NON-CEMENT REFRACTORY CASTABLES CONTAINING NANO-SILICA: PERFORMANCE, MICROSTRUCTURE, PROPERTIES

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In this study, the effect of nano-silica sol content on the self-flow characteristics, microstructure, physical and mechanical properties of high-alumina self-flowing non-cement castable has been studied. The self-flow characteristics such as: self-flow value and working time has been evaluated. The bulk density, apparent porosity, mechanical properties and microstructure of fired castables at different temperatures has been investigated. The results show that the proper nano-silica content for achieving self-flowing performance of such castables and sufficient strength is 10-11 %. By increasing of firing temperature up to 1000°C, porosity and pore sizes of castable tend to decrease, because of complete dehydration of reminder hydroxyl groups, which can lead to increasing of strength. Because of using nanometer-sized colloidal silica particles with high surface area, the solid phase sintering of the nano-sized particles and also, mullite formation can occurr in the low temperatures up to 1300°C.

INTRODUCTION

Most castables and gun mixes use calcium aluminate cement (CAC) to bond the refractory aggregate together. The amount of CAC in the mix can vary from relatively low quantities to 10% or more, depending on the manufacturer and the mix. The presence of CAC is evident by CaO in the chemical composition of the material. For most CAC products, the CaO content will be in the range of 0.8 to 3.0%. These castables and gun mixes are blended with water to a proper consistency and installed in place. The added water reacts with the CAC, forming hydrated phases that provide low-temperature bonding of the refractory material. At low temperatures, the CAC materials are very dense and have very low permeability. As the refractory is heated, the physically bonded water is first driven off, followed by the chemically bonded hydrated water. Because several hydration phases are present, the complete dehydration process occurs over a broad temperature range (210 to 620°C). As each of these phases gives up its chemically bonded water, bonding strength decreases, and permeability and porosity increase until all water has been removed. Recently, new pumpable refractory products have been developed based on a patented sol-gel bonding nanotechnology containing no CAC. Nano-silica is one of the most popular binders for refractory, monolithic and castable applications. Nano-silica sol or colloidal silica is a stable water-based suspension, containing up to 40 wt.% of nano-metric spherical amorphous silica particles (3-15 nm diameter). These materials have been broadly used in the formulations of coatings, catalysts as well as high temperature binders for fibrous isolating, investment casting and refractory castables [1-4]. The water-based colloid (colloid silica) surrounds the refractory particles and, after gelling, forms a network encapsulating the refractory particles. 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. Gelation can also be induced by pH changes and a salt or water-miscible organic solvent addition, named gelling agents [1, 5, 6]. 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. The resulting structure is highly permeable and allows the composition to be easily dried, reducing cracks and explosive spalling [4-7]. Therefore, the use of nano-silica in refractory castables may reduce the problems presented by the current hydraulic binders. One of the main advantages of gel-bond compositions is their self-flow characteristics. This enables them to be installed by a pump. The wet mix coming out of the pipes flow freely on the surface and find its own level. No vibration is needed to make the material move and thus provides a great advantage in installations. Since the colloidal silica is compatible with silica and alumino-

silicate compositions, the gel-bond refractories have been successfully developed for a wide variety of compositions ranging from high alumina to alumina-silicate with or without silicon carbide and graphite, as well as all silica compositions. This compatibility provides a wide range of applications [1, 7-12].

Despite the advantages concerning gel-bonded present in the literature, further understanding of this bonding system is still required [1, 4-7]. In this work, the effect of nano-silica sol content on the self-flow characteristics, physical and mechanical properties of high-alumina self-flowing non-cement castable has been studied. Also, the microstructure of these castables has been investigated.

EXPERIMENTAL

Raw materials and composition

The composition prepared for experiments was high alumina self-flowing non-cement castable. The source of raw materials together with the composition and particle size distribution used for mixing of this castable is shown in Table 1. The particle size distribution was optimized by following the packing model found in literature [5]. Also chemical composition of raw materials is listed in Table 2. The nano-silica sol used is product of Bee Chems. Co. (India) which its specification is shown in Table 3.

