Colloidal Alumina as a Novel Castable Bonding System

M.A.L. Braulio, C. Tontrup, J. Medeiros, V.C. Pandolfelli

The increasing use of colloidal silica replacing traditional refractory castable binders, such as calcium aluminate cement and hydratable alumina brings into discussion the potential of adding colloidal alumina as a bonding agent, as some applications do not allow silica in the refractory composition. In this context, a systemic study was conducted in order to ensure the use of higher colloidal alumina solid contents (up to 4 mass-%) aiming mainly at the development of refractory castables for aluminium or petrochemical applications. The colloidal alumina bonding effect was compared to the ones attained for cement or hydratable alumina, pointing out a suitable mechanical strength performance coupled with lower drying spalling likelihood. Therefore, a novel refractory binder is proposed in order to produce high-performance nano-structured refractory castables.

1 Introduction

Calcium aluminate cement is the most usual and robust refractory castable binder. Nevertheless, over the last few years non-cement bonding systems containing hydratable alumina, colloidal silica, phosphates, etc. have been applied [1, 2]. Considering that hydraulic binders (cement and hydratable alumina) impose particular processing requirements due to their hydrate decomposition during the castable drying stage [3–5], colloidal silica has become an alternative to minimize this drawback [6]. In addition, the decomposition of cement and hydratable alumina hydrates result in mechanical strength decay at temperatures ranging from 600 – 1000 °C [7–8], whereas for the colloidal silica-containing castables, the mechanical strength level is kept or even increased as a consequence of its higher sinterability [9].

Colloidal silica is a stable dispersion of nano-scaled amorphous silica particles and can be set by gelling or coagulation [10, 11]. For colloidal suspensions, the bonding mechanism takes place due to van der Waals attraction (and also hydrogen bond, in some cases) among the nano-scaled particles,

when they are forced to get together in a high solid content water suspension [9]. This mechanism can be induced by water release, while the castable is drying [12].

Despite the advantages, adding colloidal silica to refractory castables always implies that silica will be present in the final product, which would inhibit its use in various steel plant applications [12]. In this context, colloidal alumina would be a most suitable refractory binder candidate. Due to colloidal alumina processing advances, stable aqueous suspensions containing up to 60 mass-% of alumina particles with average particle size of approximately 80 nm are now available. Thus, the reduction of the water amount in the suspension allows for the production of refractory castables containing a higher amount of colloidal alumina, but with lower overall water content.

Up to this moment, only few studies in the literature mention the possibilities of adding colloidal alumina as a refractory binder and also the advantages associated with its high sinterability [13, 14]. Besides that, in these publications its addition was restricted to contents lower than 1 mass-%, most likely due to processing difficulties, such as high

water demand and low flowability and workability.

Taking these aspects into account, a systemic study aiming to increase the amount of colloidal alumina addition to refractory castables is still required and is the target of this work. Aspects related to the castable mixing, curing, drying and the mechanical behaviour at intermediate temperatures (up to 1000 °C) were considered in order to figure out the possibilities of using colloidal alumina to produce high-performance nano-structured refractory castables for petrochemical and aluminium applications.

2 Materials and techniques

A free-flow high-alumina castable composition was designed according to the Alfred particle packing model (q = 0,21) [15]. The castables' matrix comprised 19 mass-% of two fine reactive alumina

M.A.L. Braulio, V.C. Pandolfelli
Federal University of São Carlos
Materials Engineering Department
Materials Microstructural Engineering
Group
13565-905 São Carlos (SP), Brazil
(FIRE Associate Laboratory)

C. Tontrup
Evonik Degussa GmbH
63457 Hanau-Wolfgang, Germany

J. Medeiros
PETROBRAS Research Center (CENPES)
21941-915, Rio de Janeiro (RJ), Brazil

Corresponding author: V.C. Pandolfelli
E-mail: vicpando@power.ufscar.br

Tab. 1 Properties of the colloidal alumina dispersions

Suspension	Primary particle size [nm]	Specific surface area [m²/g]	Aggregate size – stabilized dispersion [nm]	Surface charge	pH range	Stabilizers
CA30	13	100	80	cationic	< 5	acid, no pepticizer
CA40	13	100	80	anionic	6 – 9	citric acid
CA50	13	100	80	anionic	6 – 9	phosphor-based
CA60	20	65	80	anionic	6 – 9	citric acid

sources (*Almatis*/DE, CL370 and A1000SG) and 81 mass-% of tabular alumina added as aggregates and also in the matrix (Almatis / DE, $D_{max} < 6$ mm). Compositions containing or not an electrosteric polycarboxilate-based dispersant (*BASF*/DE) were evaluated.

