Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 3479–3497

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Review paper

Nano-bonded refractory castables

M. Nouri-Khezrabad[a,]*, M.A.L. Braulio[b], V.C. Pandolfelli[b], F. Golestani-Fard[a,c], H.R. Rezaie[a,c]

[a]*School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Narmak, Tehran 16844, Iran*
[b]*Federal University of São Carlos, Materials Microstructural Engineering Group, km 235, Rod. Washington Luís, FIRE Associate Laboratory, São Carlos 13565-905, SP, Brazil*
[c]*Center of Excellence for Advanced Materials, Iran University of Science and Technology, Narmak, Tehran 16845-195, Iran*

Received 17 October 2012; received in revised form 12 November 2012; accepted 13 November 2012
Available online 23 November 2012

Abstract

Calcium aluminate cement (CAC) contents higher than 3 wt% in refractory castables can have some drawbacks in the various processing steps (mainly drying) and also in their refractoriness when in contact with SiO_2. The use of colloidal silica as an alternative binder has been studied by many researchers in recent years and recently reports have also explored the use of colloidal alumina for the same purpose. This article reviews the recent developments in nano-bonded refractory castables focusing on the use of colloidal silica or alumina. In the first part of the paper, a comparison of different binding systems for refractory castables is shown. The benefits of replacing CAC or hydratable alumina by colloidal binders are discussed. In the second part, the advantages of colloidal silica/alumina as a refractory binder are highlighted. Meanwhile, the characterization techniques and functional mechanisms of these binders are presented in order to understand the behavior of these systems. Finally, in the last section, the challenges for suitable use of colloidal binders are discussed and the future direction of nano-structured refractory castables is outlined.

Keywords: A. Suspensions; E. Refractories

Contents

1. Introduction 3480
2. Benefits 3482
    2.1. Mixing behavior 3482
    2.2. The rheological behavior. 3482
    2.3. Setting mechanism 3484
        2.3.1. Colloidal silica 3484
        2.3.2. Colloidal alumina 3487
    2.4. The drying and thermogravimetrical behavior 3488
    2.5. Permeability 3489
    2.6. Mechanical properties. 3490
        2.6.1. Cold mechanical properties 3490
        2.6.2. Thermomechanical properties 3490
    2.7. Hot elastic modulus 3491
    2.8. Sinterability. 3492

---

*Corresponding author. Tel./fax: +98 21 77240291.
E-mail addresses: nouri@iust.ac.ir (M. Nouri-Khezrabad), vicpando@ufscar.br (V.C. Pandolfelli).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.11.028

3. Final remarks and challenges for the future . . . 3494
Acknowledgments . . . 3495
References . . . 3495

1. Introduction

Monolithic ceramics have evolved over the years into a widely used class of refractories that associates performance and cost-effectiveness [1]. In the monolithic family, refractory castables comprise a large group of materials whose application has grown significantly in the last 30 years. Progressing from rather simple mixes, today they comprise some very complex and technical formulations, used in a variety of very demanding and harsh industrial applications. Nowadays, their market share has been increasing and, in many instances, has overcome brick and shaped refractories. Furthermore, for many applications it is the most appropriate choice due to better performance and easier installation [2].

Refractory castables can be classified based on different aspects including CaO content, the binder source, chemical composition, fluidity, bulk density, etc [3]. Their binding system plays a relevant role in different processing steps, including workability, dry-out and service performance. Therefore, all efforts are conducted to improve the bonding agents [4,5].

Different sorts of binding systems have been developed throughout the years starting with hydraulic bonding, in which higher amounts of calcium aluminate cement (CAC) were used, towards coagulating binders such as colloidal silica or alumina (Table 1) [4]. Hydraulic bonding via CAC is the most applied mechanism due to its suitable rheological properties and green mechanical strength. Detailed information about this binder has been described in a recent review [6]. Nevertheless, there are some drawbacks related to the use of CAC in systems containing microsilica and/or magnesia, as the presence of CaO coupled with these other oxides results in low melting point phase formation at high temperatures [7,8]. Other important concerns for cement-based castables arise during the curing and dewatering steps, which must be carefully conducted in order to reduce the explosive spalling likelihood [9–12]. In order to minimize these drawbacks, the properties of the refractory castables were improved by decreasing the cement content, giving rise to a shift from regular cement castables towards LCC (low cement castables), ULCC (ultra low cement castables) and lately cement-free castables [13–16].

Table 1
Progress in binding system for refractory castables [4].

Binding mode	1920s	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s	2010s
Hydraulic	Conventional cement bonded castables (Silicate cement, low purity CA cement)									
					Pure CA cement bonded castables (CA cement with improved purity)					
							High purity CA cement bonded castables (High purity CA cement+uf-Al_2O_3)			
							ρ-Al_2O_3 bonded castables			
								Hydratable Al_2O_3 bonded castables		
Chemical				Phosphate bonded castables [H_3PO_4 or $Al(H_2PO_4)_3$+MgO or CA]						
				Water glass bonded castables [Na_2O nSiO_2+Na_2SiF_6]						
					Sulphate, chloride bonded castables [$Al_2(SO_4)_3$+CA, $MgCl_2$ or $MgSO_4$]					
Polymerization					Polyphosphate bonded castables [$Na_5P_3O_{10}$ or $(NaPO_3)_6$+MgO, CaO or CA]					
							Resin bonded castables (Phenol resin, Novalac resin+cross linker)			
Hydraulic+Coagulating						Low cement castables (CA cement+Clay, CA cement+uf-SiO_2)				
Coagulating						Clay bonded castables (Ca-clay or Na-clay+CA)				
							Ultralow cement castables (uf-SiO_2+uf-Al_2O_3+CA)			
							Cement-free castables (non-cement castables) (uf-SiO_2, uf-Al_2O_3+electrolyte, uf-SiO_2+MgO)			
							Sol bonded castables (silica sol, alumina sol+electrolyte)			
Carbon bonded									MgO–C castables	
Nano engineered										In progress

Different calcium-free binding systems such as hydratable alumina (HA), colloidal silica (CS) and colloidal alumina (CA) have been developed for refractory castables [17–21]. Hydratable aluminas (HA) are amorphous mesophase transition aluminas which are produced by flash calcining gibbsite [$Al(OH)_3$], leading to a high specific surface area transition phase (ρ-alumina) [22–24]. When in contact with water, this alumina source rehydrates forming pseudo-boehmite (a poorly crystallized boehmite) and bayerite, which provides a suitable green mechanical strength to the structure [24]. This calcium-free binder is usually combined with microsilica in refractory castables to induce the mullite formation and improve the hot mechanical strength [25]. Although HA overcomes the low-melting point phase generation associated with microsilica-containing CAC-bonded castables, there are still some drawbacks attributed to this binder. Comparing to equivalent CAC formulations, HA-bonded castables demand longer mixing time and high water contents due to the high specific surface area of the binder [26,27]. 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 [28,29].

The fast development of nanotechnology in recent years has suggested that the refractory industry could also benefit from it [30–32]. For refractory castables, the use of nano-powders and colloidal suspensions has been of great interest during recent years, mainly to improve the refractory's bonding and densification at lower sintering temperatures [18,19,33–35]. Nano-powders use in refractory castables has been the subject of various reports in the literature [34–40]. However, the nano-scaled powder dispersion drawback in the matrix has been a challenge in terms of using these additives [35,37]. Therefore, adding nano particles could improve the castable properties, as long as the nano agglomeration problem is kept under control. The high price of commercially available nano powder products can also be another hindrance. Thus, nano-particles containing aqueous suspensions (colloidal binders) are preferred to nano-powders [35].

Among colloidal suspensions, silica sol has been of greatest interest for refractory castable applications [18,41–44]. One of the reasons for its use is the possibility of mullite formation at low temperatures for alumina-rich systems. Actually, the reaction activity of nanometer SiO_2 in silica sol is extremely high. Colloidal particles can be absorbed on the surface of active α-Al_2O_3 ones and fill in their packing gaps, which can reduce the temperature of mullite formation, with suitable densification at about 1100 °C [43]. Another reason for applying colloidal silica to refractory castables is related to its high solid contents, ranging from 15–50 wt% of silica [45].

The fact of increasing the use of colloidal silica as a binder has initiated a discussion concerning the possibility of adding colloidal alumina for the same purpose. Despite the colloidal silica advantages, its addition always implies that SiO_2 will be present in the final product, which would inhibit its use in various steel plant applications [19,45]. This drawback has been the driving force towards using colloidal alumina [19,46]. At first, the addition of colloidal alumina had been restricted to contents lower than 1 wt% [34,35], most likely due to processing difficulties such as high water demand and low flowability and workability. However, trying to overcome these limitations, recently higher colloidal alumina solid contents (up to 4 wt%) could be added to the refractory castable [19]. For lower solid contents in the composition, the role of colloidal alumina as a binder may be insufficient whereas if it exceeds 4 wt%, higher water amounts are required for mixing and the mechanical properties may be spoiled [46,47].

In addition to colloidal silica and alumina, there is also a report related to the use of mullite and spinel sols as a bonding agent in high alumina ULCC castables [48]. These sols with low solid content (about 5 wt%) in water suspension were used as an additive for CAC containing castables in order to evaluate their effect on physical and mechanical properties, as well as slag corrosion and thermal shock resistance.

Similar to any other bonding agent, colloidal suspensions have their own advantages and disadvantages. Their consolidation mechanism does not result in hydrated phase generation (as in CAC or HA ones) and lead to a high permeable and porous structure. This effect can be technologically useful as it reduces the overall processing time and the composition can be safely and quickly dried, reducing the risk of explosive spalling [18]. The volumetric stability of colloidal binders at high temperatures is another advantage compared

Table 2
Properties of some available colloidal binders (alumina or silica) in comparison with calcium aluminate cement and hydratable alumina.

Binder type	Chemical specification (wt%)	Surface area (m^2/g)	Aggregate size	Surface charge	pH range	Stabilizer	BD (g/cm^3)
Colloidal alumina [51]	Al_2O_3: 40	100	80 nm	Anionic	6–9	Citric acid	1.5
Colloidal silica [52]	SiO_2: 40 $Na_2O < 0.4$	200	15 nm	Anionic	10	Na-stabilized	1.3 >
Calcium aluminate cement [53]	Al_2O_3: >69 CaO: <30 $SiO_2 > 0.3$ $Fe_2O_3 < 0.3$	0.4	−45 μm: 82 wt% D_{50} = 13 μm	–	–	–	2.9–3.05
Hydratable alumina [21]	Al_2O_3: 90 Na_2O: 0.5 LOI: 6.5	270	D_{50} = 2.5 μm	–	–	–	3.2

to CAC-based castables. According to the literature [49], CAC addition results in the formation of calcium dialuminate (CA_2) and calcium hexaluminate (CA_6) at temperatures above 1100 °C which in turn leads to a theoretical volumetric change of +13.6 and +3.01% [49], respectively. This expansion level can be a problem and must be mastered to avoid any crack formation in use. Conversely to CAC, colloidal binders show high volumetric stability after firing due to the lack of CA_2 or CA_6 in their structure. Even though colloidal silica can lead to mullite formation, which has a similar expansion behavior [50], the particles' nano-scaled dimension can lessen the overall expansion [37]. In addition, the nano-nature of colloidal binders improves the castable's sinterability due to their higher specific surface area. Table 2 shows the properties of two commercially available colloidal binders (CS and CA) compared with calcium aluminate cement (CAC) and hydratable alumina (HA).

As mentioned above, replacing CAC or hydratable alumina by colloidal binders has various advantages. Referring to the studies carried out in the literature, the next section of the paper aims to review some of these benefits.

2. Benefits

The current section reviews some advantages and properties of colloidal binders from mixing through in-service conditions, whereas any available comparison with hydraulic binders (CAC and HA) are also considered. As more attention was drawn towards colloidal silica compared to colloidal alumina, some parts will only discuss the colloidal silica behavior which indicates the need for further investigation of the role of colloidal alumina as a castable binder.

2.1. Mixing behavior

By using a two-step water addition method [54], Ismael et al. [18] compared the mixing behavior of high alumina self-flow castables containing CAC, HA (hydratable alumina) or colloidal silica (CS) as a binder. The results showed lower torque values and shorter mixing times for colloidal silica (Fig. 1). The higher viscosity of this nano-scaled binder (about 10 mPa. s) when compared to water keeps the particles apart and makes the mixing process easier. Additionally, colloidal silica does not result in chemical reactions during the mixing step such as calcium aluminate hydrates (for CAC) and alumina gel formation (for HA), that can change the ionic force and the suspension's viscosity.

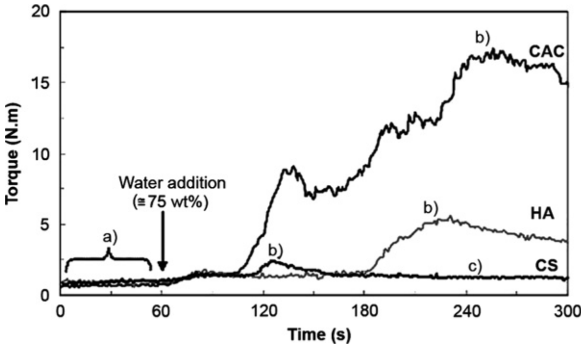

Fig. 1. Mixing behavior for castables containing different hydraulic binders: (a). dry mixing; (b) castable turning point and (c) addition of the total water remaining and castable homogenization [18].