For the compositions, MgO sintered powder (d_{50}=15 µm) was used as a gelling agent (0.4 wt.% of the nano-silica sol). For the study of nano-silica addition on self-flow characteristics and other properties of non-cement castables, the nano-silica sol was used in amounts of 8, 9, 10, 11, 12 and 13 volume-to-weight percent (volume of sol added in cubic centimeters to a 100 g batch).

Self-flow measurements

Self-flow value and working time measurement was performed according to ASTM C 1446-99. Based on this standard, after dry mixing of the batch for 30 s in a planetary mixer (Hobart), all the water (distilled) was added within 10 s while the mixer was running. The wet mixing was conducted for 5 min at a slow speed (Hobart, speed 1). After mixing, the prepared castable, was transferred to a sealed container and care was taken to keep the moisture constant. Ten minutes after addition of water, the mixed castable was poured into a standard cone with a base diameter of 100 mm according to ASTM standard number C-230. The cone was then elevated to allow the mix to flow, and after 60 s the patty diameter was measured. The percentage increase in spreading diameter after 60 s is taken as the self-flow value according to the following formula:

$$\text{Self-flow (\%)} = (D_2 - D_1) \times 100/D_1 \qquad (1)$$

where D_2 is the final average diameter after removal of mould and D_1 is the initial diameter (100 mm). The castable is considered as self-flow, when the above value lies within the range of 80-110% of the base diameter. During the self-flow evaluation, the ambient temperature was controlled to be in the range of 20-24°C [12].

Table 2. Chemical composition of raw materials

Oxide (wt.%)	Tabular Alumina	Microsilica	Reactive Alumina
Al_2O_3	99.4	0.47	99.8
Na_2O	0.36	0.01	0.06
CaO	0.05	0.3	0.02
MgO	0.10	0.22	0.02
SiO_2	0.02	96.45	0.03
Fe_2O_3	0.10	0.44	0.03

Table 1. Raw materials and composition of the high alumina non-cement castable studied

Raw materials		Source (Type)	wt.%
Tabular Alumina	2-5 mm	Alcoa Chemicals, T-60	10.8
	1-2 mm		10
	0.5-1 mm		15.6
	0-0.5 mm		6.7
	≤ 45 µm		33.3
Microsilica	d_{50}= 0.25 µm	Elkem, 971U	3.6
Reactive Alumina	d_{50}= 1.90 µm	Alcoa Chemicals, CTC-20	20

Table 3. Specification of nano-silica sol

SiO_2 Content (%)	Silica: Soda (w/w), %	Titrable Alkali (w/w), %	pH	Surface Area (m^2/g)	Average grain size (nm)
40 ± 0.5	77	0.32	9.5	250	3.03

Castable preparation

The raw materials were dry mixed in a planetary mill for 4 min, nano-silica sol was added during mixing, and the whole composition was wet mixed for an additional 4 min. Compositions of castables were cast into standard mold without vibration. After aging at 20°C for 24 h in the mold, the specimens were taken out of the mold, air dried for 24 h and oven dried at 110°C for 24 h. then, the specimens were fired at 1000, 1300 and 1500°C for 3 hours respectively.

Test methods

Dried and fired samples were tested for apparent porosity (A.P), cold crushing strength (C.C.S) and cold modulus of rupture (M.O.R). Apparent porosity results were obtained through the Archimedes method using kerosene as the immersion liquid for dried samples and water for fired samples (in accordance with ASTM C 830-93). In addition, the C.C.S. and M.O.R (3-point bent) testing were performed in accordance with ASTM C 133-97. An average of five samples was considered for all such tests. For microstructural evaluation, scanning electron microscopy (SEM) (Cambridge S-360) was performed on polished sections after gold coating. Energy dispersive X-ray spectroscopy (EDX) accompanied SEM observation to allow the identification of the crystalline phases. For characterization and detection of phases, X-ray diffraction (XRD) analyses (Cu Kα, Ni-filtered radiation, Philips model No. PW1050) were carried out on fired samples.