Regarding the colloidal alumina suspensions (*Evonik Degussa GmbH*/DE), initial tests were carried out using a source containing 50 mass-% of solids (CA50, VP Disp. W 650 ZXP). Afterwards, different colloidal alumina sources were evaluated containing: 30 mass-% of solids (CA30, VP Disp. W 630 X), 40 mass-% of solids (CA40, VP Disp. W 640 ZX) and 60 mass-% of solids (CA60, VP Disp. W 460 ZX). The typical properties of these alumina dispersions are shown in Tab. 1. The colloidal alumina dispersions contain fumed aluminium oxide produced by a high temperature flame process. The water content for suitable moulding was based on an initial free-low value of 60 %.

In order to figure out the likelihood of using colloidal alumina as a novel refractory castable binder, calcium aluminate cement (Secar71, *Kerneos*/USA) or hydratable alumina (AlphaBond300, Almatis/DE) containing castables were prepared (containing 2 or 4 mass-% of these traditional binders). Tab. 2 shows the differences among the compositions.

After mixing [16], the castables were shaped into 40 mm x 40 mm cylindrical moulds and the mechanical strength was evaluated after curing for 24 h at 50 °C (in a humid environment and at room conditions), followed by drying at 110 °C for 24 h. Mechanical strength tests were also carried out after firing at intermediate temperatures (1 day curing at 50 °C, 1 day drying at 110 °C and a heat treatment for 5 h at 350, 600, 800 and 1000 °C at a rate of 1 °C/min). The mechanical evaluation was conducted according to the ASTM C496-90 standard (Splitting Tensile Strength of Cylindrical Concrete Specimens) in MTS testing equipment (MTS Systems, Model 810, USA).

In addition, prismatic samples (25 x 25 x 150 mm³) were prepared and, after drying and firing (1 day curing at 50 °C, 1 day drying at 110 °C and firing at 800 °C for 5 h), their hot modulus of rupture (800 °C) was evaluated in HBTS 422 equipment (3-point bending test, *Netzsch*/DE), according to the ASTM C 583-8 standard. The erosion resistance was also measured considering the same firing temperature (800 °C for 5 h) and following the ASTM C704 standard (1 kg of no. 36-grit silicon carbide to erode samples of 10 cm by 10 cm by 2,5 cm thick, leading to a weight loss which is converted to a volume one).

Finally, as the drying stage is a key safety concern during refractory castable applications, thermogravimetrical evaluations were carried out up to 800 °C after 1 d of curing at 50 °C and 1 d drying at 110 °C. The test was performed under a heating rate of 20 °C/min, aiming at the evaluation of the spalling likelihood. The thermogravimetric device was developed in the authors' research group and used to evaluate the mass loss during drying (W) and the drying rate (dW/dt) [3, 4].

3 Results and discussion

Initial rheological tests were carried out in a paddle mixer developed at the authors' research group [17] by adding 1 mass-% of free water, 8 mass-% of colloidal alumina suspension CA50 (4 mass-% of solids + 4 mass-% of water) and 0,2 mass-% of the electrosteric dispersant. Nevertheless, the mixture did not attain the turning point and, thus a further 0,2 mass-% of the dispersant and 0,3 mass-% of free water was added. The resultant initial free-flow value for this condition was 30 %. Considering that the colloidal alumina suspension already contains its own stabilizer, an additional composition containing no further additive was produced (with 1,3 mass-% of distilled water and 8 mass-% of CA50) and the initial free flow value attained was 60 %. Based on this result, all colloidal alumina-bonded castables evaluated in this work were moulded without adding any dispersant.

In order to evaluate the colloidal alumina bonding effect during curing, three different contents were selected (3, 4 or 5 mass-% of solids of CA50) and the castables were cured at 50 °C (in humid environment). Additionally, two different curing conditions were investigated (humid environment or air, at 50 °C) for the best solid content (4 mass-%). For the castables containing 3 or 4 mass-% of colloidal alumina solids, the total water content (free + suspension) was 5,3 mass-%, whereas the composition containing 5 mass-% of colloidal alumina solids comprised 6,0 mass-% of water in total, as the addition of 1 mass-% of distilled water

Tab. 2 Castable compositions evaluated in this work

Raw materials	q = 0,21 Content [mass-%]	References			
		2 CAC	4 CAC	2 HA	4 HA
Tabular alumina (D < 6 mm)	81	79	77	81	81
Reactive alumina	19	19	19	17	15
Calcium aluminate cement	-	2	4	-	-
Hydratable alumina	-	-	-	2	4
Accumulated R2 (PSD)	0,037	0,033	0,031	0,037	0,038
Discrete R2 (PSD)	0,011	0,011	0,011	0,011	0,011
Water content [mass-%]	5,3	4,4	4,4	5,0	5,4

was found to be required to wet the castable. Fig. 1 shows the mechanical strength results attained for these conditions. For all of them, the green mechanical strength level was suitable for the castable demoulding after 1 day of curing, pointing out the likelihood of using colloidal alumina as a refractory castable binder. According to previous work [7, 18], an initial splitting tensile strength higher than 1 MPa would be enough to avoid crack generation during demoulding.