It is worth pointing out that the total liquid content required for suitable mixing of colloidal bonded castables is selected by taking into account the water amount of the colloidal suspension, as they add some part of it to the castable system.

2.2. The rheological behavior

Badiee and Otroj [55] studied the effect of silica sol content on the flow behavior of tabular alumina self-flow castables. The flowability results (Fig. 2) showed that sol contents within the range of 9–11 volume-to-weight percent (volume of sol added in cubic centimeters to a 100 g batch) led to self-flow values in the range of 80–110%. The results of working time for the above-mentioned range of sol contents are also presented in Fig. 3. With the increase in the sol content, the working time of castable increases, which has been attributed to the dispersing effect of nano-silica sol and the higher water content of the castable (however, high sol contents had a deteriorating effect on porosity and mechanical properties as mentioned by the authors). As the suggested working time for suitable

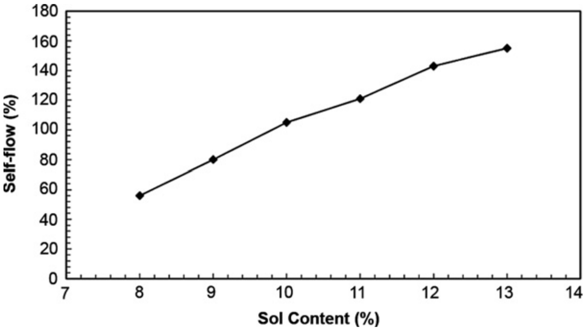

Fig. 2. Self-flow values of tabular alumina castables containing different amounts of silica sol as binder [55].

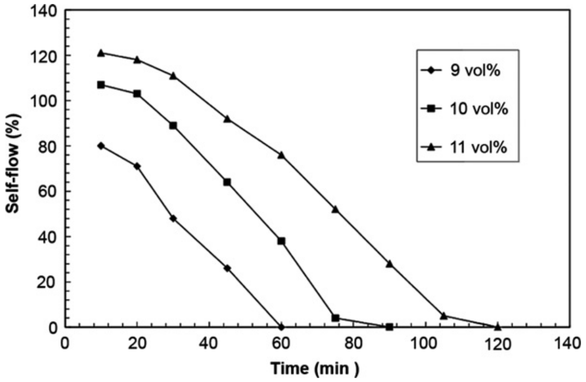

Fig. 3. The effect of silica sol content on self-flow value of tabular alumina castables as a function of time [55].

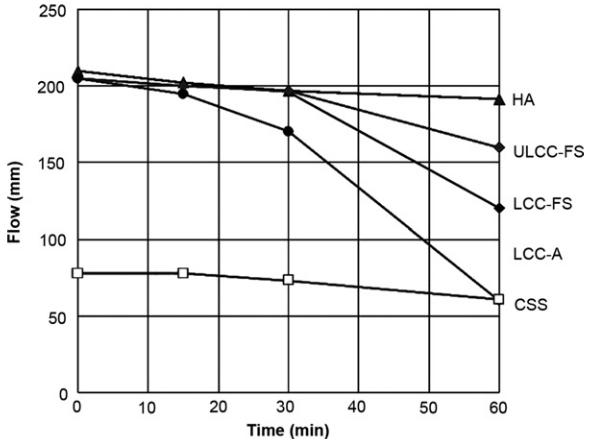

Fig. 4. Flow properties of different castable systems moulded with a similar range of water content (HA: hydratable alumina binder, ULCC-FS and LCC-FS contains fume silica, LCC-A contains reactive alumina and calcium aluminate cement; CSS: colloidal silica system) [45].

placement of self-flowing castables is actually between 30 to 100 min, compositions containing at least 10 vol% silica sol content will present proper working time. Using the same method (flow table test), Parr and Wohrmeyer [45] compared the flow value of colloidal silica bonded (CSS) castables with those of hydraulic bonded compositions, including hydratable alumina binders (HA) and CAC-based (LCC and ULCC). According to Fig. 4, the LCC-A castable (containing reactive alumina) showed the highest flow decay. Furthermore, the silica fume containing systems (LCC-FS and ULCC-FS) presented a similar flow profile over time, but the colloidal silica system (CSS) kept a stable flow, albeit at a lower value than the other castables. The reason for the different colloidal silica flow behavior shown in Fig. 3 and Fig. 4 can be attributed to the distinct conditions of each piece of research, including differences in particle packing, water content, amount and size of the MgO setting agent and so on.

Although the flow table test has been the most frequently used technique to characterize the rheological behavior of castables [56], this test cannot bridge the large existing gap found between advances in castable technology and the rheological behavior characterization considering that flow values involve complex measurements of viscosity and yield stress [57]. Among the different available sorts of rheological techniques [58], the oscillatory test method was found to be useful to study the rheological behavior of colloidal suspensions [59,60].

Concentrated colloidal suspensions commonly show viscoelastic behavior, which can be characterized by dynamic rheological measurements (or oscillatory techniques). During oscillation measurements, a frequency-dependent shear stress or strain is applied to a suspension and the shear moduli are obtained.

The complex shear modulus (G^*) has a real and an imaginary component, as given by:

$$G^* = G' + iG'' \qquad (1)$$

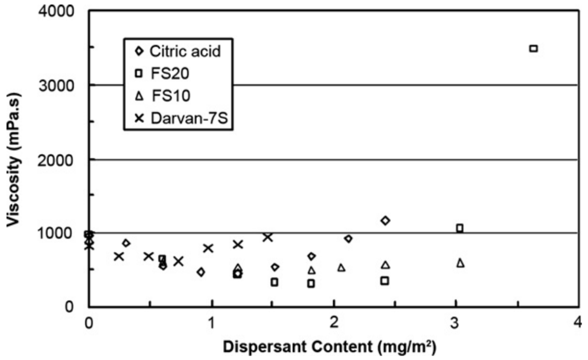

Fig. 5. Alumina–silica sol suspension viscosity as a function of dispersant content [63].

The G' modulus indicates the fraction of mechanical work reversibly stored as elastic energy during the test, whereas G'' points out the fraction that is irreversibly lost as shear heating in the viscous flow. When $G'' > G'$ for all the frequency spectrum, it implies that the material behaves predominantly as a viscous fluid, whereas if $G' > G''$ the elastic solid behavior prevails [60].

An oscillatory test was used to evaluate the rheology and setting behavior in both CAC [61] and colloidal bonded castables [62,63]. Anjos et al. [63] studied the viscosity and viscoelastic behavior of alumina–silica sol suspension systems containing various dispersants (citric acid, polietilenglicol FS10, policarboxilate FS20 and sodium polimetacrilate Darvan 7-S). Reduction in the suspension viscosity was observed for all tested dispersants (Fig. 5). Performing the oscillatory test with the optimized amounts of the above-mentioned dispersants showed that FS10, which is a poliethileneglicol-based polymer, reduced the initial values of G' and G'', which were constant during the testing time (Fig. 6). This effect can favor the moulding step of the castable, as it affects the material's workability.

Other reports suggest that gel-bonded castable compositions containing silica sol does not need dispersing additives [1,42]. According to Zhu et al. [64], around pH 10, colloidal silica can work as a dispersant for alumina particles via electrostatic repulsion, giving rise to a Newtonian behavior for the suspension (Fig. 7). This kind of dispersion is ruled by electrostatic repulsion and steric interaction resulting from the absorption of colloidal particles with a negative charge on the surface of large alumina particles.

While studying the bonding effect of colloidal alumina on alumina-based castables, Braulio and co-workers [19] reported that no dispersant addition is required for colloidal alumina. Adding 0.2 and 0.4 wt% of an electrosteric additive resulted in free-flow value of 30% whereas in compositions containing no additive, this value was found to be 60%. This result was attributed to the fact that colloidal alumina suspension already contains its own stabilizer.

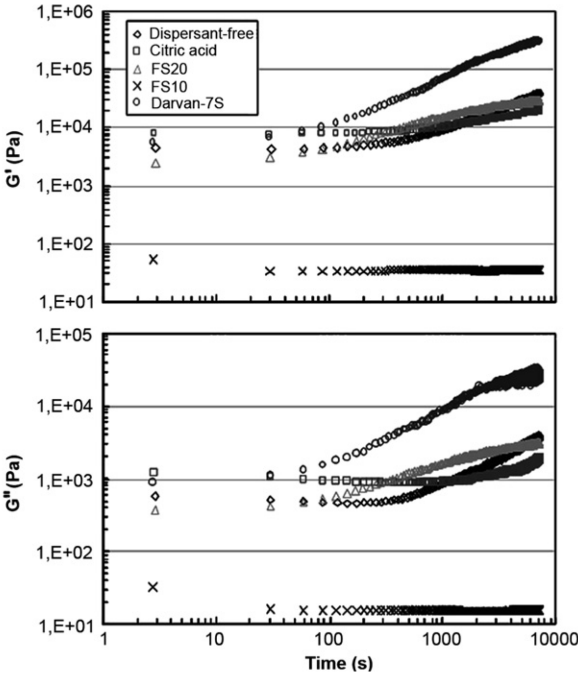

Fig. 6. Storage (G′) and loss (G″) moduli as a function of time for alumina–silica sol suspensions with different dispersant additives at 25 °C [63].

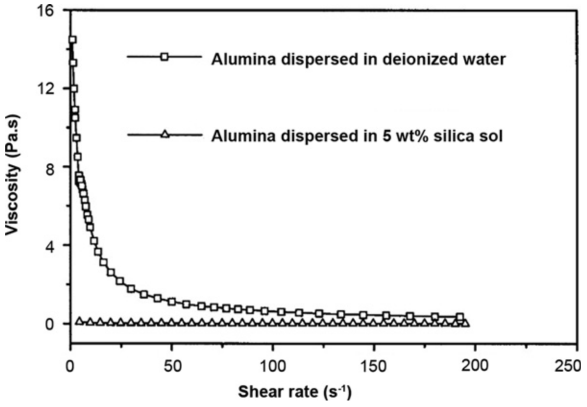

Fig. 7. Viscosity vs shear rate for 60 wt% alumina slurries in deionized water and in 5 wt% silica sol close to pH = 10 [64].

2.3. Setting mechanism

The main role of colloidal binders in refractory castables is related to the setting process, therefore its mechanism needs to be understood. These aqueous suspensions of nano-particles do not result in hydrated phases during this step. When combined with other refractory particles, the colloidal ones are linked together in branched chains, in a process known as gelation. The different setting mechanisms for colloidal silica/alumina are discussed as follows.

2.3.1. Colloidal silica

Undoubtedly, the best summary of the colloidal silica chemistry is provided by Iler [65]. According to this author, the internal structure of silica sol particles is formed by siloxane network (–Si–O–Si–) whereas the surface layer is covered by many silanol groups (–SiOH) and hydroxyl groups (–OH). Colloidal silica particles can be linked together using different setting mechanisms, such as gelling and coagulation, providing initial strength when applied to ceramic systems. As shown in Fig. 8, the gelling process takes place when siloxane groups are formed at the interface of nanometric particles at the expense of silanol groups through the following reaction

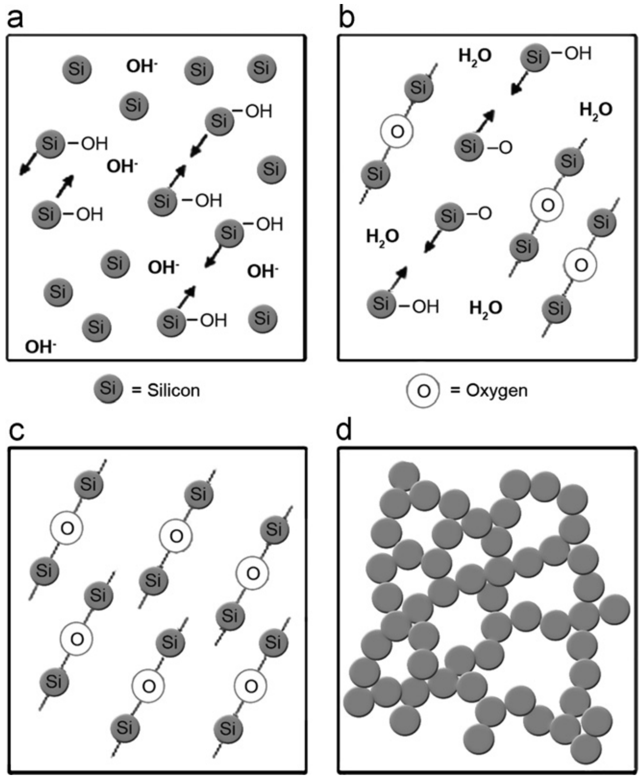

Fig. 8. Colloidal silica gelling mechanism [18].

$$-\mathrm{SioH}+\mathrm{HOSi}-\rightarrow-\mathrm{SiOSi}-+\mathrm{H_2O} \qquad (2)$$

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 electrolytes and organic liquids and the temperature [65]. Colloidal silica suspensions are commonly stabilized via electrostatic repulsion achieved by controlling the pH. Therefore, the setting process must start with the destabilization of the suspension, which allows the particles' contact. This can occur in different ways including pH change, adding setting agents, water drying of the suspension and freezing the sol [65,66].