RESULTS AND DISCUSSION

The effect of nano-silica sol on the self-flow characteristics

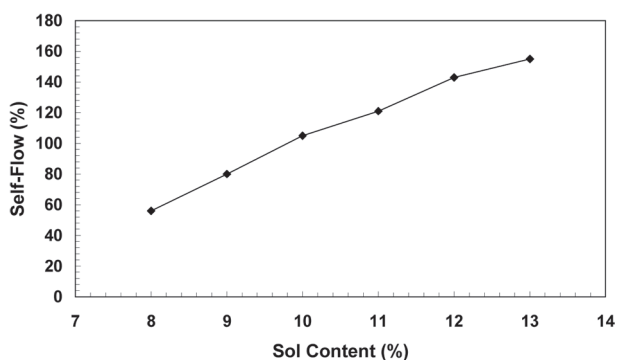Self-flow value against nano-silica sol content was plotted in Figure 1. It can be seen from Figure 1 that the flow value is enhanced with the increase of sol content because of increasing of liquid in the composition. Less than 9 % sol content, castable can not flow under its weight (self-flow value < 80 %) and considered to be vibrocast. Also, more than 11 % sol content, segregation of a liquid phase from the mixed batch material occurs (self-flow value > 110 %). Therefore, at sol content within the range of 9-11%, the self-flow value of castable lies within the range of 80-110 % which castable shows self-flowing behavior.

In Figure 2, the effect of sol content on self-flow value as a function of time is shown. The results indicate that with increase of sol content, the working time of castable tends to increase. This effect can be attributed to the dispersing effect of nano-silica sol and an increase of liquid phase in the castable composition. Generally, the first step in the setting of a self-flowing castable is a loss of flow, i.e. it becomes impossible to place without external force such as vibration. This time is recognized as working time. Control of the working time has always been one of the most important but also perhaps the most difficult aspect of refractory self-flowing castable technology which, can be controlled by additives such as accelerators or retarders. However, in gel-bonded castables the control of the working time is done via the sol content and the particle size distribution. The working time long enough for appropriate placement of self-flowing castables is actually between 30 to 100 min. Therefore, castables containing more than 10 % sol content will have adequate working time and can be installed properly.

The effect of nano-silica sol on the physical and mechanical properties

The effect of the sol content on the bulk density and apparent porosity of castable after drying and firing at various temperatures are shown in Figures 3 and 4. From these results, one can see that the addition of nano-silica sol increase the apparent porosity and hence, decrease the bulk density of the castables at all temperatures. Higher

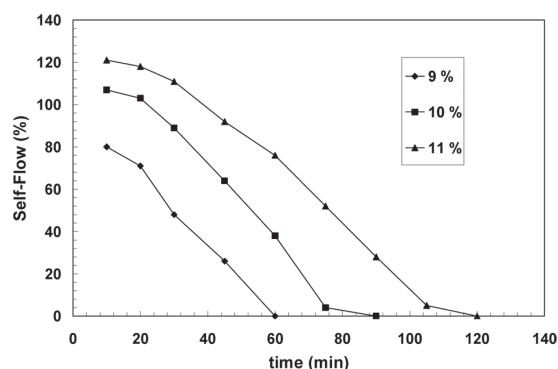Figure 1. Variation in self-flow value with nano-silica sol content

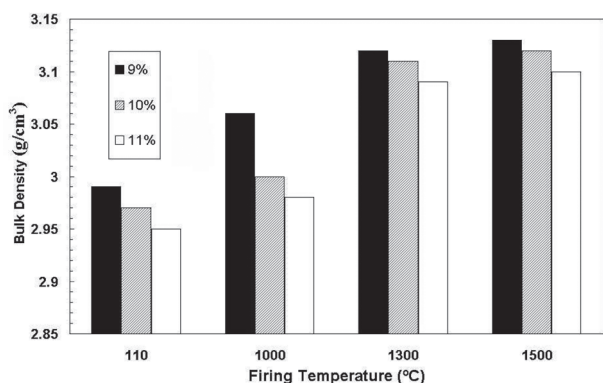Figure 2. The effect of sol content on self-flow value as a function of time