Regarding the colloidal alumina content, the best result was attained when 4 mass-% of solids was added. This optimum amount might be related to the lack of enough bonding when adding a lower solid content (3 mass-%) and the high water content (6 mass-% in total) for a higher solid one (5 mass-%). Concerning the curing environment, better mechanical strength at 50 °C or at 110 °C was attained when the castables were cured in air. Thus, the 4 mass-% solid content was selected for further evaluation and all colloidal alumina-bonded castables were cured at 50 °C in room conditions.

Another aspect that could affect the castable mechanical strength is the colloidal alumina source. For the suspensions containing lower solid contents (30 or 40 mass-%), a mixture of one of them plus the reference colloidal alumina source (50 mass-%) was designed, in order to keep the water content constant. Tab. 3 shows the features of each prepared composition containing different colloidal alumina suspensions, keeping the total colloidal solid amount constant (4 mass-%).

When changing the colloidal alumina source, the green mechanical strength was not significantly affected (Fig. 2a). A slightly better green mechanical strength was detected for the compositions containing colloidal alumina sources with higher solid contents (50 or 60 mass-%). Nevertheless, when firing at higher temperatures (350, 600, 800 and 1000 °C), castables containing the mixture CA40+CA50 or CA60 showed the best results (Fig. 2b). Conversely to calcium aluminate cement or hydratable alumina-bonded castables, which, in general, show a drop in the mechanical strength at this temperature range, due to their hydrate decomposition, colloidal alumina-bonded castables increased the mechan-
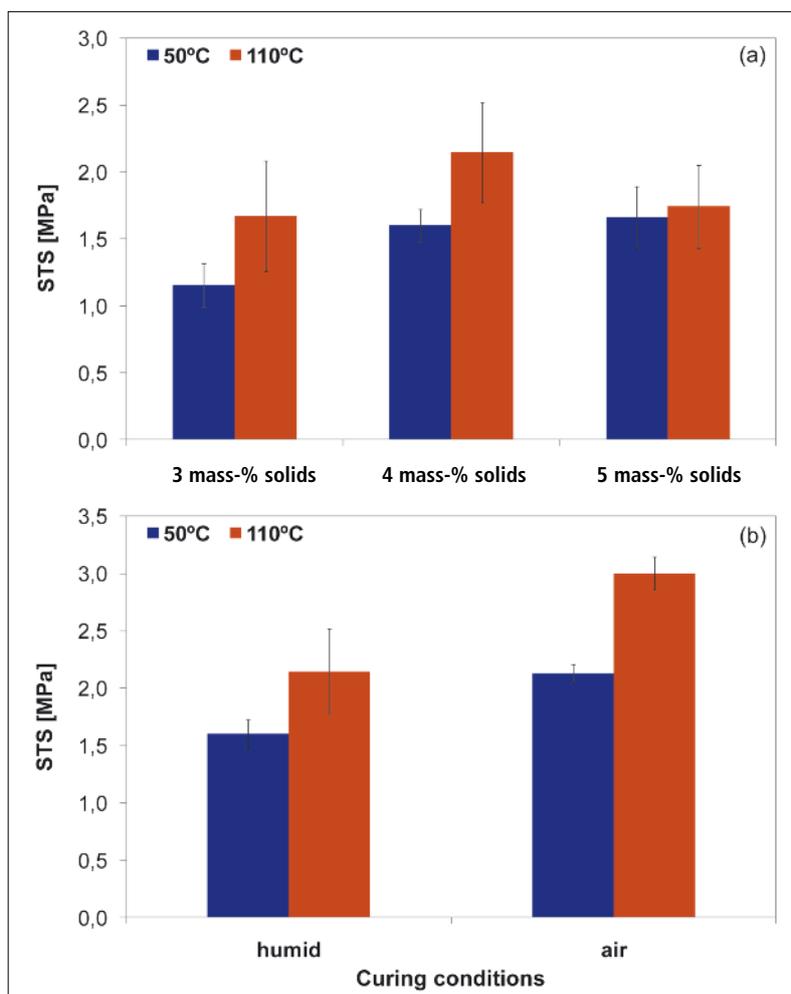

Fig. 1 Splitting tensile strength (STS) after curing at 50 °C and drying at 110 °C for (a) different colloidal alumina solid contents (3, 4 or 5 mass-%) and (b) different curing conditions (humid or air environment), where blue means 1 d curing at 50 °C; and red means 1 d curing at 50 °C followed by 1 d drying at 110 °C

ical strength up to 800 °C, most likely as a consequence of its lower starting sintering temperature. However, at 1000 °C, a drop in the mechanical strength was detected, but the mechanical strength levels for the CA40 + CA50 and CA60 compositions were still high. Considering these aspects, this sort of binder has a great potential to be used as a refractory binder of high-performance refractories for petrochemical or aluminium production application, as their working temperatures are close to 800 °C.

