Novel Engineering Route to Improve the Green Mechanical Properties of Nano-Bonded Refractory Castables

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The use of colloidal silica as a CaO-free binding system for refractory castables has been increasing recently. Nevertheless, the resultant low green mechanical strength of these castables has hindered their application in relevant areas. The current paper provides a novel engineering route to improve the green mechanical properties of colloidal silica bonded refractories. To attain this purpose, calcium aluminate cement (CAC) and/or hydratable alumina (HA) were used as gelling agents. Splitting tensile test showed that although using HA resulted in a more significant increase in the mechanical strength of the samples when compared to CAC, using a combination of both additives (CAC+HA) had the most positive impact on the green mechanical properties of the castables, leading to strength levels as high as the reference cement-bonded system (CAC-Ref). XRD and DTG tests were carried out to evaluate the hydration behaviour of the selected additives. The results indicated that CAC enhanced the hydration of HA based on the accelerated dissolution of the gel layer formed on HA particles, which was induced by the $Al(OH)_4^-$ common ion effect. Nevertheless, XHR-SEM results showed that HA on its own is an efficient gelling agent for colloidal silica bonded refractory castables, providing a unique hybrid gelled nanostructure in the matrix.

1 Introduction

Calcium aluminate cements (CAC) have been the most usual refractory castable binders due to their suitable rheological properties and green mechanical strength. Nonetheless, CAC amounts higher than 3 mass-% may extend the drying time and also reduce the refractoriness of silica-containing systems [1, 2]. Therefore, products bonded with hydratable alumina (HA) or colloidal binders (colloidal silica or alumina) were developed as alternatives to cement [3–5].

Hydratable aluminas (HA) are amorphous mesophase transition aluminas which are produced by flash calcining gibbsite [$Al(OH)_3$] [3]. Although HA overcomes he low-melting point phase generation associated with microsilica-containing CAC-bonded castables, there are still some drawbacks attributed to this binder. HA-bonded castables demand longer mixing time and high water contents due to the high specific surface area of the binder [6]. Moreover,

after hardening, HA-containing castables results in a much less permeable structure when compared to CAC-based ones, which leads to higher explosive spalling likelihood during the water dry-out [7, 8].

Based on that, colloidal silica-bonded products were presented as an alternative to overcome the drawbacks of other binder systems [4, 9]. Details of the benefits of this nano-binder have been shown in a review paper by Nouri-Khezrabad et al. [10], where the main differences have been compared to the aforementioned traditional hydraulic ones.

Contrary to hydraulic binders like CAC and HA, colloidal silica does not give rise to hydrated phases during setting step. When combined with other refractory particulate materials, colloidal silica particles can be linked together using different setting mechanisms, such as gelling and coagulation, providing initial strength when applied to ceramic systems [11]. Gelling process takes place when siloxane groups are

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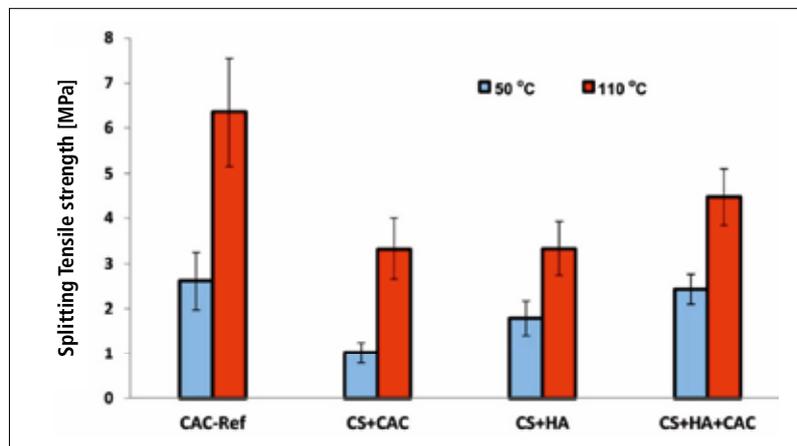Corresponding author: M. Nouri-Khezrabad
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Tab. 1 Specification of colloidal silica binder used in the experiments

Silica Content [mass-%]	Particle Size [nm]	Specific Surface Area [m²/g]	Stabilizing Agent	pH
50	20–100	80	Sodium	9,3

Fig. 1 Mechanical properties of nano-bonded castables containing HA, CAC or HA+CAC as setting additives. A reference composition (CAC-Ref presenting 4 mass-% CAC as a binder) was also prepared and evaluated. The samples were cured (50 °C) or dried (110 °C) for 24 h before testing

formed at the interface of nanometric particles at the expense of silanol groups through the following reaction:

$$- SiOH + HOSi- \rightarrow -SiOSi- + H_2O$$
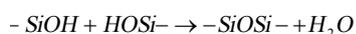
Regarding the coagulation, an additive bridges the particles causing close-packing clumps. Both setting mechanisms are influenced by the pH change, particle size and concentration of silica, the presence of additives and the temperature [11].

