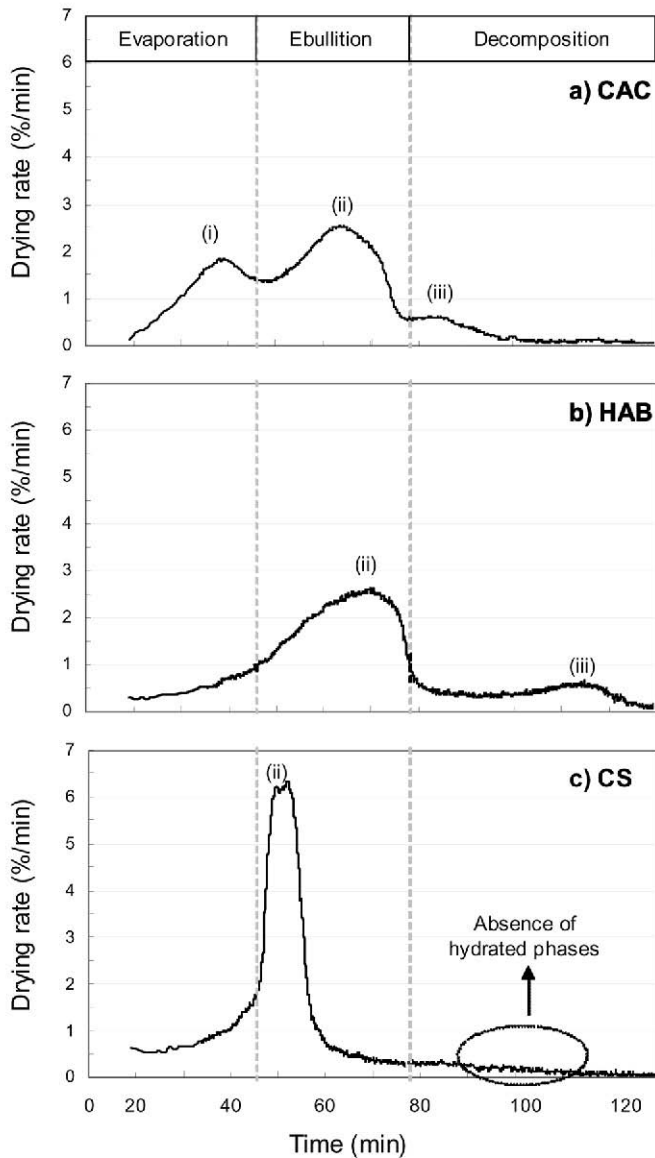


Figure 6. Drying rate (dW/dt) as a function of heating time ($5^{\circ}\text{C}/\text{min}$) for castables prepared with different binders, cured at 50°C .

The dewatering of low permeability refractory castables, such as CAC bonded ones, is carried out in several stages, driven by different mass and energy transport mechanisms. In the first stage (from room temperature up to around 100°C) (**Figure 6a**-segment i), the main drying mechanism is the free water evaporation. The second stage (from 100 up to $250\text{-}300^{\circ}\text{C}$) corresponds to the free water ebullition and decomposition of low temperature hydrates and gel (**Figure 6a**-segment ii). The third one is usually related to the decomposition of hydrated products, such as C_3AH_6 and AH_3 (**Figure 6a**-segment iii) [22].

The CS and HAB compositions were cured in an open atmosphere during which some drying occurred; therefore, the amount of free water removed and deleted by evaporation (first stage) during the dewatering test was reduced. In the second stage, indicated by segment (ii) in **Figure 6 a, b and c**, the drying rate becomes highly sensitive to the permeability level, as a higher amount of steam can be entrapped in low permeability structures, raising the pressure inside the castable. If the vapor rate formation is greater than the structure's

ability to expel it, the modulus of rupture of the castable can be exceeded, leading to material spalling.

Due to the difference among the castables' permeability values (**Figure 4**), the water removal was facilitated in colloidal silica containing castables. Therefore, they were dried much more easily and quickly, and likely generated lower pressure levels. The lower permeability of the HAB samples required higher temperatures to expel the water vapor from the bulk of the solid, increasing the risk of explosive spalling during drying.

The absence of the third stage in the CS curve is a good evidence of the non-existence of high temperature chemically bonded water in colloidal silica containing castable, which reduces the damage risks during heating.