Considering the suitable mechanical strength levels attained for the colloidal alu-

Tab. 3 Characteristics of the compositions containing different colloidal alumina sources (solid content in the suspension: 30 mass-% – CA30, 40 mass-% – CA40, 50 mass-% – CA50 and 60 mass-% – CA60)

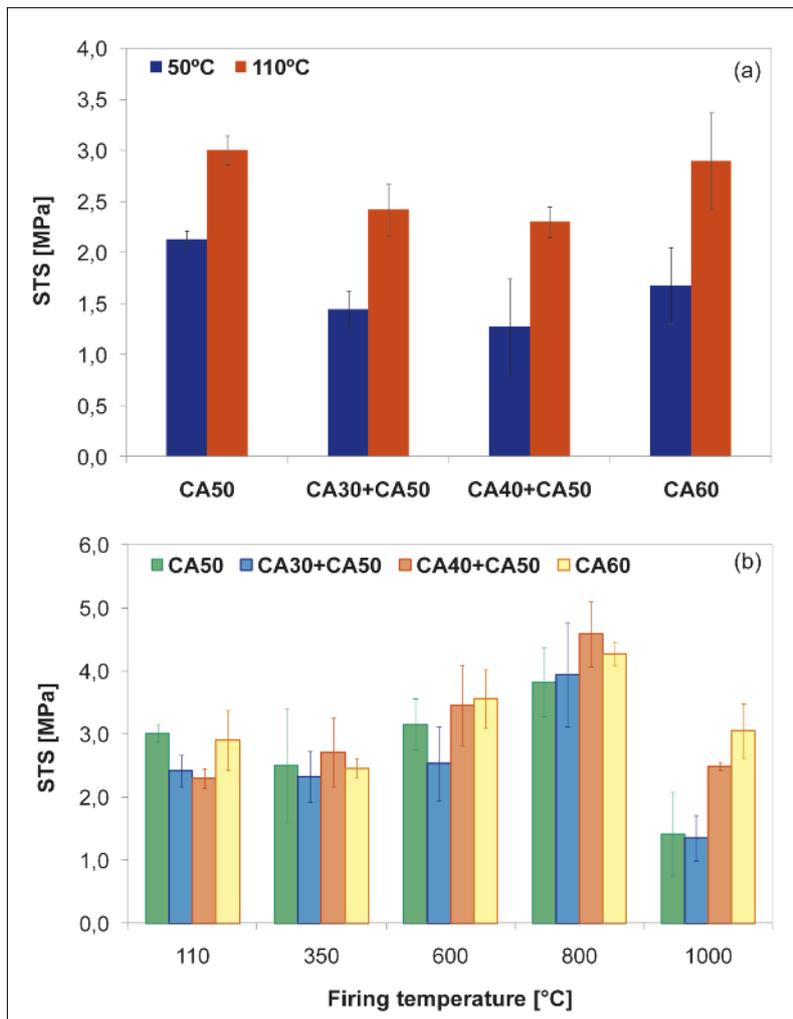| Composition | Colloidal alumina source (solid content – [mass-%]) | | | | Initial water content [mass-%] |
| | CA30 | CA40 | CA50 | CA60 | |
	water from the suspension [mass-%]				
CA30+CA50	0,5 [1,2]	-	3,5 [3,5]	-	0,6
CA40+CA50	-	1,0 [1,5]	3,0 [3,0]	-	0,8
CA50	-	-	4,0 [4,0]	-	1,3
CA60	-	-	-	4,0 [2,7]	2,6