Fig. 9 shows the effect of pH on the gel time of a colloidal silica sol. The point of zero charge for silica is about pH 2, which means silica surface has a negative charge above this value. At the beginning of the gelation process, the surfaces of particles must collide with each

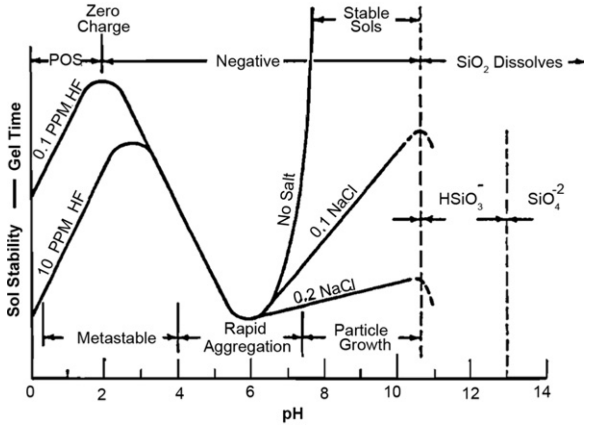

Fig. 9. Effect of pH on the gel time of a colloidal silica-water system [65].

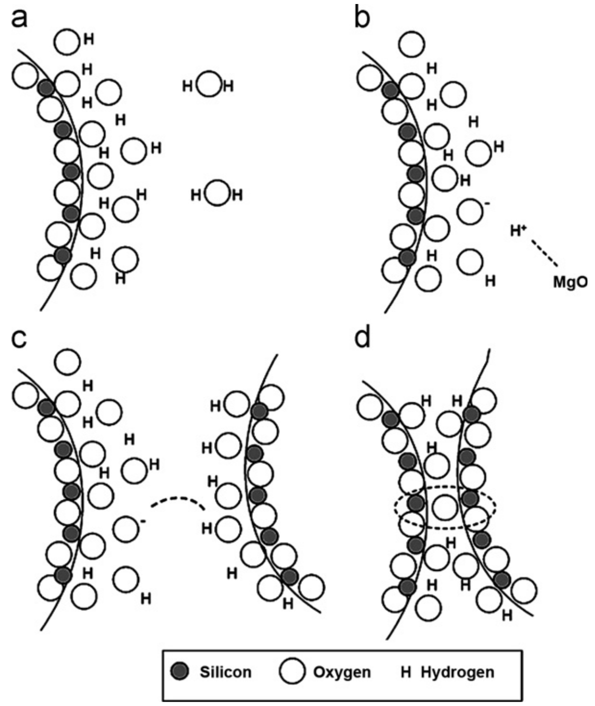

Fig. 10. Schematic representation of colloidal silica consolidation through gelling mechanism: (a) colloidal silica particle surface, (b) MgO addition, (c) siloxane bonds formation and (d) siloxane bonding (–Si–O–Si–) [62].

other so that siloxane bonds can form. The reaction which produces siloxane bond formation is catalyzed by hydroxyl ions and, therefore, the reaction rate speeds up between pH 3 and 5 as the hydroxyl ion concentration increases. Above approximately pH 6, the concentration of hydroxyl groups is no longer the limiting factor and the charge on the particles begins to have an effect. At these pH levels, silica particles are highly negatively charged and effective collisions between particles become less frequent as a result of mutual repulsion between electric double layers. Gel time at pH 8–10 is very long and commercial sols stabilized at these pH levels can be indefinitely stable [65–67]. As a result, changing pH of the suspension in the pH range of 3–5 will induce the aggregation of silica sol.

Above pH 3.5, where commercial silica sols starts bearing a negative charge, the addition of salts, oxides or water-miscible organic liquids reduces the overall net repulsion effect and both coagulation and gelling are greatly accelerated. Two mechanisms of aggregation are generally considered: particle-to-particle attraction by van der Waals forces and particle-to-particle bridging by the flocculating or coagulating agent. Bridging usually occurs because the agent is cationic and thus attracted to the negatively charged silica surface. Nevertheless, the mechanism by which silica particles are held together depends on the type of the setting agent [65]. In colloidal silica bonded castables, sintered MgO has been the most frequently used additive as a setting agent [18,23,41,42,55,62,63]. MgO favors anionic reaction by the formation of $Mg(OH)_2$ and withdrawal of hydrogen ions from Si–OH groups, which, as a result, provides a higher siloxane bond formation, increasing the colloidal silica gelation rate (Fig. 10) [62].

The effect of MgO on the silica sol setting is so fast that preparing a homogenous suspension in high-MgO castables containing silica sol is difficult [62,68]. During mixing, silica particles are immediately gelled around the magnesia ones forming an impermeable external layer which hinders the powder dispersion [62]. Nevertheless, Hamedani et al. [68] attained a suitable rheological condition by adding extra water to the magnesia castable mix, but this approach may not be appropriate as it affects other castables′ properties such as mechanical strength and porosity.

Besides MgO, Anjos et al. [62] tested some other setting agents in alumina and microsilica silica sol containing systems. The tested compounds were oxides (MgO and CaO), hydroxides ($Mg(OH)_2$ and $Ca(OH)_2$) and salts ($MgCl_2$, $MgSO_4$, $CaCl_2$ and $CaSO_4$). Oscillatory tests were used to evaluate the systems. Among the selected additives, MgO was the most suitable. MgO addition in the range of 0.3–0.6 wt% and curing temperatures of 25 °C were the suggested parameters for high-alumina and microsilica-containing systems. However, all other setting agents also sped up the colloidal silica consolidation except $CaSO_4$ in the alumina–colloidal silica system (Fig. 11). The tested oxides favor the colloidal silica consolidation through the gelling mechanism due to their basicity and insolubility. CaO is a stronger basic oxide when compared to MgO, but the latter one is less soluble in water, which explains its greater efficiency to induce gelling. Soluble compounds, such as salts, when added to the suspension release ions that could act as coagulating agents, as schematically shown in Fig. 12. The higher the salt solubility, the higher the cation release is and its efficiency as a coagulating agent. Calcium sulfate presented a small effect on the increase in the coagulation rate, most likely because it is almost insoluble in water.

For the tested hydroxides, the OH^- released in the medium catalyzes the formation of siloxane bonds, accelerating the

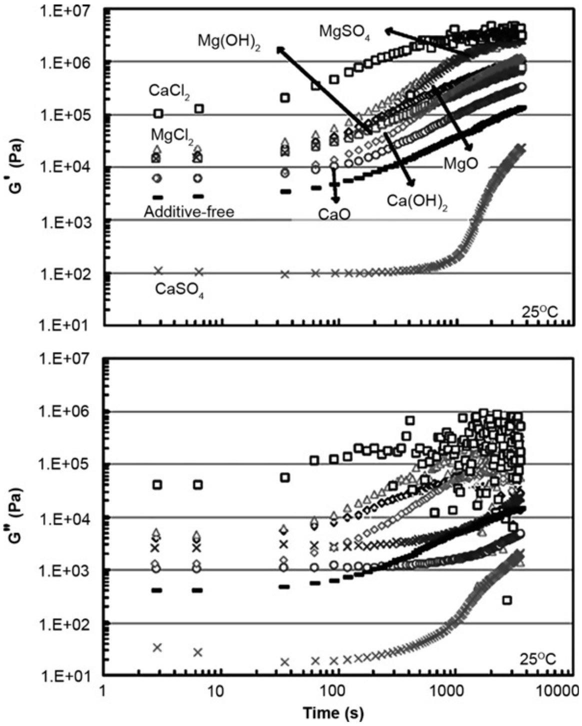

Fig. 11. Storage (G′) and loss (G″) moduli as a function of time for alumina–colloidal silica suspensions with different inorganic compounds as setting agent at 25 °C [62].

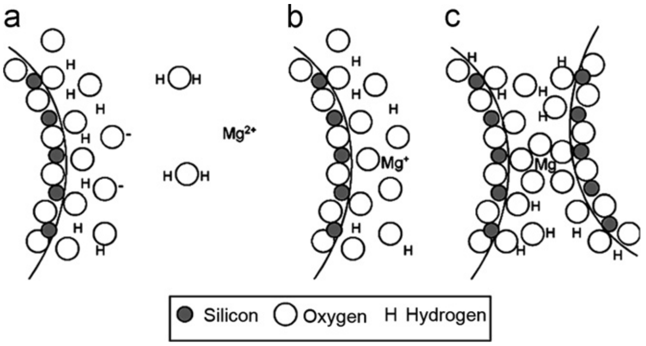

Fig. 12. Schematic representation of colloidal silica consolidation through the coagulating mechanism: (a) colloidal silica particle and magnesium soluble salt addition, (b) reaction between the cation and silica surface and (c) Mg^{2+} acting as a bridge by reacting with two particles [62].

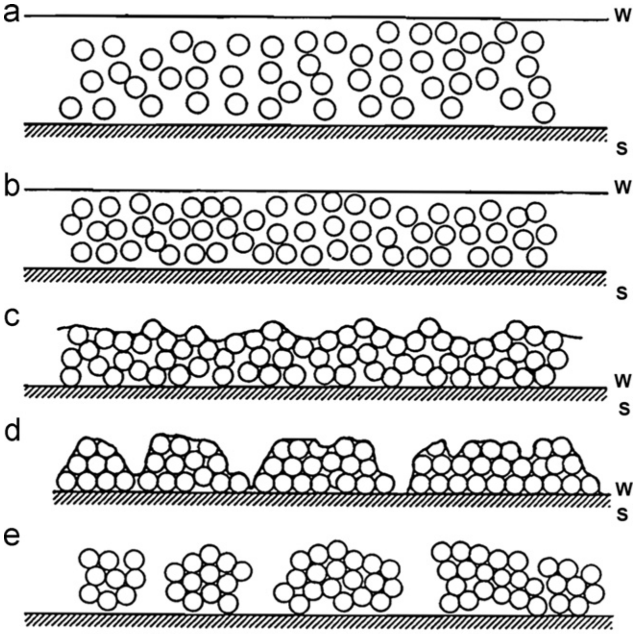

Fig. 13. gelling process by drying, W: water surface, S: solid substrate [65].

gelling. $Ca(OH)_2$ resulted in a higher gelling rate as its basicity is greater than the $Mg(OH)_2$ one [62].

The literature also reports on the use of CAC as the setting agent of colloidal binders [42,69–71]. When CAC is mixed with colloidal silica, the Ca^{2+} and Al^{3+} ions, which are released due to the cement dissolution, give rise to the reduction in the overall net repulsion effect (same as Mg^{2+} mechanism in Fig. 10) and so the gelling rate is accelerated. Therefore, the workability can be affected by the amount of added CAC [72].

Although polymeric agents can be used as a flocculating agent of colloidal binders [65], there is no report in the literature for application of these agents in colloidal-bonded refractory castables. Nevertheless, cationic polymers are used for the flocculation of commercial silica sol particles because of the highly negative charge of silica surface [65]. For example, cationic starch has been applied as the setting agent of silica sol to produce an alumino-silicate fibre based product [73].

Colloidal particles of opposite charges can be used as linking agents. Therefore, colloidal alumina particles with a positive charge can flocculate silica sol particles [65,74]. The literature also reports on the use of phosphates as the setting agent of colloidal silica bonded refractories [1,75].

It is possible to induce gelling by drying the suspension without the assistance of special agents. During water evaporation, the suspension concentration increases, forcing particles to approach each other (Fig. 13) [65]. The stages by which sol is converted to dried gel are: (a) solidification of sol to a three-dimensional gel network of branched chains of silica particles in which the liquid is retained by capillary forces; (b) strengthening of particle–particle bonds at their points of contact by particle coalescence; (c) shrinkage of the three-dimensional silica network as water evaporates; (d) development of stresses in the silica network as three-dimensional shrinkage progresses; and (e) fracture of the dried silica gel into fragments. As shown in Fig. 13, the shrinkage of silica gel is easily observed when a thin layer of sol is dried on a smooth surface. At a certain stage, a clear, coherent gel film is formed, and as the drying step progresses, this film shrinks leading to crack formation in the drying direction, resulting in a fragile, fibrous or hairlike residue of silica gel [65].

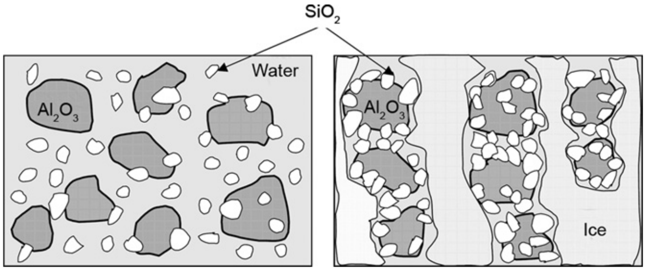

Fig. 14. A schematic view of freeze-gelation process of alumina ceramics by silica sol [76].