Figure 3. The effect of sol content on the bulk density of castable after firing at various temperatures
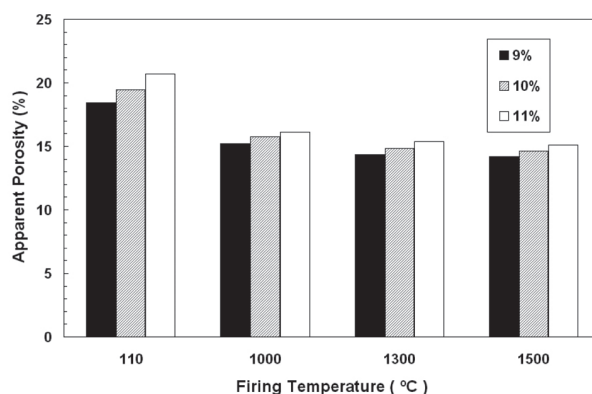

Figure 4. The effect of sol content on the apparent porosity of castable after firing at various temperatures

sol content leads to higher liquid content in the castable composition. Therefore, the removal of moisture during drying causes increasing of porosity in the body, which results in decreased bulk density. On the other hand, the results indicate that with increase of firing temperature, the apparent porosity of all compositions tends to decrease. The porosity of non-insulating industrial refractories typically falls in the broad range of 2 to 30 %. Porosity provides the openings for the penetration and reaction of working face refractories that are directly exposed to service conditions such as molten metal and slag or dross, cement clinker, spray injected liquid alkali and molten glass. Therefore, mix changes that result in lower porosity will, in general, reduce or slow down the reactivity in service and extend the service life.

The results of C.C.S and M.O.R of castable containing different amount of nano-silica sol after drying and firing at different temperatures are shown in Figures 5 and 6. It is found that higher contents of sol have a disadvantage in the strength development. Also, the results show that with increase of firing temperature, the mechanical strength of all compositions tends to increase.

A very important characteristic is the green strength development of a castable. It is created by the formation of hydrates of the clinker phases. In practice the higher cold

crushing strength leads to the higher erosion resistance of castable and prolonged life time. The results showed that despite the absence of hydraulic binders in composition of gel-bonded castables cold crushing strength and bending strength after drying are reaching to 37 and 3.5 MPa respectively. These strengths are reasonable values for field applications and may be attributed to the highly packed structure.

Generally, several factors can affect the apparent porosity and strength of these castables, including sol content, initial packing density and phases developed during sintering. As mentioned earlier, higher sol content leads to higher liquid content in the castable composition. Therefore, the removal of moisture from the cast shape during drying causes higher porosity in the body, which results in decreased strength.

The tendency of decrease in C.C.S up to 1000°C for cement bonding castables may happen due to the dehydration of high alumina cement and then, breaking of cement-hydrated bonds. The results show that the apparent porosity of nano-silica bonded castables is decreased and hence, C.C.S is increased after firing at 1000°C. This shows the advantage of using sol bonding instead of cement bonding, where strength degradation is observed up to 1000°C. A sharp increase of the C.C.S
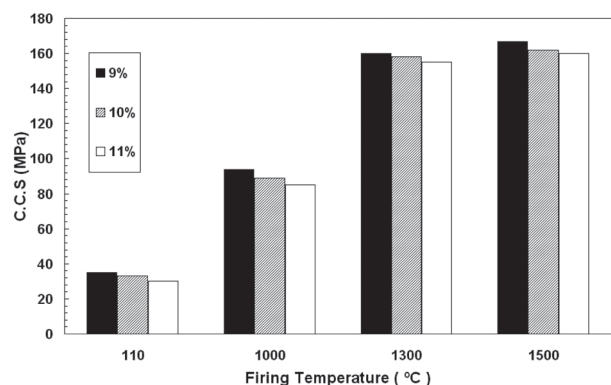