In spite of the advantages of the colloidal silica, there are still some problems which hinder the potential applications of this binder. Although various gelling agents can be used [12], the available setting times are still too long and the as-cast green mechanical strength levels are lower than those attained for CAC-based castables [13]. This would be a problem for demoulding the cast products as they may easily crack or be damaged during their handling.

Considering these aspects, the objective of this work was to overcome the challenge of low green mechanical strength of colloidal silica bonded castables by using small amounts of CAC and/or HA.

2 Experimental

The castable compositions were prepared with a mixture of reactive aluminas as matrix powders (CT3000SG and CL370 C, Almatis/US) and tabular alumina (Almatis U.S, D$_{max}$ <6 mm) as coarse aggregate grains. The particle-size distribution of castables was adjusted to Alfred packing model with a distribution coefficient (q) of 0,21. The colloidal silica (CS) binder used in the experiments was Bindzil 50/80 (Eka Chemicals/SW) and its features are pointed out in Tab. 1. 0,5 mass-% Calcium aluminate cement (Secar 71, Kerneos/FR) or 2 mass-% hydratable alumina (Alphabond 300, Almatis, US) were used as gelling agents. A dual additive system based on mixture of 1,5 mass-% HA and 0,5 mass-% CAC was also tested. Citric acid (Labsynth/BR) was employed as the setting retarder to provide enough workability for the castable. The total water content of the castables was 4,5 mass-% (4 mass-% available in 8 mass-% colloidal silica and 0,5 mass-% added as distilled water). Castables were prepared by gradually adding colloidal silica binder to the dry raw materials in an Eirich mixer (model R02E) and mixing for 4 min. A colloidal silica-free castable containing 4 mass-% calcium aluminate cement was also prepared as a reference (CAC-Ref).

The samples for mechanical test evaluation were cast in cylindrical moulds (40 mm high and 40 mm in diameter) and kept in a chamber at 50 °C (without humidity) for 24 h during curing and at 110 °C for 24 h

(drying). The splitting tensile strength of the castables was measured according to the ASTM C496-90 standard in a MTS Universal Testing System, Model 810. A constant loading rate of 42 N/s (1000 kPa/min) was used. The splitting tensile strength was calculated by:

$$\sigma = \frac{2P}{\pi h d}$$

where, σ is the splitting tensile stress [MPa]; P is the maximum load [N]; h [mm] and d [mm] are the height and diameter of the samples, respectively.

For XRD and TG tests, alumina-colloidal silica suspensions containing HA, CAC or HA + CAC as additives were prepared. XRD measurements were carried out in Bruker equipment (model D8 Focus, CuKα radiation [λ = 1,5418 Å] and a nickel filter, using 40 mA, 40 mV and scanning step = 0,02). TG evaluations of the cured materials were conducted in a Netzsch STA 449 device, using a heating rate of 10 °C/min with a synthetic air (80 % N$_2$ – 20 % O$_2$) flow of 50 cm³/min and α-Al$_2$O$_3$ as a correction standard.

Additionally, the microstructures of the alumina-colloidal suspensions containing HA, CAC and HA+CAC after curing at 50 °C for 24 h were observed using high resolution scanning electron microscope (XHR SEM, Model Magellan-400L, FEI/ US).

3 Results

Fig. 1 shows the splitting tensile strength of high alumina colloidal silica-bonded castables containing HA, CAC or HA+CAC after curing for 24 h at 50 °C and drying at 110 °C for another 24 h. The results were compared with a reference CAC-bonded castable with 4 mass-% of calcium aluminate cement binder. Although using HA as setting agent resulted in significant increase in green strength comparing to CAC, a dual additive system based on mixture of CAC and HA (CS+HA+CAC) had the greatest improve on green mechanical properties leading to strength levels as high as the reference cement-bonded castable.