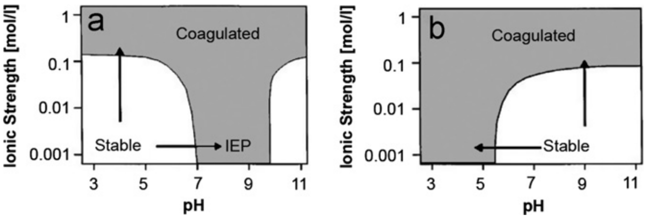

Fig. 15. Stability limits for an aqueous alumina suspension (a) without a specific adsorbing deflocculant and (b) with 0.35 wt% citric acid as deflocculant. The arrows indicate the two strategies to destabilize the suspensions by either changing the pH or the ionic strength of the suspension [85].

Sol freezing is another method which leads to gelation. This is simply because the particles become concentrated between growing ice crystals until they are squeezed together leading to interparticle bonding [65]. Fig. 14 shows a schematic view of an alumina–water–silica sol system before and after freezing [76]. By using colloidal silica, this phenomenon has evolved to a new forming method in ceramic industry called "Freeze gelation process" [76–80]. Although several applications such as refractory lining of gas turbine chamber have benefited through this process [81,82], there is no published work in the literature about the potential application of the method in other areas of the refractory industry.

2.3.2. Colloidal alumina

Unlike colloidal silica, there is not a comprehensive source of information about colloidal alumina and its behavior. In addition, most of the published work is related to alumina suspensions with submicron sizes but not nano-scaled ones. This aspect indicates that the available results cannot be reliably generalized for the nano scale.

The surface charge of colloidal alumina particles depends on the pH, solid loading and the electrolyte source used for stabilizing the suspension [83,84]. For plain alumina suspensions, as the concentration of alumina in the slurry increases, a change in the surface charge sign from positive to negative occurs. With a further increase in slurry density, the magnitude of total negative charge also increases [83,84]. Considering the available data, the setting mechanisms of colloidal alumina binders are discussed as follows.

Fig. 15(a) [85] shows the stability limits at 24 °C for a plain alumina suspension with an average particle size diameter of 0.5 μm. The suspension is stable at low pH and low ionic strengths. The arrows in Fig. 15 indicate the possible reaction paths that might be used in order to modify a low viscous suspension from the stable state to the coagulated one. By increasing the pH in the deffloculated free system (Fig. 15a), the suspension coagulates at pH 7, whereas increasing the ionic strength at a constant pH=4 also leads to the same effect.

Another aspect is shown in Fig. 15b in which a surfactant, e.g., citric acid, has been added to the suspension. Citric acid shifts the isoelectric point (IEP) of alumina from pH 9 to pH 3.5. The suspension is now stable at high pH and low ionic strengths. Therefore, it might now be destabilized by either shifting the pH from the alkaline to the acidic pH range or by increasing the ionic strength, e.g., at pH 9. This is the dominant situation for most of the commercial colloidal aluminas available on the market (Table 2). Therefore, destabilization of an electrostatically stabilized colloidal alumina suspension may be attained by one of the following mechanisms:

1. Changing the pH (ΔpH mechanism): the suspension is initially dispersed at a pH value where the particles have a high surface charge and then coagulated through a pH shift toward the system's isoelectric point;
2. Changing the ionic strength (ΔI mechanism), which involves an increase in the liquid's ionic strength at a fixed pH value far from the isoelectric point, leading to the coagulation of the suspension because of the compression of the particle's electric double layer.

The internal reactions that result in an in situ pH shift or ionic strength increase can either be autocatalyzed or catalyzed by specific enzymes [85]. By using the above-mentioned mechanisms, Studart et al. [86], studied the in situ coagulation of high-alumina zero-cement self flow castables. The authors used an autocatalytic hydrolysis of gluconic acid lactone (GAL) in water to result in a pH shift in castables. Moreover, gradual dissolution of hydroxyaluminum diacetate (HADA) particles in water was used to induce coagulation through a combined mechanism of pH shift and ionic strength increase. On the other hand, urea was combined with a natural source of the enzyme urease (Jack bean – JB – powder) to accomplish coagulation by an increase in the liquid's ionic strength. The results showed that the internal reactions involving pH shift cause an abrupt decay in the fluidity of castables, and is inappropriate for the development of initially self-flow compositions (Fig. 16). On the other hand, compositions containing urea and JB powder were effectively coagulated by the ΔI mechanism and exhibited initial free-flow values higher than those obtained with cement-containing castables

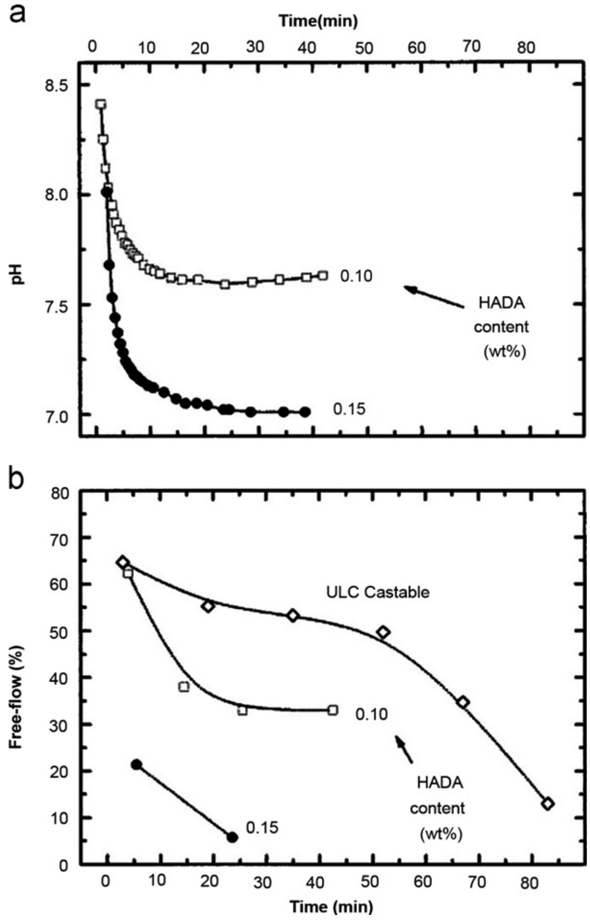

Fig. 16. Effect of hydroxyaluminum diacetate (HADA) particles on (a) pH and (b) free-flow values of alumina castables (15.9 vol% water) as a function of time. The lower chart also shows free-flow decay obtained for ultralow cement (ULC) reference composition (1 wt% of CAC) [86].

(Fig. 17). Eq. (3) highlights how the enzyme-catalyzed hydrolysis of urea in water is carried out:

$$NH_2CONH + 2H_2O \xrightarrow{urease} 2NH_4^+ + CO_3^{2-} \quad (3)$$

This reaction causes a significant increase in the solution's ionic strength, mainly due to the release of ammonia ions leading to compression of double layer and hence coagulation.

The positive effect of urea on coagulation of colloidal alumina has also been confirmed by other reports [85,87–89]. Balzer and co-workers [88] used urea and observed a rapid coagulation in ΔpH and a slow coagulation in Δ*I* based samples of alumina suspensions. This result is in tune with the above-mentioned flow results of Studart and colleagues [86] for castables. Balzer et al. [88] also reported that Δ*I* samples are followed by particle rearrangement (aging) which should lead to denser-packed regions in the network, increasing the overall strength. Tsai and Hseih [89] studied the gelation of colloidal suspensions prepared from γ-alumina fume powder by using several gelling agents including urea (Table 3). The results showed that urea and formamide were quick to cause gelation and easy to burn-off.

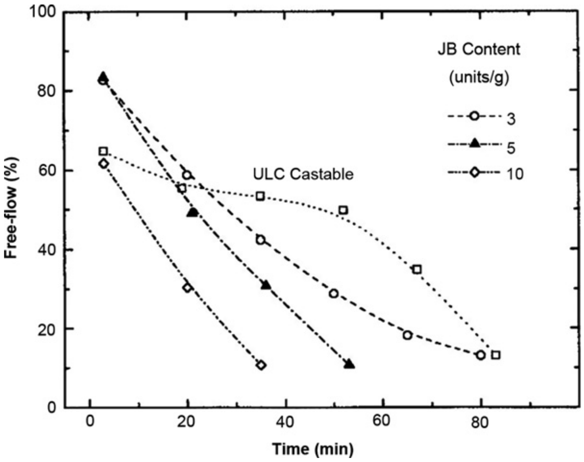

Fig. 17. Free-flow values as function of time of alumina castables (15.2 vol% liquid) coagulated with 2 wt% urea and different contents of Jack bean powder. The free-flow results obtained for ultralow-cement (ULC) reference composition (1 wt% of CAC) [86] are also presented.

Table 3
Gelation time and burn-off temperatures of various gelation agents (2.5 wt%) used in colloidal alumina suspension prepared from γ-alumina fume powder [89].

Gelation agent	Gelation time (h)	Burn-off temperature (°C)
Urea	4.8	300
Formamide	2.7	400
Ammonium carbamate	3.8	350
Biuret	9.1	450
Glycinamide hydrochloride	5.4	550
Sulfamide	5.7	> 800

2.4. The drying and thermogravimetrical behavior

The setting process of hydraulic binders (cement and hydratable alumina) yields hydrated phases leading to particular processing requirements during the castable's drying stage, due to the water release at temperatures in the range of 110–650 °C [10,11,28]. Colloidal silica and colloidal alumina do not generate hydrated phases and provides a faster and safer water drying-out step due to the formation of a high permeable and porous structure [18,19,45]. This effect is so remarkable that according to Gordeeva and co-authors [90], high temperature heat treatment of silica sol binding castables can be performed without preliminary drying at 100 °C.

Braulio et al. [46] compared the thermogravimetrical behavior of hydraulic bonded (CAC or HA) high alumina self-flow castables with the colloidal ones (Fig. 18). After 1 day of curing at 50 °C and 1 day of drying at 110 °C, the test was performed up to 800 °C under a heating rate of 20 °C/min, aiming to evaluate the spalling likelihood by measuring the mass loss during drying (W) and the drying rate (dW/dt). According to Fig. 18a, colloidal silica (CS) or colloidal alumina (CA) result in the lowest weight loss. In addition, the derivative of the weight loss curves (Fig. 18b) highlights that the amount of phase decomposition is lower than the ones observed for cement or hydratable alumina-bonded compositions. Therefore, colloidal alumina and colloidal silica would lead to safer and faster drying, reducing the lining installation or maintenance time.

Magliano et al. [91] reported that silica sols with average particle sizes lower than 14 nm are not suitable for isolated use in nano-bonded refractory castables due to the negative effects associated with their high reactivity. The smaller particle size and higher solid content of this sol induces drying shrinkage and results in internal stresses that can lead to crack formation.

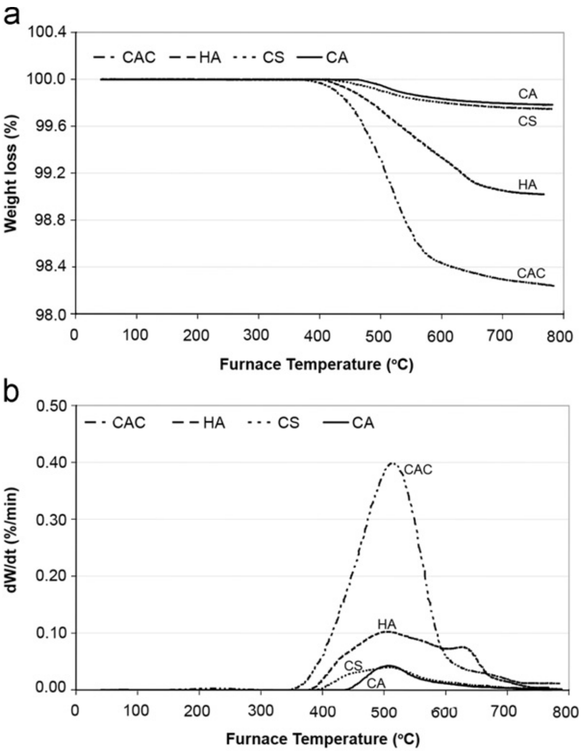

Fig. 18. (a) Weight loss and (b) drying rate (20 °C/min up to 800 °C) of castables containing 4 wt% of calcium aluminate cement (CAC), hydratable alumina (HA), colloidal silica (CS) or colloidal alumina (CA). All castables were previously dried at 110 °C for 24 h [46].

2.5. Permeability

Permeability is one of the most important properties to forecast the drying behavior and chemical attack of refractory castables [92,93]. Permeability of refractory ceramics is usually expressed by constants derived from two main models: Darcy's law and Forchheimer's equation (Table 4) [94]. The basic difference between these models is based on the fluid pressure dependence with its velocity. Darcy's law, which was formulated based on experiments conducted at low velocities, considers only the viscous effects on the fluid pressure drop and results in a linear fitting between the pressure gradient and the fluid velocity through the porous medium. Forchheimer's equation, on the other hand, considers that the pressure gradient shows a parabolic trend with the fluid velocity due to the inertia and turbulence effects. Although Darcy's law has appeared to be widely applied in the literature because of its simplicity [94,95], Forchheimer's equation has yielded more-realistic and more-reliable permeability constants, as discussed by Innocentini et al. [94–96].