Fig. 2 Splitting tensile strength (STS) of different colloidal alumina sources (a) after curing at 50 °C and drying at 110 °C, and (b) after firing at intermediate temperatures (350, 600, 800 and 1000 °C)
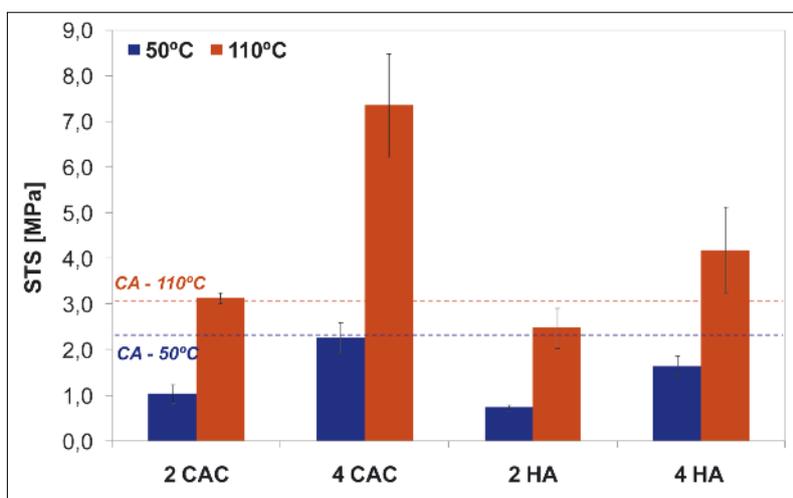

Fig. 3 Splitting tensile strength (STS) after curing at 50 °C and drying at 110 °C for castables containing 2 or 4 mass-% of usual refractory binders (calcium aluminate cement (CAC) or hydratable alumina (HA)). The dotted lines indicate the mechanical strength levels attained for a colloidal alumina (CA) containing composition

mina-containing castables, compositions containing traditional binders (calcium aluminate cement – CAC – or hydratable alumina – HA) were prepared according to Tab. 1. The green mechanical strength (after curing under humid environment for CAC and no wet environment for the HA at 50 °C and after drying at 110 °C) of these castables are shown in Fig. 3. The increase in the binder content (from 2 to 4 mass-%) led to higher mechanical strength levels for both binders. Compared to them, colloidal alumina containing castables (CA50 – 4 mass-% of solids, cured at room conditions) can develop similar mechanical strength levels than 4 mass-% of calcium aluminate cement and higher than 4 mass-% of hydratable alumina, after curing at 50 °C. Nonetheless, as these hydraulic binders result in stable hydrates after drying at 110 °C, their mechanical strength levels are higher than the one attained for colloidal alumina in this condition.

Besides this benefit, hydraulic binders usually show a drop in the mechanical strength level at intermediate temperatures (ranging from 350 °C up to 1000 °C), due to their hydrates decomposition [3–8]. Fig. 4 illustrates the effect of this behaviour in the mechanical strength and apparent porosity of these traditional binders (CAC and HA) compared to the best colloidal-alumina containing compositions (Fig. 2, CA40 + CA50 and CA60). For cement-bonded castables (Fig. 4a), the increase in the firing temperature reduced the mechanical strength level mainly for the composition containing 4 mass-% of this binder (4 CAC) due to its dehydration. In agreement with this result, the apparent porosity increased as a function of the temperature (Fig. 4b). Conversely, as colloidal alumina does not have a hydraulic setting, its apparent porosity level was kept constant regardless of the firing temperature, whereas its mechanical strength level increased up to 800 °C, highlighting a bonding effect of this source. Due to these opposite behaviours, the mechanical strength levels of both binders were similar at 800 °C, pointing out that colloidal alumina can be an alternative to cement when applied to aluminium or petrochemical producing equipment.