XRD and DTG tests were carried out to detect the formation of any possible hydrated phases of calcium aluminate cement or hydratable alumina in the samples. Fig. 2 shows the X-ray diffraction patterns of the powders obtained from gelation of alu-

mina-colloidal silica suspensions with CAC, HA or HA+CAC after curing at 50 °C for 24 h. The results clearly showed the formation of the gibbsite phase [$Al(OH)_3$] in the CS+HA+CAC sample, whereas this phase was not detected in the CS+HA one. This means that CAC has accelerated the hydration of HA particles, as $Al(OH)_3$ is the main phase formed when HA reacts with water. Another interesting aspect was that the usual cement hydrated phases could not be detected and the anhydrous compounds (CA and CA_2) were still present in the CS+CAC and CS+HA+CAC materials. The XRD results were also confirmed by the DTG profiles shown in Fig. 3.

Trying to evaluate the XRD and DTG results, two main questions arose: Firstly, why HA did not hydrate in CS+HA sample? And secondly, what is the mechanism by which CAC accelerates the hydration of HA? In order to answer these questions, a comprehensive literature review on hydration of HA and CAC as well as coagulation of colloidal silica by calcium ions was performed.

Formation of an aquo-hydroxo gel layer over HA surface immediately after contacting with water has been reported in the literature [14–17]. Subsequently, the water should slowly diffuse through the formed gel in order to contact the fresh HA and progress the hydration. The properties of the aquo-hydroxo gel layer formed on HA particles are mainly a function of pH and temperature. By increasing these parameters, the structure of this gel layer changes from a microporous gel to a dense crystalline one [16, 17].

As a result, the hydration obstacle of HA in the presence of colloidal silica was attributed to the high crystallinity order of the formed gel layer over HA particles. The high pH (>10 according to experimental measurements) or curing temperature (50 °C) of alumina-CS-HA system may lead to a gel layer with high crystalline order. The dense gel layer would not allow water to diffuse through it easily and so the hydration halts after formation of the gel layer. In order to partially support the statements above, a similar HA+CS sample was cured at room temperature and its hydration was evaluated using XRD measurements. Formation of the $Al(OH)_3$ phase was clearly observed in the obtained X-ray diffraction patterns (Fig. 4). Furthermore, this result corrobo-
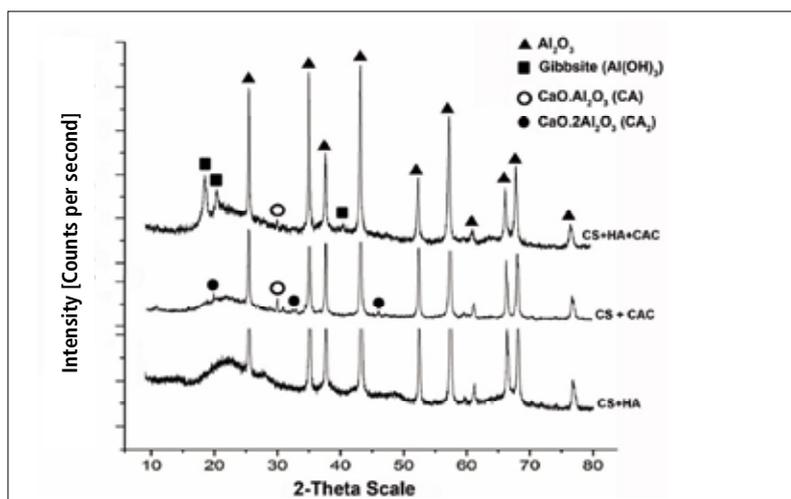

Fig. 2 XRD patterns of the powders obtained from gelation of alumina-colloidal silica suspensions containing CAC, HA or HA+CAC (as setting agents) after curing at 50 °C for 24 h
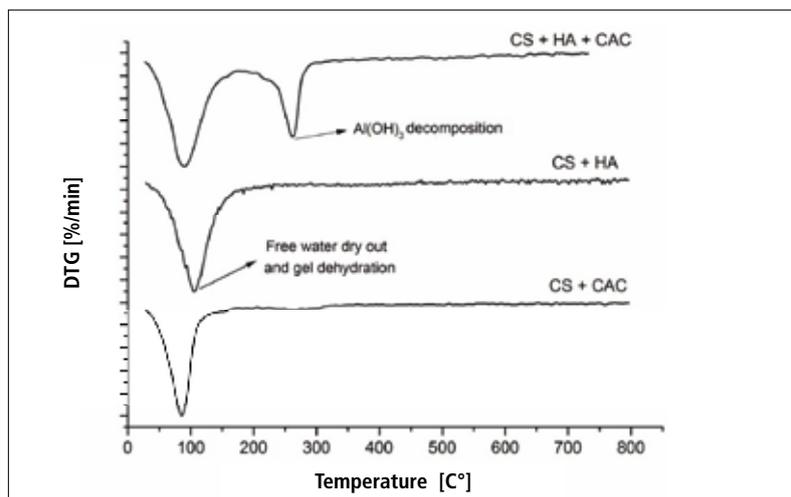