Forchheimer's equation for compressible fluids has been successfully used to evaluate the permeability of nano-bonded refractory castables [18,23]. The Darcyan (k_1) and non-Darcyan (k_2) permeability constants were attained by

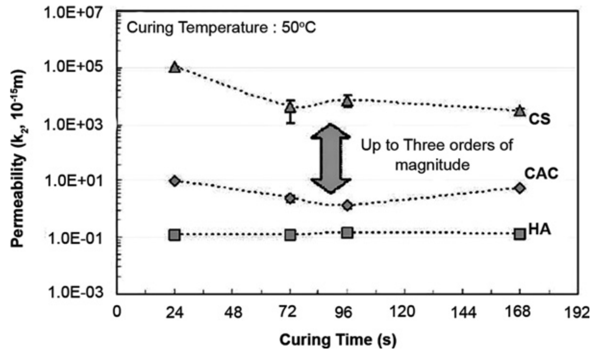

Fig. 19. Permeability measurements (k_2) as a function of time for different binders of hydratable alumina binder (HA), calcium aluminate cement (CAC) and colloidal silica (CS), cured at 50 °C [18].

Table 4
Commonly used equations for permeability evaluation of refractory ceramics [94].

Model	Equation*	
	For incompressible fluids	For compressible fluids
Darcy	$(P_i - P_o/L) = (\mu/k_1)v_s$	$(P_i^2 - P_o^2/2PL) = (\mu/k_1)v_s$
Forchheimer	$(P_i - P_o/L) = (\mu/k_1)v_s + (\rho/k_2)v_s^2$	$(P_i^2 - P_o^2/2PL) = (\mu/k_1)v_s + (\rho/k_2)v_s^2$

*Where P_i is the fluid pressure at the sample entrance (Pa); P_o the fluid pressure at the sample exit (Pa); v_s the fluid velocity, given by the volumetric flow rate (Q) divided by the specimen cross-sectional area (A), orthogonal to the fluid flow (m/s); L the sample thickness (m); μ the viscosity of the fluid (Pa s); ρ the density of the fluid (kg/m^3); k_1 the Darcian or viscous permeability constant (m^2); k_2 the non-Darcian or inertial permeability constant (m); and P the fluid pressure at which v_s, μ and ρ are measured or calculated (usually P_i or P_o) (Pa).

a polynomial fitting between the airflow and air pressure values using Forchheimer's equation.

Fig. 19 compares the permeability of different binding systems of CAC based, hydratable alumina binder (HA) and colloidal silica (CS) [18]. Results attained by Parr and Wohrmeyer [45] are in tune with those shown in Fig. 19, indicating higher permeability levels for CS and thus an easier way for water release. Additionally, these authors [45] stated that even after polypropylene fiber addition to LCC and ULCC based castables, their permeability level is still lower than that of colloidal silica bonded ones.

2.6. Mechanical properties

2.6.1. Cold mechanical properties

Oscillatory tests can define when the gelling starts, but are not always suitable to evaluate the time required for demolding and the mechanical strength during curing [60,63]. Anjos et al. [63] developed the normal force test technique to analyze the demolding time of colloidal-bonded refractory castables. The test comprises the measurement of the normal force (Fn) generated in a sample as a response to an uniaxial elastic deformation. The measurement expresses the difficulty that a blade-shaped sensor faces to penetrate the sample's surface at a rate of 1 mm/s for 20 s. Fig. 20 shows the normal force test results for alumina–silica sol suspensions containing different MgO contents as a setting agent. The suspension with 0.6 wt% of MgO was the only one that reached a constant normal force rate after approximately 35 min, which can be associated with the demoulding time.

According to the literature [18,45], the green mechanical strength of colloidal silica bonded castables is very low compared to the hydraulic bonded ones. Nevertheless, as presented by Braulio et al. [46] (Fig. 21), colloidal alumina containing castables can develop similar mechanical strength to calcium aluminate cement and higher than hydratable alumina after curing at 50 °C (Fig. 21). Fig. 21 also shows that colloidal alumina performs better compared to the colloidal silica one. As the hydraulic binders (CAC or HA) result in stable hydrates after drying at 110 °C, their mechanical strength levels are higher than those attained for colloidal alumina or silica samples. However, this behavior changes by increasing the firing temperature up to 1000 °C, leading to higher mechanical strength for colloidal binder containing castables, whereas for CAC and HA ones, a decrease can be detected (Fig. 22) [46]. The decomposition of cement and hydratable alumina hydrates results in a mechanical strength decay at firing temperatures ranging from 600 to 1000 °C [45,97], whereas for the colloidal binder containing castables the mechanical strength level is kept or even increased as a consequence of the higher sinterability. Fig. 22 attests this behavior by comparing the mechanical strength of calcium aluminate cement (CAC), hydratable alumina (HA), colloidal silica (CS) and colloidal alumina (CA) as a function of the firing temperature [46]. The higher strength of colloidal silica at 1000 °C could be a consequence of the earlier mullite formation. For colloidal alumina, the mechanical strength attained after firing at 800 °C is similar to the CAC one, pointing out that this nano-scaled suspension can be an alternative for the cement when applied to aluminum or petrochemical industries [46].

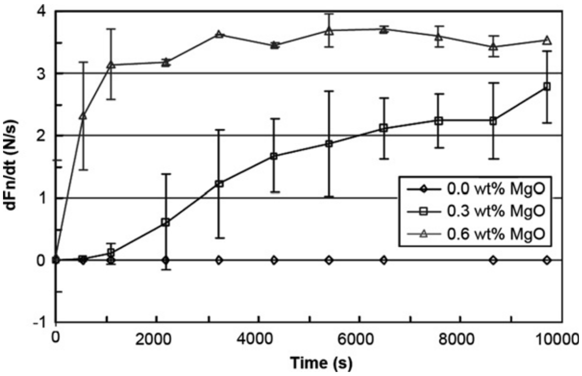

Fig. 20. Normal force rate as a function of time for alumina–silica sol suspensions with different MgO contents at 25 °C [63].

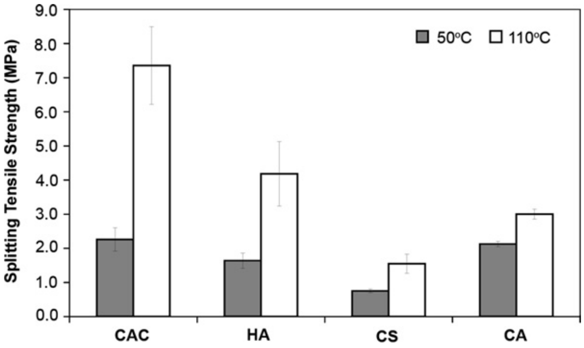

Fig. 21. Splitting tensile strength after curing at 50 °C and drying at 110 °C for castables containing 4 wt% of usual refractory binders (calcium aluminate cement – CAC – or hydratable alumina – HA) or 4 wt% of solids of colloidal silica (CS) or alumina (CA) [46].

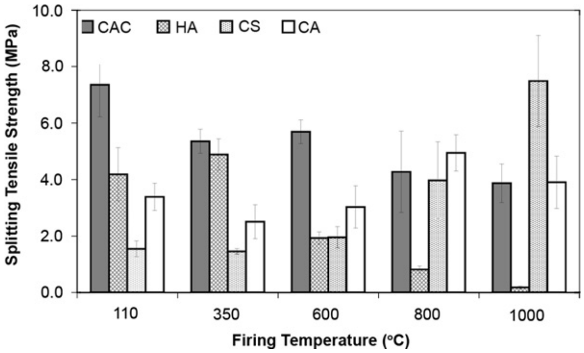

Fig. 22. Splitting tensile strength as a function of the firing temperature, for calcium aluminate cement (CAC) or hydratable alumina (HA)-bonded castables compared to colloidal binder-containing compositions (CS: colloidal silica; CA: colloidal alumina) [46].

2.6.2. Thermomechanical properties

As highlighted by various authors [17–20,33,41–45,55], adding colloidal silica can induce the formation of the

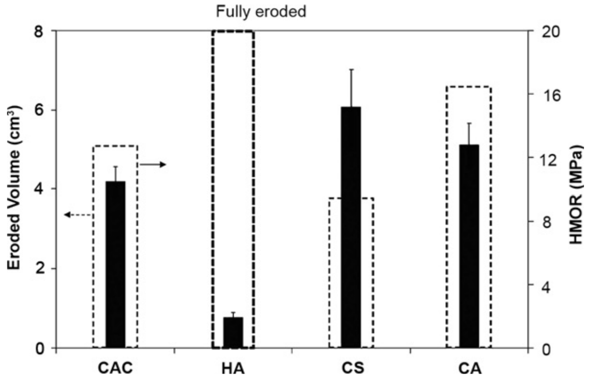

Fig. 23. Eroded volume and hot modulus of rupture of castables containing 4 wt% of calcium aluminate cement (CAC), hydratable alumina (HA), colloidal silica (CS) or colloidal alumina (CA), previously fired at 800 °C [46].

in situ mullite phase at high temperatures and hence improves the high temperature properties of the refractory castable. Fig. 23 compares the erosion resistance and hot modulus of rupture (HMOR) at 800 °C for castables containing hydraulic binders and those with colloidal binders [46]. The results indicate that calcium aluminate cement and colloidal alumina present quite a similar behavior, however better than the hydratable alumina one. Colloidal silica showed the best results in both tests (lowest eroded volume and highest HMOR).

The sample profiles after the erosion evaluation are shown in Fig. 24, pointing out the lower wear resistance for the hydratable alumina-bonded castable. This behavior might be a consequence of the weak link between the castable matrix and aggregate [46].

Braulio et al. [98] recently produced a nano-engineered refractory castable by using colloidal binders (CB: colloidal alumina or silica) and a boron-based sintering additive (SA) that could meet the requirements of wide temperature range applications from 800 to 1400 °C. Fig. 25 compares the HMOR behavior of this castable (Colloidal binder + sintering additive: CB + SA) with the sintering additive-free (CB) and also CAC-based castables (CAC and CAC + SA). For the cement-containing castable with no additive (CAC), low mechanical strength values were observed at lower temperatures (800–1000 °C), which is the region where the hydrates have already been decomposed and the sintering is limited for such compositions. By adding the sintering additive to the cement-containing castables (CAC + SA), the densification was anticipated, as at 800 °C it showed a remarkable HMOR value. Nevertheless, when increasing the testing temperatures, a steep decrease in the hot mechanical strength took place, as a consequence of liquid formation for the cement-bonded compositions. Meanwhile, the colloidal binder-based castables showed a distinct behavior. For the additive-free sample (CB), an increase in the hot modulus of rupture was observed up to 1000 °C, but followed by a decrease up to 1400 °C. On the other hand, by adding both the colloidal binder and the sintering additive (CB + SA), the hot modulus of rupture values were always kept considerably high, regardless of the testing temperature. This statement was based on the assumption that HMOR values above 10 MPa at 1400 °C are considered suitable for refractory castables. The authors also pointed out that the key issue to attain full temperature range (800–1400 °C) high performance is to master the addition of both colloidal binder and sintering additive, as the composition containing only colloidal binder is not enough to provide a constant level of mechanical strength at high-temperature ranges.

The above-mentioned nano-bonded castable was used in practice for low temperature applications of 800–1250 °C in a petrochemical FCC unit and in an alumina calciner. The results (Fig. 26) showed about 5–6 fold improvement in thermomechanical and erosion resistance compared to the CAC based reference castables (Ref composition), which were already being used in these plants.

2.7. Hot elastic modulus

The measurement of hot elastic modulus has been a suitable way to follow in situ the chemical and microstructural evolutions of castables during thermal treatment [99,100]. By using the bar resonance method (ASTM C1198 standard), Braulio et al. [98] evaluated the effect of a sintering additive on the formation of transient or permanent liquid and the castable densification during CAC or colloidal bonded castables heating-up step. Fig. 27 [98], shows the in situ elastic modulus evaluation up to 1000 °C and also during cooling. For the cement-bonded compositions (Fig. 27(a)), the elastic modulus values after drying at 110 °C are high, but due to cement-hydrate decomposition, a drop is noticed up to temperatures slightly lower than 400 °C. For the sintering additive-free castable (CAC), the elastic modulus did not increase at higher temperatures, indicating that no densification occurred. Conversely, when adding the sintering additive (CAC + SA), the elastic modulus increased in the temperature range of 600 to 900 °C, pointing out some liquid phase formation and densification of the sample. Nevertheless, above 900 °C, the elastic modulus decreased, highlighting that the formed liquid started to affect the hot properties.

For the colloidal bonded castables, (Fig. 27b), the initial elastic modulus values were lower than for the cement-bonded compositions followed by a slight drop in the elastic modulus close to 300 °C due to the $Al(OH)_3$ decomposition. By adding the sintering additive (CB + SA), an outstanding increase in the elastic modulus was attained at temperatures above 700 °C. The authors pointed out two advantages of colloidal binders-containing castables when compared to the cement-bonded ones: (i) no drop in the elastic modulus took place up to 1000 °C, indicating a liquid generation that sped up the castable densification without deteriorating its hot property, and (ii) the final elastic modulus value (close to 170 GPa, which is usual for technical ceramics, but not for typical refractory castables) was higher than for the CAC-based composition (~140 GPa).