Besides the similar behaviour when compared to cement at 800 °C, colloidal alumina showed greater likelihood to replace hy-
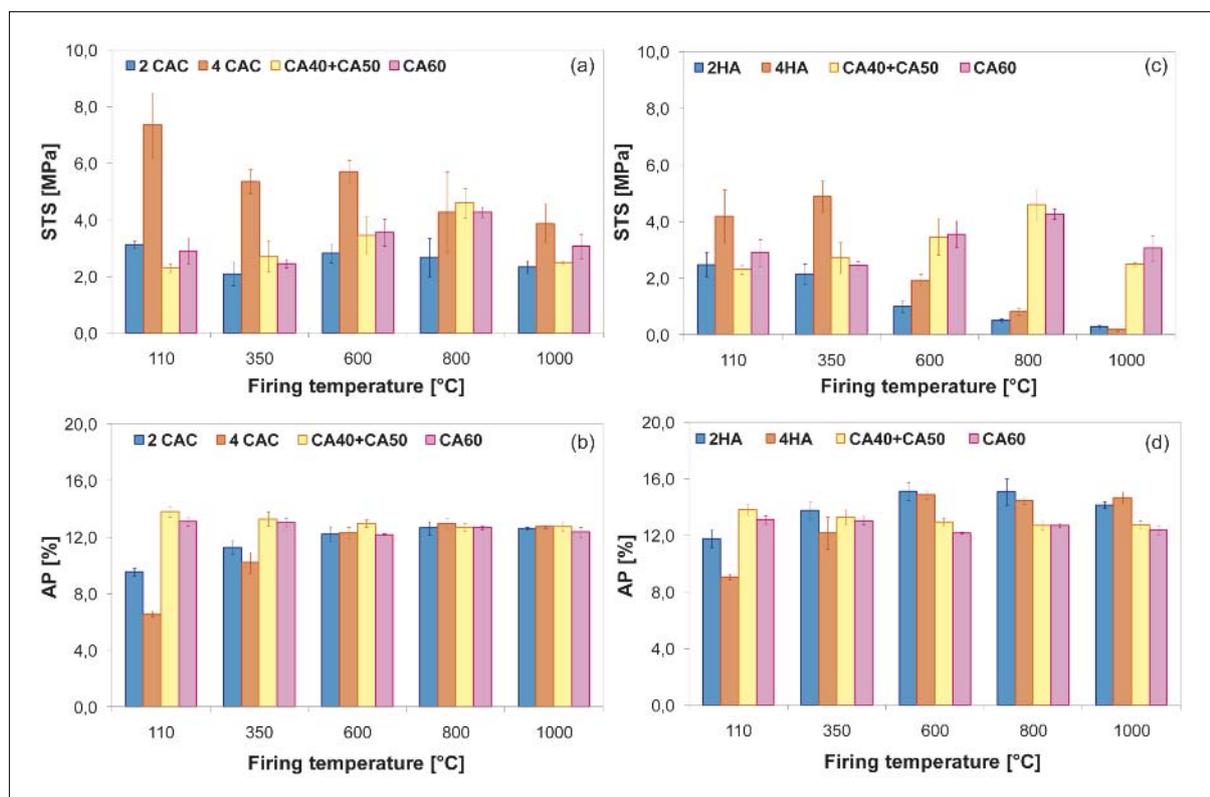
Fig. 4 Splitting tensile strength (STS, a and c) and apparent porosity (AP, b and d) as a function of the firing temperature, for calcium aluminate cement (CAC) or hydratable alumina (HA)-bonded castables compared to colloidal alumina-containing compositions (CA40 + CA50 or CA60)

dratable alumina as a castable refractory binder. According to Fig. 4c and 4d, hydratable alumina shows a considerable drop in the mechanical strength and an increase in the apparent porosity as a function of the firing temperature. As a consequence, from 600 °C upwards, the mechanical strength level for the colloidal alumina compositions is higher than those attained for hydratable alumina and this difference becomes higher when increasing the temperature. The apparent porosity level is also lower for firing temperatures higher than 600 °C.

Considering the technological potential of using colloidal alumina as a refractory binder, additional tests (cold erosion and hot modulus of rupture – HMOR) were carried out for the castables containing 4 mass-% of binders (calcium aluminate cement (CAC), hydratable alumina (HA) or colloidal alumina (CA)) and previously fired at 800 °C (Fig. 5). The HMOR tests were also conducted at this temperature. Fig. 5 indicates that calcium aluminate cement and colloidal alumina behaved quite similarly, whereas hydratable alumina presented a lower performance. Concerning the erosion results, the lowest

eroded volume level was attained for cement containing composition. On the other hand, the colloidal alumina-bonded castable showed a better hot mechanical strength. For the hydratable alumina composition, the hot modulus of rupture was very low compared to the others and its samples were fully eroded. The sample profiles after the erosion evaluation are shown in Fig. 6, pointing out the inferior wear resistance for the hydratable alumina-bonded castable. This behaviour might be a consequence of a poor link between the castable matrix and aggregates.
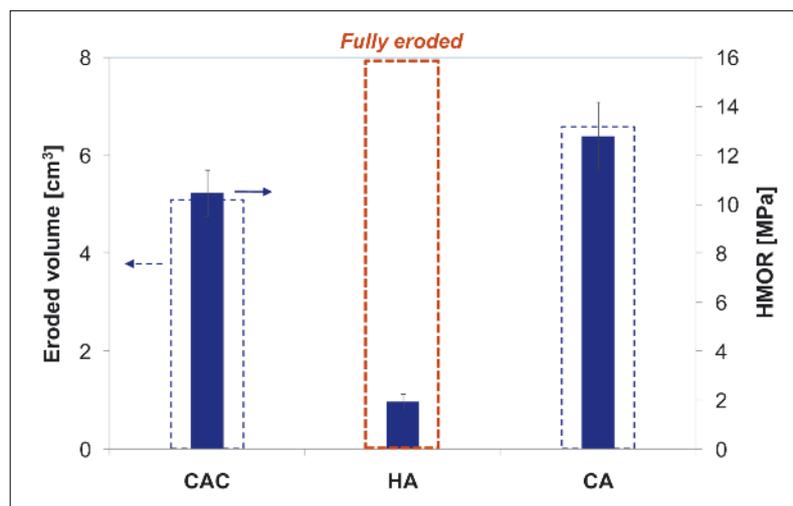