Fig. 3 DTG curves of the powders obtained from gelation of alumina-colloidal silica suspensions containing CAC, HA or HA+CAC after curing at 50 °C for 24 h
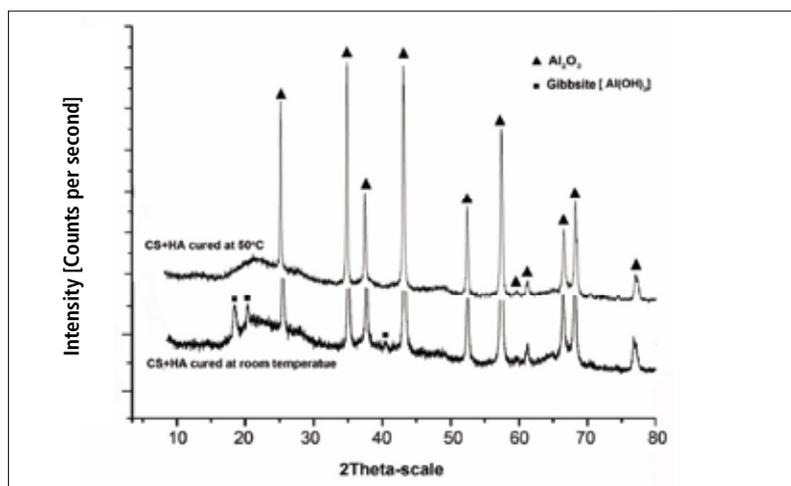

Fig. 4 X-ray diffraction patterns of the powders obtained from gelation of alumina-colloidal silica suspensions containing HA after curing at room temperature or 50 °C for 24 h
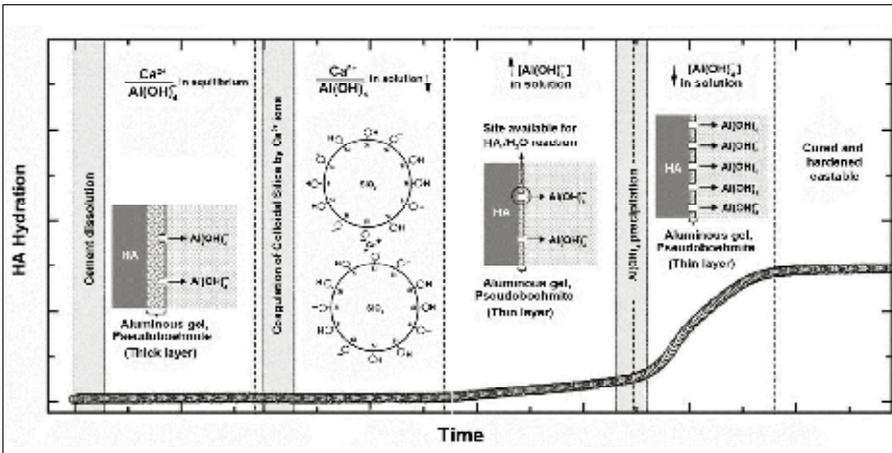
Fig. 5 Schematic diagram illustrating the most likely hydration mechanism of hydratable alumina (HA) in the presence of calcium aluminate cement and colloidal silica (adapted from [20])
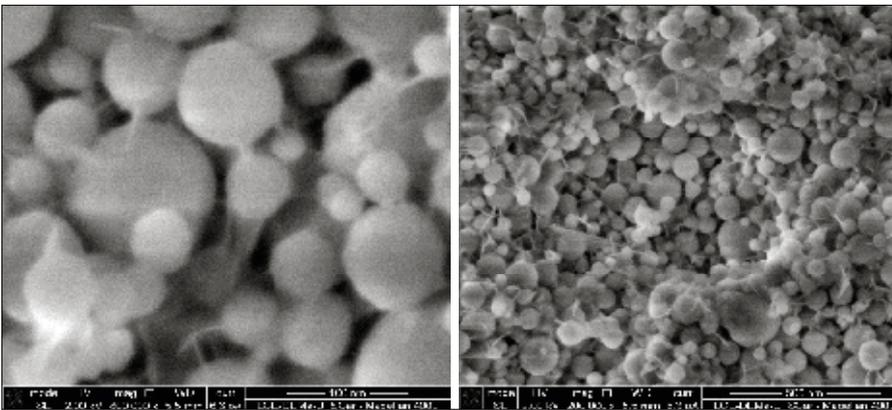