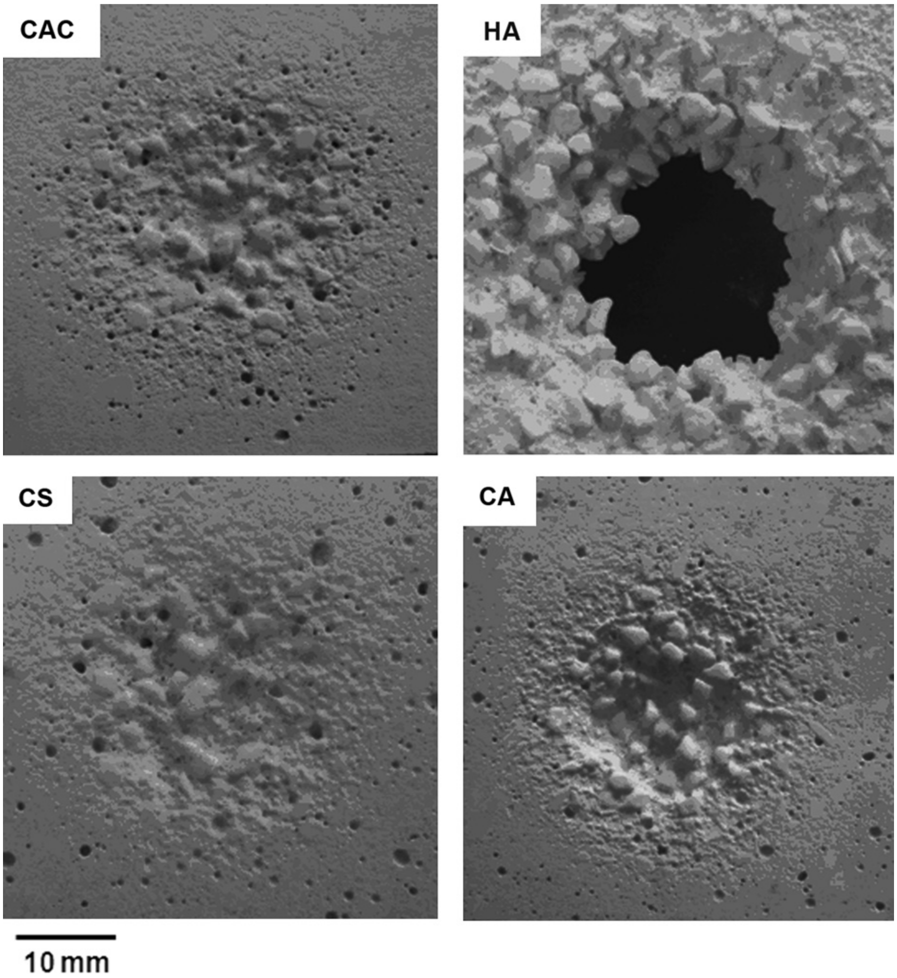

Fig. 24. Erosion sample profiles for castables containing 4 wt% of calcium aluminate.cement (CAC), hydratable alumina (HA), colloidal silica (CS) or colloidal alumina (CA), previously fired at 800 °C [46].

Nonetheless, this high elastic modulus level concerned the authors regarding to the castable's thermal shock behavior, as strong materials, in general, result in catastrophic failures owing to their ability to store elastic energy. Therefore, the elastic modulus was measured as a function of thermal shock cycles (up to 6 cycles with $\Delta T = 800$ °C for samples fired at 800 °C and $\Delta T = 1000$ °C for samples fired at 1250 °C). As Fig. 28 shows, almost no decrease in the elastic modulus as a function of cycles was detected, pointing out a high thermal shock resistance. On the other hand, reference castables presented low elastic modulus values and their percentual elastic modulus loss after six cycles was much higher than the one attained for the nano-engineered composition (40 and 43% for FCC and calciner references, respectively vs only 8–9% for the nano-engineered castable).

Based on the above-mentioned results (Figs. 26–28), Braulio and co-workers [98] concluded that a transient liquid has been formed in the castables containing colloidal binder and sintering additive, leading to fast densification by which a multi-applicable full temperature range refractory castable was attained.

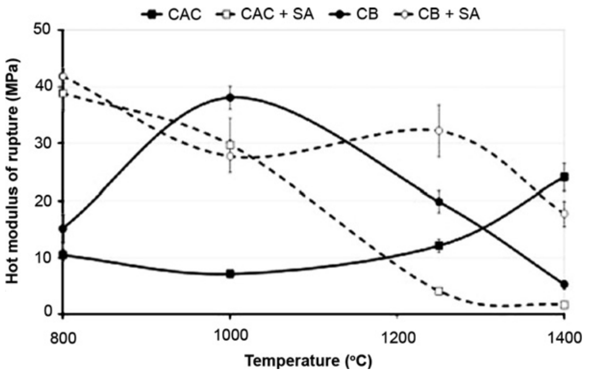

Fig. 25. Hot modulus of rupture (testing temperatures of 800, 1000,1250 and 1400 °C) for the cement-bonded castables (CAC with or without Sintering Additive(SA)), and for colloidal-bonded compositions CB with or without SA [98].

2.8. Sinterability

As mentioned before, nano-scaled particles provide high reactivity for the castable system due to their high specific surface area. As a novel alternative to induce sintering

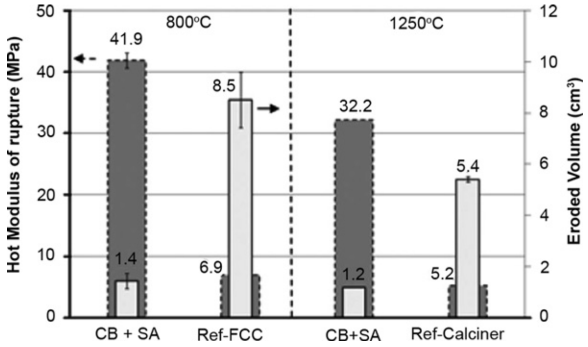

Fig. 26. Hot modulus of rupture and eroded volume for samples fired at 800 or 1250 °C, CB+SA stands for the designed nano-engineered refractory castable containing colloidal binder and sintering additive, Ref -FCC is the vibratable castable petrochemical reference and Ref -Calciner is the gunning refractory calciner reference [98].

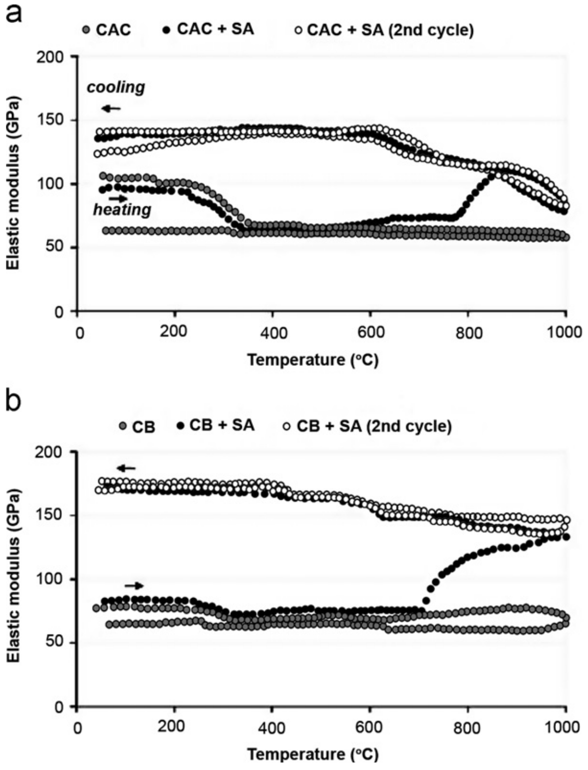

Fig. 27. In situ elastic modulus evaluation up to 1000 °C (heating and cooling cycles): (a) for CAC-containing compositions, with or without sintering additive (SA) and (b) for colloidal bonded castables, with or without sintering additive (SA). For the castables containing sintering additive a second heating cycle (2nd cycle) was also conducted [98].

at lower temperatures, colloidal binders with high solid concentrations present a certain potential to lower the self agglomeration problems commonly detected in nano powders [35,37].

Braulio et al. [101] studied the effect of alumina particle size on the expansion behavior of low-cement alumina–magnesia castables (Fig. 29). The in situ formation of spinel ($MgAl_2O_4$) in these castables results in volume expansion that requires a microstructural control [102,103]. Adding alumina powders with very high surface areas (nano alumina powder—NAP, hydratable alumina—HA and colloidal alumina—CA) resulted in lower overall linear expansion levels when compared to the reference containing a bimodal micronized reactive alumina (REF). Among all castables, the one containing colloidal alumina presented the lowest expansion and the highest delay on the starting expansion temperature due to its higher sintering effectiveness. Meanwhile, the composition containing nano alumina powder did not behave as expected due to the nano particles' agglomeration. This is an example that the benefits of adding nano powders would only be feasible if suitable dispersion can be attained.

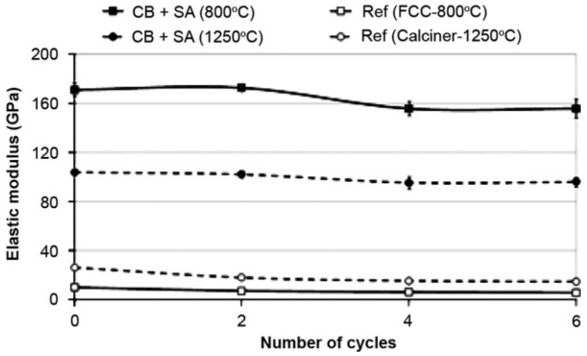

Fig. 28. Elastic modulus measurement as a function of thermal shock cycles ($\Delta T = 800$ or1000 °C). CB+SA stands for the designed nano-engineered refractory castable containing colloidal binder and sintering additive, Ref -FCC is the vibratable castable petrochemical reference and Ref -Calciner is the gunning refractory calciner reference [98].

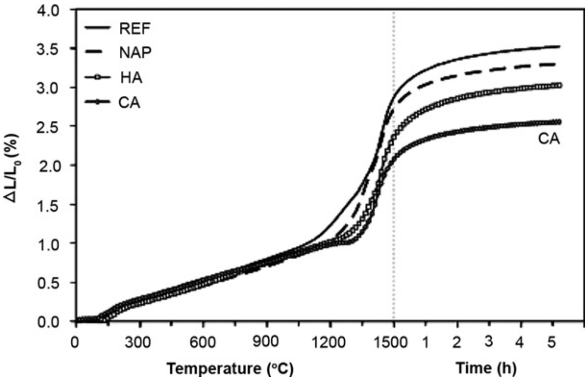

Fig. 29. Expansion behaviour of alumina–magnesia castables containing different fine reactive aluminas. Reference castable with reactive alumina CL370 (REF) and others containing mixtures of CL370 with either nano alumina powder (NAP) or hydratable alumina (HA) or colloidal alumina (CA). All castables contain 1 wt% of microsilica and 6 wt% of calcium aluminate cement [101].

In other related work, Braulio et al. [104] evaluated the effect of colloidal alumina solid content (CA40, CA50 and CA60 in which the numbers indicate the solid content of each suspension: 40, 50 and 60 wt% of solids, respectively) on the overall expansion level of alumina–magnesia low cement castables. Fig. 30 shows the attained results for three different colloidal alumina suspensions and thus distinct nanoscaled particle contents (the CA solid

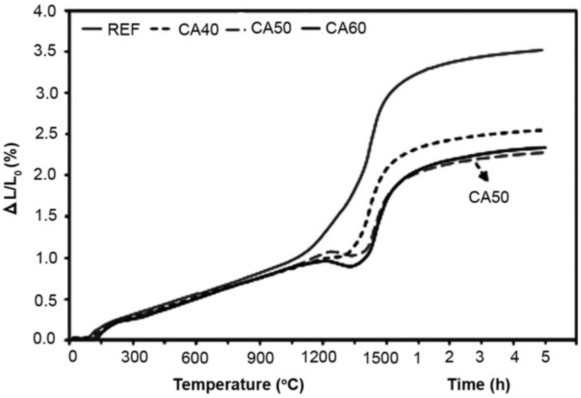

Fig. 30. Linear expansion of alumina-magnesia low cement castables containing different colloidal alumina sources [104].

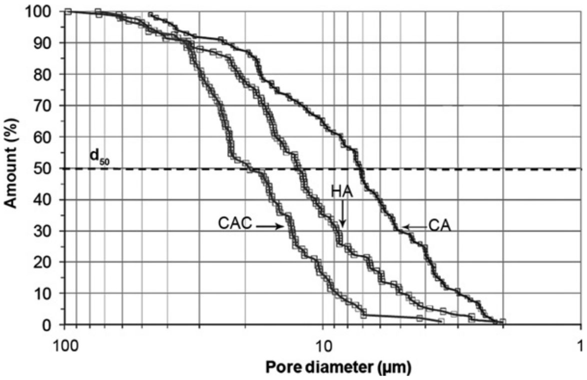

Fig. 31. Pore diameter distribution of the alumina–spinel castable containing CAC, colloidal Alumina (CA) or hydratable alumina (HA) [105].

contents were calculated by considering a constant water amount of 4.1 wt% totally provided from colloidal alumina, leading to solid amounts of 2.7 wt% for CA40, 4.1 wt% for CA50, and 6.1 wt% for CA60). The increase in the colloidal alumina solid content resulted in the reduction of the overall linear expansion from CA40 to CA50. Nevertheless, a further increase (CA60) did not lead to lower expansion, indicating a limited sintering effect of colloidal alumina suspensions. The authors also pointed out that 3 wt% of colloidal alumina is the optimum content to provide a suitable spinel expansion accommodation without any drawbacks. Higher amounts would lead to additional problems related to high water consumption, higher costs and lower flowability, as it reacts with magnesia.