Fig. 5 Eroded volume and hot modulus of rupture (HMOR) of castables containing 4 mass-% of calcium aluminate cement (CAC), hydratable alumina (HA) or colloidal alumina (CA), and previously fired at 800 °C
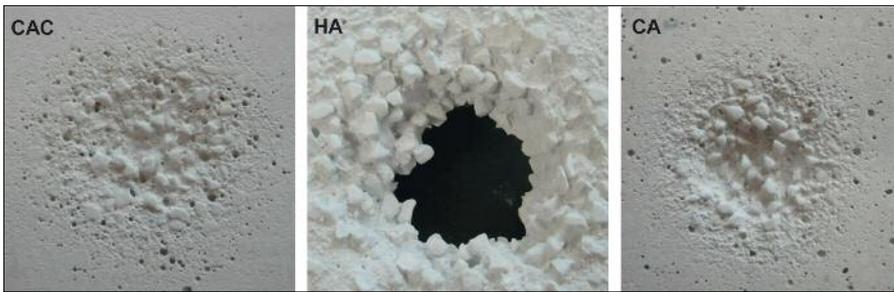
Fig. 6 Erosion sample profiles for castables containing 4 mass-% of calcium aluminate cement (CAC), hydratable alumina (HA) or colloidal alumina (CA), and previously fired at 800 °C

Due to the similar behaviour of cement and colloidal alumina at the aimed application temperature (800 °C), thermogravimetric tests were also conducted (under a heating rate of 20 °C/min) in order to figure out which binder would be safer regarding the spalling likelihood. According to Fig. 7a, colloidal alumina (CA) results in the lowest weight loss, as it is not a hydraulic binder.

In addition, the derivative of the weight loss curves highlights that the phase decomposition amount as well as the final decomposition temperature are lower than the ones observed for the cement or hydratable alumina castables. Therefore, besides the benefits attained in terms of mechanical strength, the use of colloidal alumina would imply in a safer and faster drying,
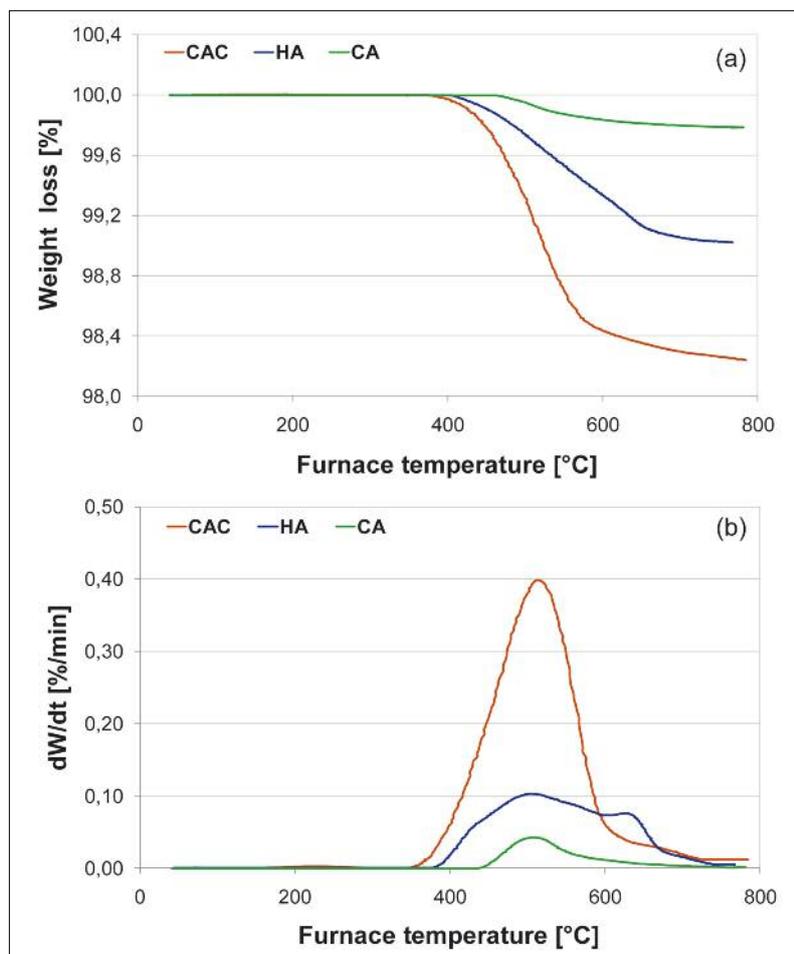
reducing the lining replacing or maintenance time.