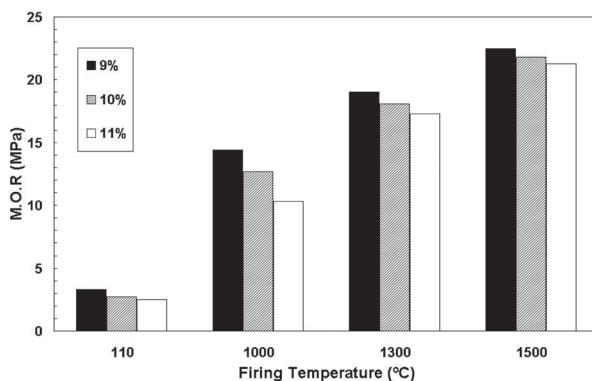Figure 5. The effect of sol content on the C.C.S of castable after firing at various temperatures

Figure 6. The effect of sol content on the M.O.R of castable after firing at various temperatures
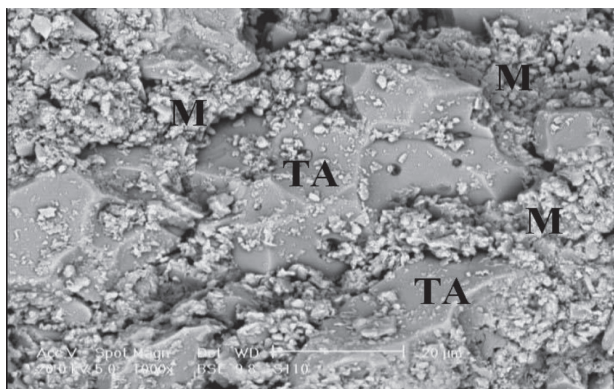
Figure 7. SEM micrograph of gel-bonded castable containing 10 wt. % nano-silica sol dried at 110 ºC. TA: tabular aggregates; M: matrix

Figure 8. SEM micrograph of gel-bonded castable containing 10 wt. % nano-silica sol fired at 1000°C

value at low firing temperatures (1300°C) is observed and is probably due to the enhanced ceramic bonding. Products sintered at 1500°C show the highest strength values because of a higher degree of sintering.

Microstructural evaluation

The microstructure of high alumina gel-bonded castable containing 10 wt.% nano-silica sol after drying at 110°C is shown on Figure 7. This figure reveals that the microstructure of these castables consisting of tabular aggregates (TA) and agglomerates of fine alumina, microsilica and colloidal silica in the matrix. This figure shows high packing and well dispersed particles in a microstructure, in which the fine particles occupy the voids between the coarser particles, enabling a decrease of porosity and thus an increase of the green strength. When combined with other particles, nano-silica particles can be linked together in branched chains, in a process known as gelation, 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
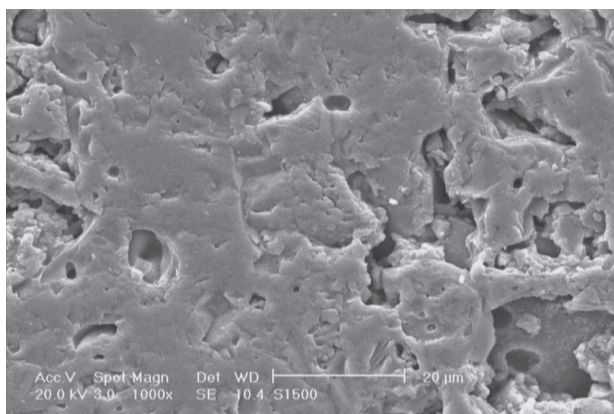
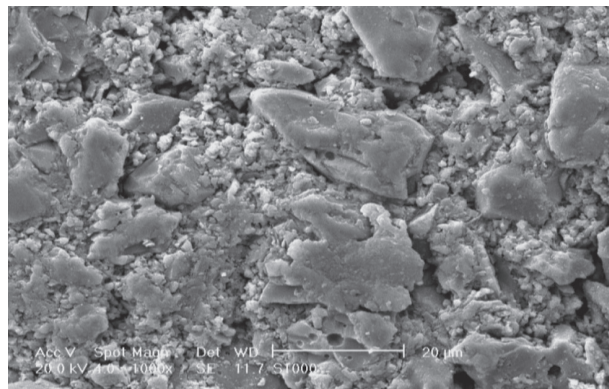Figure 8 shows a general view of gel-bonded castable containing 10 wt.% nano-silica sol after firing at 1000°C, which is similar to those dried at 110°C. There are two main differences between the 110 and 1000°C microstructures which can be attributed to dehydration after firing at 1000°C which produces lower porosity and smaller pore sizes resulting in higher strengths.