Sako and co-workers [105] found that the higher sinterability of colloidal alumina bonded alumina–spinel castables improves their slag corrosion resistance compared to CAC or HA bonded ones. As the corrosion mechanism was similar for the three compositions, the differences observed in their corrosion resistance were attributed to the refractory contact to the liquid. The colloidal alumina presence resulted in more densified structure, due to its higher specific surface area and sinterability. Furthermore, by measuring the castable's pore size (Fig. 31) it was shown that colloidal alumina containing castables present higher amount of smaller pores compared to CAC or HA ones. Therefore, the better performance of the colloidal-alumina bonded-castable was associated with the lower physical infiltration degree due to a denser structure and higher amount of small pores. Therefore, the chemical interaction between the molten slag and the refractory was restricted to the interface regions, decreasing the corrosion wearing rate.

3. Final remarks and challenges for the future

Despite all the advantages of adding colloidal binders solutions to refractory castables (including faster drying, higher sinterability, volumetric stability, lack of agglomeration, good mechanical strength at intermediate temperatures, better thermomechanical properties at high temperatures, etc.), there are still some drawbacks which hinder the potential applications of these binders. Although various gelling agents can be used, the available setting times are still long and the as-cast green mechanical strength levels are lower than those attained for CAC-based castables. Special attention has to be drawn to colloidal alumina due to the lack of information when compared to colloidal silica. Therefore, some possible suggestions for future research can be outlined in three main areas as follows:

- Colloidal silica:
  i. An important challenge for silica sol-bonded castables will be finding new gelling agents which could improve the setting time and green strength without spoiling the drying speed. Based on this review, one may conclude that low hydration resistant compounds (e.g., MgO and CaO) can induce the setting through gelation mechanism. Therefore, compounds having low hydration resistance (such as doloma, aluminum carbide, different kinds of cements, etc) can be evaluated as gelling agents. Cationic polymers must also be tested, although the setting is based on coagulation mechanism;
  ii. Besides the gelling agent source, the use of a complementary binder can be useful to improve the green mechanical strength. Binders with silicate structure (such as alkali-activated aluminosilicate ones or geopolymers) can reinforce the gellated structure as well as speed up the setting time. The binder must be carefully selected by considering the alkali amount as the thermomechanical properties of the castable cannot be spoiled;
  iii. The freeze gelation process of colloidal bonded castables could overcome the main drawbacks of setting time and green strength. Although the process can be used for making some precast refractory shapes, its use in practical industrial applications is so far difficult. A future challenge

could be to develop new installation techniques based on a freeze gelation process;

- Colloidal alumina:
  - iv. Conversely to colloidal silica, there is not a comprehensive source of information about colloidal alumina behavior. The use of this suspension in refractory castables could be optimized by a fundamental understanding of the gelation mechanism. Therefore, a systematic study on this subject has to be carried out taking into account the surface chemistry of colloidal alumina particles in the composition;
  - v. Similar to colloidal silica, an important challenge for using colloidal alumina binders would be to find new setting agents for castables. Based on this review, the ionic strength increase might be a promising alternative for castables. Since it is proportional to charge and concentration of the ions in the aqueous media, using multivalent ionic compounds such as Fe^{3+} or Al^{3+} salts can increase its value and the compression of the double electrical layer. The use of these salts (nitrates and sulfates) has already been reported in the literature for applications such as water treatment [106,107], but there is no report for colloidal alumina-bonded castables;
  - vi. Special attention must be drawn to design nano-engineered castables by considering the customer requirements and conditions. An example of this challenge was reported in this review for a castable containing colloidal alumina and sintering additive when applied to petrochemical and aluminum industries. Novel additives can provide an outstanding technological opportunity for designing nano-engineered castables to be used in ferrous and non-ferrous industries;
- Other colloidal binders
  - vii. Testing the potential benefits of adding other colloidal particles such as zirconia, spinel, mullite and titania sols may be recommended. However, a main challenge for these colloids is that they are usually not commercially available and so using them may not be economically reasonable. Nevertheless, scientific evaluations can be feasible to identify ways for using them in the future.

Acknowledgments

The Brazilian authors are grateful to CNPq, Magnesita Refratários S. A., Petrobras and Alcoa for providing research funds for most of the results presented in this paper.

References

[1] S. Banerjee, Monolithic Refractories, a Comprehensive Handbook, World Scientific/The American Ceramic Society, Westerville, 1998 311p.

[2] L. Krietz, Refractory castables, in: C.A. Schacht (Ed.), Refractories Handbook, Marcel Dekker Inc., New York, 2004, pp. 259–285.

[3] M. Ishikawa, Refractory castables, Taikabutsu Overseas 19 (3) (1999) 7–13.

[4] N. Zhou, S. Hu, S. Zhang, Advances in modern refractory castables, CN-Refractories 13 (2) (2004) 3–12.

[5] N. Zhou, New castables and their role in advancements in monolithic refractories, Interceram 55 (1) (2006) 24–26.

[6] W.E. Lee, W. Vieira, S. Zhang, K. Ghanbari, H. Sarpoolaky, C. Parr, Castable refractory concretes, International Materials Reviews 46 (3) (2001) 145–167.

[7] B. Myhre, A.M. Hundere, On the influence of superfines in high alumina castables, in: Proceedings of 39th International Colloquium on Refractories, Aachen, Germany (1996) pp. 184–188.

[8] B. Myhre, B. Sandberg, The use of microsilica in refractory castables, in: Proceedings of International Seminar on Monolithic Refractory Materials, Tehran, Iran (1997) pp. 113–140.

[9] W.E Lee, R.E. Moore, Evolution of in situ refractories in the 20th Century, Journal of the American Ceramic Society 81 (6) (1998) 1385–1410.

[10] M.D.M. Innocentini, F.A. Cardoso, A.E.M. Paiva, V.C. Pandolfelli, Dewatering refractory castables, American Ceramic Society Bulletin 83 (7) (2004) 9101–9108.

[11] M.D.M. Innocentini, F.A. Cardoso, A.M.M. Akiyoshi, V.C. Pandolfelli, Drying stages during the heating of high-alumina, ultra-low cement refractory castables, Journal of the American Ceramic Society 86 (7) (2003) 1146–1148.

[12] F.A. Cardoso, M.D.M. Innocentini, M.M. Akiyoshi, V.C. Pandolfelli, Effect of curing conditions on the properties of ultralow cement refractory castables, Refractories Applications and News 9 (2) (2004) 12–16.

[13] S. Banerjee, Recent developments in monolithic refractories, American Ceramic Society Bulletin 77 (10) (1998) 59–63.

[14] J.S. Masaryk, Development and use of low cement self flow castables, in: Proceedings of. UNITECR' 93, Sao Paulo, Brazil (1993) pp. 527–538.

[15] K. Bhattachariya, P. Chintaiah, D.P. Chakraborty, M.S. Mukhopadhyay, Ultra low cement castables: a new generation of trough bodies for increased cast house life, Interceram 47 (4) (1998) 249–251.

[16] A.R. Studart, R.G. Pileggi, W. Jhong, V.C. Pandolfelli, Processing of zero cement self-flow high alumina refractory castables by matrix rheological control, American Ceramic Society Bulletin 77 (12) (1998) 60–66.

[17] S. Banerjee, Versatility of gel-bond castable/pumpable refractories, Refractories Applications and News 6 (1) (2001) 3–5.

[18] M.R. Ismael, R.D. Anjos, R. Salomão, V.C. Pandolfelli, Colloidal silica as a nanostructured binder for refractory castables, Refractories Applications and News 11 (4) (2006) 16–20.

[19] M.A.L. Braulio, C. Tontrup, J. Medeiros, V.C. Pandolfelli, Colloidal alumina as a novel castable bonding system, Refractories Worldforum 3 (3) (2011) 136–141.

[20] A.R. Souri, B. Mirhadi, F. Kashani Nia, The effect of nano-structured colloidal silica on the properties of tabular alumina castables, Interceram 57 (6) (2008) 414–416.

[21] M.W. Vance, K. J. Moody, Steelplant refractories containing alphabond hydratable alumina binders, Alcoa Technical Bulletin, USA,1996.

[22] Y. Hongo, ρ-alumina bonded castable refractories, Taikabutsu Overseas 40 (4) (1988) 226–229.

[23] M.R. Ismael, R. Salomão, V.C. Pandolfelli, A combined binding system for refractory castables based on colloidal silica and hydratable alumina, American Ceramic Society Bulletin 86 (2007) 58–61.

[24] W. Ma, P.W. Brown, Mechanisms of reaction of hydratable aluminas, Journal of the American Ceramic Society 82 (2) (1999) 453–456.

[25] B. Myhre, B. Sandberg, Mullite formation in tabular alumina based refractory castables with hydraulic alumina as binder, in: The American Ceramic Society 97th Annual Meeting, OH, USA, 1995.

[26] R. Lorenz, G. Buchel, A. Buhr, J. Aronni.; R. Racher, Improved workability of calcia free alumina binder alphabond for non-cement castables, in: Proceedings of the 47th International Colloquium on Refractories, Aachen, Germany (2004) pp. 67–71.

[27] New Almatis Alphabond 300 Global Product Data Sheet, GP-RCP/015/R04/1207/MSDS 834, 2004.

[28] F.A. Cardoso, M.D.M. Innocentini, M.F.S. Miranda, F.A.O. Valenzuela, V.C. Pandolfelli, Drying behavior of hydratable alumina-bonded refractory castables, Journal of the European Ceramic Society 24 (5) (2004) 797–802.

[29] M.D.M. Innocentini, A.R.F. Pardo, V.C. Pandolfelli, Permeability of high-alumina refractory castables based on various hydraulic binders, Journal of the American Ceramic Society 85 (6) (2002) 1517–1521.

[30] R.G. de Sa, W.E. Lee, Nanotechnology for the refractories industry—a foresight perspective, The Refractories Engineer, May Issue (2007) 12–19.

[31] A.M. Garbers-Craig, How cool are refractory materials?, Journal of the South African Institute of Mining and Metallurgy 108 (9) (2008) 491–506

[32] V. Antonovič, I. Pundiene, R. Stonys, J. Česniene, A review of the possible applications of nanotechnology in refractory concrete, Journal of Civil Engineering and Management 16 (4) (2010) 595–602.

[33] M. Anderson, Better refractories through nanotechnology, Ceramic Industry Magazine 155 (10) (2005) 29–35.

[34] T.R. Lipinski, E. Drygalska, C. Tontrup. The influence of additions of nanostructured Al_2O_3-powder on the high temperature strength of high alumina refractories, in: Proceedings of UNITECR'09; Salvador, Brazil (2009) pp. 3.

[35] T. R. Lipinski, C. Tontrup, The use of nano-scaled alumina in alumina-based refractory materials, in: Proceedings of UNITECR'07; Dresden, Germany (2007) pp. 391–393.

[36] S. Otroj, R. Marzban, Z.A. Nemati, N. Sajadi, M.R. Nilforoushan, Behavior of alumina–spinel self-flowing castables with nano-alumina particles addition, Ceram-Silikaty 53 (2) (2009) 98–101.

[37] M.A.L. Braulio, J.F.R. Castro, C. Pagliosa, L.R.M. Bittencourt, V.C. Pandolfelli, From macro to nano magnesia: designing the in situ spinel expansion, Journal of the American Ceramic Society 91 (9) (2008) 3090–3093.

[38] V.C. Arasu, S. Adak, A.K. Chattopadhyay, C.D Kamath, Influence of Nano additives on thermo mechanical properties of alumina castables, in: Proceedings of UNITECR'09. Salvador, Brazil (2009) pp. 4.

[39] M.H. Amin-Ebrahimabadi, M. Rahimipour, The effect of nanosized carbon black on the physical and thermomechanical properties of Al_2O_3–SiC–SiO_2–C composite, Journal of Nanomaterials (2009) (2009) 5.

[40] S.H. Badiee, S. Otroj, The effect of nano-titania addition on the properties of high-alumina low cement self flowing refractory castables, Ceramics-Silikaty 55 (4) (2011) 319–325.

[41] A. Souri, F. Kashaninia, H. Sarpoolaki, Improving thermomechanical properties of tabular alumina castable via using nanostructured colloidal silica, in: Proceedings of 1st International Conference on Nanomaterials: Applications and Properties, Crimea, Ukraine (2011) pp. 254–259.

[42] S. Banerjee, C.W. Connors, Composition and Method for Manufacturing Steel-containment Equipment. US Patent 5147830. September 15, 1992.

[43] X. Jiquan, P. Yuntao, X. Dayong, M. Xuesong, The characteristics of silica-sol combining refractories, Advanced Materials Research 396–398 (2011) 288–291.