Thermo Mechanical Behavior

Thermo mechanical properties were evaluated through refractoriness under load (RUL) and creep measurements in a NETZSCH-421 device. RUL measurements were performed in pre-fired samples (at 550°C for 12 hours) and the analysis was carried out under continuous heating ($5^{\circ}\text{C}/\text{min}$) up to 1600°C , under a compressive load of 0.2 MPa. Creep samples were first sintered at 1500°C during 24 hours and then subjected to a compressive load of 0.2 MPa at 1450°C for 48 hours. **Figures 7 and 8** display these results.

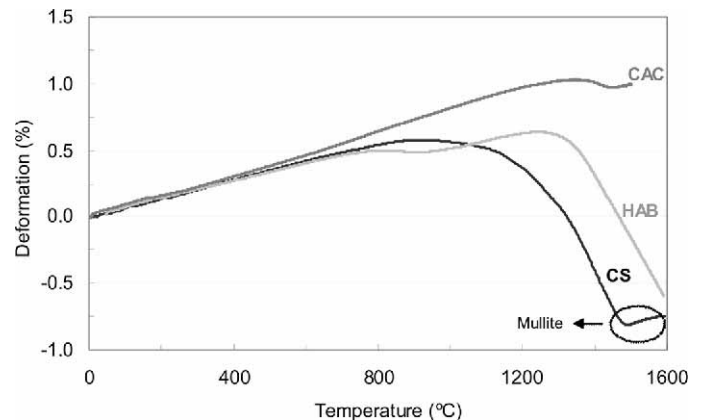


Figure 7. Refractoriness under load for calcium aluminate cement (CAC), hydratable alumina (HAB) and colloidal silica (CS) based compositions.

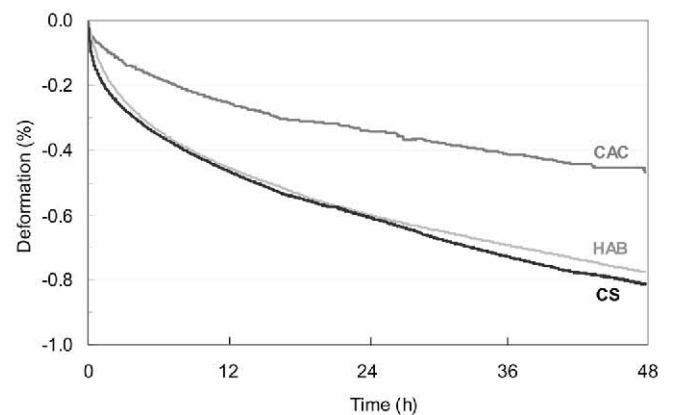


Figure 8. Creep for castables containing calcium aluminate cement (CAC), hydratable alumina (HAB) and colloidal silica (CS) for samples pre-sintered at 1500°C and tested at 1450°C .

As the samples were pre-fired at 550°C, the deformation level on the RUL test also includes sintering. The colloidal silica composition presented higher sinterability, as shown in **Figure 7**. This can be explained by its high surface area, which promoted the system's reactivity, increasing the sintering rate. The expansion detected close to 1500°C for the CS's formulation is likely to be associated to the mullite formation [23].

In order to detect the deformation under load, creep measurements were carried out. The influence of matrix content on the creep behavior of castables may explain **Figure 8**. Grain sliding deformation mechanism is more active when a large amount of fine particles is present. The system porosity is also related with the creep behavior, which explains the smaller creep deformation for the CAC composition.

CONCLUDING REMARKS

The results showed that the use of colloidal silica in refractory castable compositions can be advantageous in comparison with the refractory cement and the hydratable alumina. Lower torques values were required during the mixing step and an earlier turning point was attained, compared to the other compositions analyzed. The mechanical strength values as a function of curing time for the CS bonded system showed a lower sensitivity to curing conditions, as a shorter drying time was necessary to attain suitable properties. This effect can be technologically useful, as it provides a reduction on the full processing time.

The gelling mechanism of colloidal silica containing composition generated a high-permeability structure, facilitated water removal, preventing spalling. The drying process was favored due to the water loss which occurred during curing in open air and the absence of higher temperature chemically bonded water.

The nanometer-sized colloidal silica particles also improved the system's reactivity, increasing the castable sinterability, promoting mullite formation. Nevertheless, the porosity level developed was too high. Although the colloidal silica is a nanosized system, the results obtained showed that their contribution to the packing was low. Therefore, superior mechanical strength values could be achieved with an adequate particle-size distribution, which would result in lower porosity and consequently in high-quality performance refractory castables. This will be the subject of our next publication on colloidal silica based castables.

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