Fig. 6 XHR-SEM of cured alumina-colloidal silica samples containing HA showing a hybrid interwoven gelled nanostructure
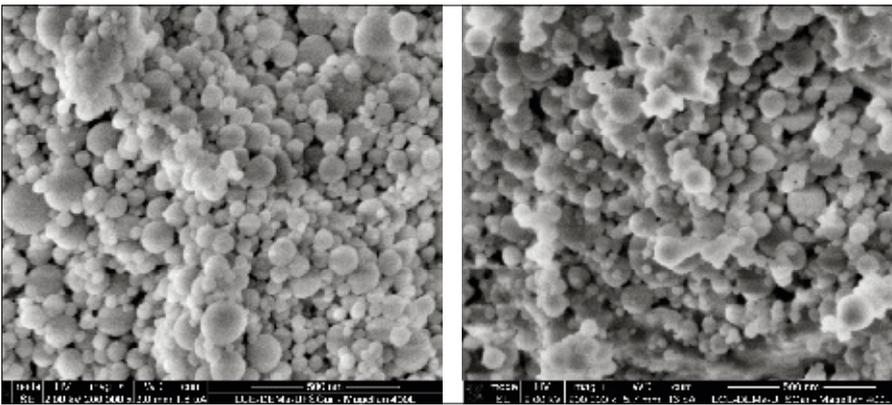

Fig. 7 XHR-SEM of cured alumina-colloidal silica samples containing CAC (left) and HA+CAC (right)

rates the discussion presented above, concerning temperature and pH dependence of the gel layer crystallinity generated during the hydration of HA.

The mechanism of hydration of HA at the presence of CAC was suggested based on the accelerated dissolution of the gel layer available on HA particles which is induced by $Al(OH)_4^-$ common ion effect. According to the proposed mechanism (Fig. 5), the cement dissolution starts immediately after contacting with water. At the same time a layer of gel is also formed on the surface of HA particles which is an obstacle for water diffusion. After moulding and during the curing step at 50 °C, the gel layer becomes

denser or less permeable, preventing liquid diffusion and further hydration of the HA particles. On the other hand, dissolution of cement continues with the tendency to keep the $Ca^{2+}/Al(OH)_4^-$ ratio in its equilibrium condition. However, simultaneously another phenomenon, i.e. colloidal silica coagulation, has started to consume the Ca^{2+} ions released by cement dissolution. The coagulation of colloidal silica by Ca^{2+} ions is a well-known process studied by several authors [18, 19]. This phenomenon decreases the $Ca^{2+}/Al(OH)_4^-$ ratio which means that $[Al(OH)_4^-]$ becomes supersaturated in the solution. As a result, $Al(OH)_3$ is precipitated from the solution and the $[Al(OH)_4^-]$ concentration decreases. This process as well as pH increase caused by presence of CAC, increase the solubility of HA gel layer leading to acceleration of HA hydration.

Analyzing the samples by high resolution scanning electron microscopy revealed interesting facts. The CS+HA composition showed a unique hybrid gelled nanostructure containing nano silica particles interwoven by polymeric chains of polysilicic acid (Fig. 6), whereas the other two systems containing CAC (CS+CAC and CS+HA+CAC) did not presented such interwoven hybrid nanostructure (Fig. 7). The interesting structure of CS+HA sample was generated due to the dissolution of the nano silica particles with the increase of the pH of the liquid medium, inducing further precipitation of these components as polymeric chains of polysilicic acid.

Considering the high pH value (>11) of the systems containing CAC, a further question may arise as why these compositions did not show a hybrid gelled nano-structure? The reason may be related to the presence of calcium ions released from CAC in the liquid medium. As mentioned in the literature [21, 22], calcium ions adsorb on a silica particles' surface and strongly reduce the solubility of amorphous silica, inhibiting the continuous dissolution and precipitation of monomeric species.

4 Conclusion

The green mechanical strength of nano-bonded refractory castables was remarkably improved by using a combined additive system based on the mixture of a small amount of calcium aluminate cement and hydrat-

able alumina as setting additives. The Al(OH)$_4^-$ common ion (released by both CAC and HA) sped up the hydration of HA, leading to the improvement of the high alumina castable's green mechanical strength. Nevertheless, based on the XHR-SEM results attained, HA may be used on its own as an efficient gelling agent for colloidal silica bonded refractory castables, providing a unique hybrid gelled nanostructure .

Acknowledgement

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