Generally, gel-bonded castables require water removal so that the gelling mechanism can take place. Water removal decreases the inter-particle separation distance, increasing particle collision probability and siloxane bond formation. Unlike CAC bonding, which produces chemically bonded water, the colloidal silica bonded material liberates chemically attached water and creates a chemical bond that does not break down through dehydration as the material is heated. Since the water is not chemically bonded, the majority of the water in the gel structure is free to be released at very low temperatures (100°C). However, a small quantity of water in the form of attached hydroxyl groups can still be released at higher temperatures (up to 1000°C). This release of water results in the formation of additional Si-O-Si bonds that further enhance strength development. These microstructural evaluations confirm the strength results at 1000°C. The

Figure 9. SEM micrograph of gel-bonded castable containing 10 wt.% nano-silica sol fired at 1300°C
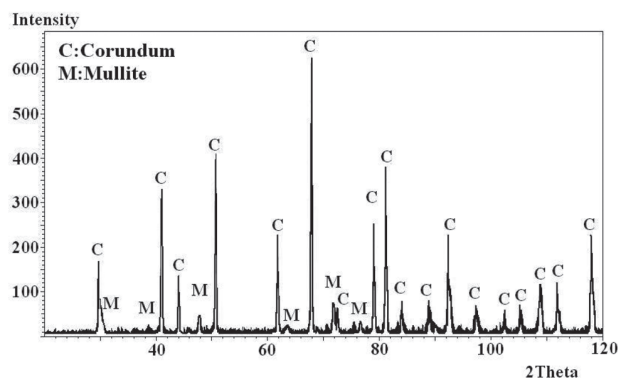

Figure 10. XRD pattern of castable fired at 1300°C.

microstructure of castable containing 10 wt.% nano-silica sol after firing at 1300°C is presented in Figure 9.

This figure shows tabular aggregates which are hold together with bonding system. Also, the XRD of castable sample fired at 1300°C is shown in Figure 10. At this temperature, mullite phase was found in addition to corundum. By comparing the XRD phases with strength properties, it can be observed that formation of mullite at 1300°C contributed towards development of strength and also influenced the other properties such as Hot M.O.R and creep resistance.

Because of the using nanometer-sized colloidal silica particles with high surface area in the composition and thus difference of special surface area energy between the matrix and the nano-silica particles, solid phase sintering of the nano-sized particles and also mullite formation can occurs at lower temperatures.

CONCLUSION

It has been shown that the nano-silica sol content has a great effect on the self-flow characteristics and other properties of gel-bonded self-flowing castables. The nano-silica sol addition can increase the working time of castable but the green strength is reduced. By increasing of the nano-silica, and thus liquid, in the batch the strength is decreased because of increasing porosity in the dried body. If the nano-silica sol content in the castable composition be used in the range of 10-11 %, a gel-bonded high alumina castable with adequate working time and reasonable strength will be obtained. Complete dehydration of hydroxyl groups after firing up to 1000 ºC leads to a decrease of apparent porosity and an increase of strength. This shows the advantage of using sol bonding instead of cement bonding. Also, the high surface area of nano-silica leads to low sintering temperaratures of castable and a considerable increase of mechanical strength. In samples fired at 1300°C mullite phase was detected that can increase the compressive strength of the castable.

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