4 Conclusions

Colloidal alumina showed great potential to be applied as a refractory castable binder. The main aspects evaluated in this study were:

- A higher colloidal alumina solid content (up to 4 mass-%) could be added, compared to previous work in the literature.
- The best condition was attained when adding 4 mass-% of solids and curing the castables at 50 °C in air.
- The mixture between two sources (CA40 + CA50) and the use of a high solid concentrated suspension (CA60) led to better mechanical strength levels at intermediate temperatures.
- Whereas cement and hydratable alumina result in a drop in the mechanical strength when firing up to 1000 °C, this behaviour is not detected for colloidal alumina. Therefore, suitable mechanical strength results (similar to cement and better than hydratable alumina) are attained at 800 °C, pointing out a greater potential for using this material in the petrochemical and aluminium industries.
- Besides the benefits related to erosion and hot modulus of rupture, a further advantage was detected in the drying behaviour, ensuring safer and faster heating up for the colloidal alumina containing castables.

Acknowledgments

Fig. 7 (a) Weight loss and (b) drying rate (20 °C/min up to 800 °C) of castables containing 4 mass-% of calcium aluminate cement (CAC), hydratable alumina (HA) or colloidal alumina (CA); all castables were previously dried at 110 °C for 24 h

References

[1] Krietz, L.: Refractories Handbook. Marcel Dekker Inc., EUA (2004) 259–285

[2] Lee, W.E.; Vieira, W.; Zhang, S.; Ghanbari, K.; Sarpoolaky, H.; Parc, C.: Castable refractory concretes. Inter. Mat. Rev. 46 (2001) [3] 145

[3] Innocentini, M.D.M.; Cardoso, F.A.; Paiva, A.E.M.; Pandolfelli, V.C.: Dewatering refractory castables. Am. Ceram. Soc. Bull. 83 (2004) [7] 9101–9108

[4] Innocentini, M.D.M.; Cardoso, F.A.; Akiyoshi, A.M.M.; Pandolfelli, V.C.: Drying stages during the heat-up of high-alumina, ultra-low refractory castables. J. Am. Ceram. Soc. 86 (2003) [7] 1146–1148

[5] Cardoso, F.A.; Innocentini, M.D.M.; Miranda, M.F.S.; Valenzuela, F.A.O.; Pandolfelli, V.C.: Drying behaviour of hydratable alumina-bonded refractory castables. J. Eur. Ceram. Soc. 24 (2004) 797–802

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

[7] Parr, C.; Bin, L.; Valdelievre, B.; Wöhrmeyer, C.; Touzo, B: The advantages of calcium aluminate cement containing castables for steel ladle applications. Proc. XXXII ALAFAR Congress 2004, p. 10

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

[9] Zhou, N.; Hu, S.; Zhang, S.: Advances in modern refractory castables. Chinas's Refr. 13 (2004) [2] 3–12

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

[11] Lidén, E.; Karlsson, S.; Tokarz, B.: Silica sols as refractory fibre binders. J. Eur. Ceram. Soc. 21 (2001) [6] 795–808

[12] Parr, C.; Wöhrmeyer, C.: The advantages of calcium aluminate cement as a castable bonding system. Lecture at St. Louis Section Meeting of American Ceramic Society, 2006

[13] Lipinski, T.R.; Tontrup, C.: The use of nano-scaled alumina in alumina-based refractory materials. Proc. UNITECR 2007, Dresden/DE

[14] Lipinski, T.R.; Drygalska, E.; Tontrup, C.: The influence of additions of nanostructured Al2O3-powder on the high temperature strength of high alumina refractories. Proc. UNITECR 2009, Salvador, Brazil

[15] Funk, J.E.; Dinger, D.R.: Particle packing, Part III: Discrete versus continuous particle sizes. Interceram 41 (1992) [5] 332–333

[16] Pileggi, R.G.; Studart, A.R.; Pandolfelli, V.C.: How mixing affects the rheology of refractory castables. Am. Ceram. Soc. Bull. 80 (2001) [6] 27–31

[17] Pileggi, R.G.; Paiva, A.E.; Gallo, J.; Pandolfelli, V.C.: Novel rheometer for refractory castables. Am. Ceram. Soc. Bull. 79 (2000) [1] 54–58

[18] Braulio, M.A.L.; Milanez, D.H.; Sako, E.Y.; Bittencourt, L.R.M.; Pandolfelli, V.C.: The effect of calcium aluminate cement on the in-situ spinel expansion. Proc. UNITECR 2007, Dresden/DE