[44] F. Cao, S. Long, X. Wu, R. Telle, Properties of sol–gel bonding castables, Key Engineering Materials (2007) 1484–1487, pp. 336–338.

[45] C. Parr, C. Wöhrmeyer, The advantages of calcium aluminate cement as a castable bonding system, in: Proceedings of St Louis Section Meeting of American Ceramic Society, USA (2006) pp. 20.

[46] M.A.L. Braulio, C. Tontrup, J. Medeiros, V.C. Pandolfelli, Colloidal alumina as a refractory binder, in: Proceedings of 35th Alafar congress, Lima, Peru (2010) pp. 10.

[47] K.R. Han, S.W. Park, C.S. Kim, J.O. Yang, Unshaped Refractory Composition Added with Alumina sol Binder, International Patent WO 2011/115352, September 2011.

[48] S. Mukhopadhyay, S. Ghosh, M.K. Mahapatra, R. Mazumder, P. Barick, S. Gupta, S. Chakraborty, Easy-to-use mullite and spinel sols as bonding agents in a high-alumina based ultra low cement castable, Ceramics International 28 (2002) 719–729.

[49] J.E. Kopanda, G. MacZura, Production processes, properties and applications for calcium aluminate cements, in: L.D. Hart, E. Lense (Eds.), Alumina Chemicals Science and Technology Handbook, Wiley-American Ceramic Society, Westerville, 1990, pp. 171–183.

[50] M. Schneider, K. Okada, J.A. Pask, Mullite and Mullite Ceramics, John Wiley, New York, 1994.

[51] Evonik Degussa GmbH Product Data Sheet, VP Disp W 640 ZX colloidal alumina, 2011.

[52] Zchimmer & Schwarz GmbH Product Data Sheet, Lithosol 1540 Colloidal silica, 2012.

[53] Almatis Calcium Aluminate Cements Global Product Data Sheet, GP-RCP/005/R06/1207/MSDS 993, 2004.

[54] R.G. Pileggi, A.R. Studart, V.C. Pandolfelli., How mixing affects the rheology of refractory castables?, American Ceramic Society Bulletin 80 (6) (2001) 27–31

[55] S.H. Badiee, S. Otroj, Non-cement refractory castables containing nano-silica: performance, microstructure, properties, Ceramics-Silikaty 53 (4) (2009) 297–302.

[56] K. Watanabe, M. Ishikawa, M. Wakamatsu, Rheology of castable refractories, Taikabutsu Overseas 9 (1) (1989) 41–53.

[57] R.G. Pileggi, A.E. Paiva, J Gallo, V.C. Pandolfelli, Novel rheometer for refractory castables, American Ceramic Society Bulletin 79 (1) (2000) 54–58.

[58] G. Schramm, A Practical Approach to Rheology and Rheometry, second ed., Gebrueder Haake GmbH, Germany, 1998.

[59] W.B. Russel, Concentrated colloidal dispersions, MRS Bulletin 16 (8) (1991) 27–31.

[60] J.A. Lewis, Colloidal processing of ceramics, Journal of the American Ceramic Society 83 (10) (2000) 2341–2359.

[61] I.R. Oliveira, F.S. Ortega, V.C. Pandolfelli, Hydration of CAC cement in a castable refractory matrix containing processing additives, Ceramics International 35 (2009) 1545–1552.

[62] R.D. Anjos, M.R. Ismael, I.R. Oliveira, V.C. Pandolfelli, Workability and setting parameters evaluation of colloidal silica bonded refractory suspensions, Ceramics International 34 (1) (2008) 165–171.

[63] R.D. Anjos, M.R. Ismael, R. Salomão, V.C. Pandolfelli, Rheometric techniques applied to refractory ceramic suspensions, Refractories Applications and News 11 (2) (2006) 8–13.

[64] X. Zhu, D. Jiang, S. Tan, Z. Zhang, Dispersion properties of alumina powders in silica sol, Journal of the European Ceramic Society 21 (16) (2001) 2879–2885.

[65] R.K. Iler, The Chemisty of Silica, Solubility, Polymerization, Colloid and Surface Properties and Biochemistry, John Wiley, New York, 1979 866p.

[66] H.E. Bergna, W.O. Robert, Colloidal Silica, Fundamentals and Applications, Taylor & Francis Group, Boca Raton, 2006 895p.

[67] H.E. Bergna, Colloid Chemistry of Silica, American Chemical Society, Washington, 1994 695 p.

[68] N. Hamedani, H. Sarpoolaky, A.R. Souri, Microstructure and properties of colloidal silica bonded magnesite castable refractories, Iranian Journal of Material Science and Engineering 8 (1) (2011) 25–31.

[69] S. Ghosh, R. Majumdar, B.K. Sinhamahapatra, R.N. Nandy, M. Mukherjee, S. Mukhopadhyay, Microstructures of refractory castables prepared with sol–gel additives, Ceramics International 29 (2003) 671–677.

[70] N. Richard, N. Lequeux, P. Boch, Low-shrinkage refractories bonded with high-alumina cement mixed with colloidal silica, Journal de Physique IV 111 (3) (1993) 1403–1406.

[71] D. Daspoddar, S.K Das, P.K Daspoddar, Effect of silica sol of different routes on the properties of low cement castables, Bulletin of Materials Science 26 (2) (2003) 227–231.

[72] M.R. Ismael, R Salomao, V.C. Pandolfelli, Colloidal silica bonded refractory castables: optimization of the particle size distribution, Refractories Applications and News 13 (1) (2008) 10–15.

[73] E. Lidén, S. Karlsson, B. Tokarz, Silica sols as refractory fiber binders, Journal of the European Ceramic Society 21 (6) (2001) 795–808.

[74] R.K. Iler, Adsorption of colloidal silica on alumina and of colloidal alumina on silica, Journal of the American Ceramic Society 47 (4) (1964) 194–198.

[75] L.E. Schulz, Thixotropic Refractory Binder based Upon Aluminum Phosphate Gelled Silica Sols, US patent 4212680, July15, 1980.

[76] D. Donchev, Controlling Porosity and Pore Size Distribution in Green Ceramics Bodies via Freeze-casting Method, Ph.D. Dissertation, Martin-Luther-Universität, 2005.

[77] M.J. Statham, F. Hammett, B. Harris, R.G. Cooke, Net-shape manufacture of low-cost ceramic shapes by freeze-gelation, Journal of Sol-Gel Science and Technology 13 (1998) 171–175.

[78] J. Laurie, C.M. Bagnall, B. Harris, R.W. Jones, R.G. Cooke, R.S. Russell-Floyd, Colloidal suspensions for the preparation of ceramics by a freeze casting route, Journal of Non-Crystalline Solids 147&148 (1992) 320–325.

[79] U. Soltmanna, H. Bottcher, D. Kochb, G. Grathwohl, Freeze gelation: a new option for the production of biological ceramic composites, Materials Letters 57 (2003) 2861–2865.

[80] F. Giese, C. Eigenbrod, D. Koch, A novel production method for porous sound-absorbing ceramic material for high-temperature applications, International Journal of Applied Ceramic Technology 8 (3) (2011) 646–652.

[81] G. Kister, Ceramic-matrix Composites for Gas Turbine Applications, Ph.D. Dissertation, University of Bath, 1999.

[82] H. Grote, W. Kollenberg, D. Nikolay, M. Tertilt, Moulding Compound for Producing a Refractory Lining, US Patent 20090221416, September 3, 2009.

[83] B.P. Singh, R. Menchavez, C. Takai, M. Fuji, M. Takahashi, Stability of dispersions of colloidal alumina particles in aqueous suspensions, Journal of Colloid and Interface Science 291 (2005) 181–186.

[84] S. Bhattacharjee, B.P. Singh, L. Besra, Effect of additives on electrokinetic properties of colloidal alumina suspension, Journal of Colloid and Interface Science 254 (2002) 95–100.

[85] L.J. Gauckler, T. Graule, F. Baader, Ceramic forming using enzyme catalyzed reactions, Materials Chemistry and Physics 61 (1999) 78–102.

[86] A.R. Studart, V.C. Pandolfelli, E. Tervoort, L.J. Gauckler, In situ coagulation of high-alumina zero-cement refractory castables, Journal of the American Ceramic Society 85 (8) (2002) 1947–1953.

[87] H.M. Wyss, S. Romer, F. Scheffold, P. Schurtenberger, L.J. Gauckler, Diffusing-wave spectroscopy of concentrated alumina suspensions during gelation, Journal of Colloid and Interface Science 240 (2001) 89–97.

[88] B. Balzer, K. Martin, M. Hruschka, L.J. Gauckler, In-situ rheological investigation of the coagulation in aqueous alumina suspensions, Journal of the American Ceramic Society 84 (8) (2001) 1733–1739.

[89] D.S. Tsai, C.C. Hsieh, Controlled gelation and sintering of monolithic gels prepared from γ-alumina fume powder, Journal of the American Ceramic Society 74 (4) (1991) 830–836.

[90] S.S. Gordeeva, A.G. Kozlovskii, Y.V. Askinazi, S.A. Suvorov, Unmolded refractories with a silica sol binder, Refractories and Industrial Ceramics 51 (4) (2010) 272–273.

[91] M. Magliano, E. Prestes, J. Medeiros, J. Veiga, V.C. Pandolfelli, Colloidal silica selection for nanobonded refractory castables, Refractories Applications and News 15 (3) (2010) 14–17.

[92] D.L. Hipps, J.J. Brown., Internal pressure measurements for control of explosive spalling in refractory castables, American Ceramic Society Bulletin 63 (7) (1984) 905–910.

[93] S.J. Glass, D.J. Green, Permeability and infiltration of partially sintered ceramics, Journal of the American Ceramic Society 82 (10) (1999) 2745–2752.

[94] M.D.M. Innocentini, A.R.F. Pardo, V.C. Pandolfelli, Influence of air compressibility on the permeability evaluation of refractory castables, Journal of the American Ceramic Society 83 (6) (2000) 1536–1538.

[95] M.D.M. Innocentini, A.R.F. Pardo., V.R. Salvini, V.C. Pandolfelli, How accurate is Darcy's law for refractories, American Ceramic Society Bulletin 78 (11) (1999) 64–68.

[96] M.D.M. Innocentini, A.R.F. Pardo, V.C. Pandolfelli, Permeability of high-alumina self-flow refractory castables; in: Proceedings of UNITECR' 99, Berlin, Germany (1999) pp. 93–96.

[97] C. Parr, L. Bin, B. Valdelievre, C. Wöhrmeywer, B. Touzo, The advantages of calcium aluminate cement containing castables for steel ladle applications, in: Proceedings of 32nd Alafar meeting, Antigua, Guatemala (2004) pp. 12.

[98] M.A.L. Braulio, G.G. Morbioli, J. Medeiros, J.B. Gallo, V.C. Pandolfelli, Nano-bonded wide temperature range designed refractory castables, Journal of the American Ceramic Society 95 (30) (2012) 1100–1104.

[99] J.M. Auvray, C. Gault, M. Huger, Microstructural changes and evolutions of elastic properties versus temperature of alumina and alumina–magnesia refractory castables, Journal of the European Ceramic Society 28 (2008) 1953–1960.

[100] J.M. Auvray, C. Gault, M. Huger, Microstructural changes and evolutions of elastic properties versus temperature in bonding phases of alumina and alumina-magnesia refractory castables, Journal of the European Ceramic Society 27 (12) (2007) 3489–3496.

[101] M.A.L. Braulio, M.F.L. Piva, G.F.L. e Silva, V.C. Pandolfelli, In situ spinel expansion design by colloidal alumina suspension addition, Journal of the American Ceramic Society 92 (2) (2009) 559–562.

[102] M. Kobayashi, K. Kataoka, Y. Sakamoto, I. Kifune, Use of alumina–magnesia castables in steel ladle sidewalls, Taikabutsu Overseas 17 (3) (1997) 39–44.

[103] M.A.L. Braulio, M. Rigaud, A. Buhr, C. Parr, V.C. Pandolfelli, Spinel-containing alumina-based refractory castables, Ceramics International 37 (2011) 1705–1724.

[104] M.A.L. Braulio, G.G. Morbioli, L.R.M. Bittencourt, V.C. Pandolfelli, Novel features of nano-scaled particles addition to alumina–magnesia refractory castables, Journal of the American Ceramic Society 93 (9) (2010) 2606–2610.

[105] E.Y. Sako, M.A.L. Braulio, E. Zinngrebe, S. VdLaan, V.C. Pandolfelli, Improved corrosion resistance of alumina–spinel castable by colloidal alumina addition, in: Proceedings of UNITECR'11 Congress, Kyoto, Japan (2011) pp. 4.

[106] U. Nowostawska, S.G. Sander, K.M. McGrath, K.A. Hunter, Effects of coagulants on the surface forces of colloidal alumina under water treatment conditions, Colloids and Surfaces A: Physicochemical and Engineering Aspects 266 (2005) 214–222.

[107] U. Nowostawska, S.G. Sander, K.M. McGrath, K.A. Hunter, Effect of trivalent metal sulfates on the coagulation and particle interactions of alumina colloids, Colloids and Surfaces A: Physicochemical and Engineering Aspects 266 (2005) 200–206.