High-performance Nano-bonded Refractories for a Wide Temperature Range*

M. A. L. Braulio, V. C. Pandolfelli, J. Medeiros, J. B. Gallo

Energy savings, safe operations, cost reductions and friendly environment are relevant topics for a sustainable industrial growth. In order to overcome these challenges, breakthrough innovation by suitable materials microstructure engineering is a key issue. Bearing in mind that technological advances must mingle basic and applied science, this work addresses the development of a nano-engineered bonded refractory for FCC petrochemical units and alumina calciners. As most of commercial refractories show densification above 1300 °C, a different composition approach was designed aiming to fulfill the sintering requirements at lower temperatures. This novel refractory comprises the use of colloidal binders and additives, in order to provide densification in lower temperatures. Considering the outstanding performance attained by these castables (high erosion, hot mechanical and thermal-shock resistances in a wide temperature range), an increase in equipment working life is expected, reducing the remarkable financial losses associated with a production halt.

1 Introduction

The improvement of the operational performance of petrochemical fluid catalytic cracking units (FCCU) or alumina refineries can result in a relevant impact on their respective production chains, as the lost income due to a production halt can reach values close to USD 0,5 million/d. Therefore, continuous efforts to maximize the campaign and reduce the unit stops must be conducted. The working life of the refractories used as lining in such equipment is one of the critical constraints that limits the unit working time.

This aspect is a consequence of the low availability of high performance materials for these applications, as the steel-making refractory market represents about 75 % of the overall market. Thus, refractories commonly used in steel shops, which show densification at temperatures above 1300 °C, are used in these units that generally operate at temperatures lower than that.

These conventional refractory castables are commonly bonded with calcium aluminate cement, that leads to ceramic bonds at high temperatures. However, over the last years, non-cement bonding systems (hydratable alumina, phosphates, colloidal silica, etc.) have also been used [1, 2]. As hydraulic binders impose specific processing restrictions, mainly on drying due to their hydrate decomposition [3, 4], colloidal silica or alumina became a potential technological alternative to minimize this shortcome [5, 6].

Due to the typical temperature decomposition profile of cement or hydratable alumina hydrates, a decay in the mechanical strength at intermediate temperatures (600–1000 °C) is generally observed [7], whereas colloidal binders can keep or even improve this property at this temperature range. Furthermore, as these binders are stable suspensions of nano-scaled silica/alumina particles [8], they show higher sinterability at lower temperatures which can speed up the refractory's densification in the usual temperature range of the target applications (800–1250 °C).

Based on these aspects, this work addressed the design of a novel engineered refractory castable by using colloidal binders and a transient sintering additive, able to induce densification at lower temperature and result in high performance materials for FCC units and alumina calciners. This approach, focused on the application requirements and typical temperatures, led to materials with

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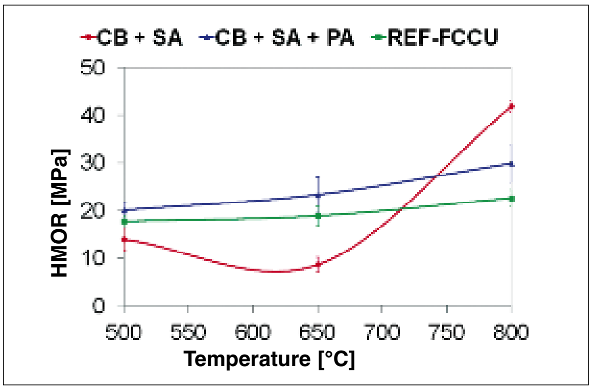

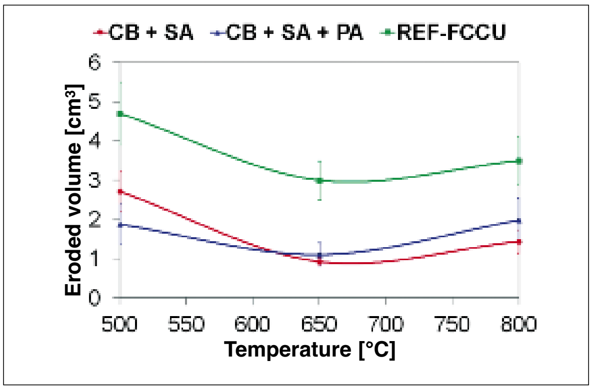

Fig. 1 Hot modulus of rupture (HMOR) and eroded volume as a function of typical petrochemical temperatures (500–800 °C) for the designed compositions (CB+SA or CB+SA+PA) and for a commercial reference (REF-FCCU)

outstanding thermo-mechanical performance (erosion resistance, hot mechanical strength and thermal shock resistance), pointing out a potential for longer refractory working life and lower maintenance stops as in these units erodible particles are conveyed at speeds as high as 50 m/s and are also prone to sudden temperature changes.

2 Materials and techniques

High-alumina free-flow castables were prepared according to Alfred's packing model (q = 0,21). The castables' matrix comprised 17–19 mass-% of two fine reactive alumina sources (*Almatis*/US, CL370 and A1000SG), 0–2 mass-% of a boron-based sintering additive (SA, under patent application) and 81 mass-% of tabular alumina (*Almatis*/DE, D_{max} <6 mm). Calcium aluminate cement-bonded references (CAC) were also prepared and 4 mass-% of this binder (Secar71, *Kerneos*/FR) was added to the composition by replacing fine tabular alumina (Almatis/DE, D_{max} <45 µm). The best commercial references currently in use at a FCCU petrochemical unit (REVAP, *Petrobras*/BR) and at alumina calciners (*Alumar*/BR) were also evaluated.

Regarding the colloidal binders (CB), nano-scaled alumina suspensions containing 40 mass-% (VP 640 ZX) and 60 mass-% (VP Disp. 460 ZX) of solids were added together (*Evonik Degussa GmbH*/DE), whereas a single suspension of colloidal silica (*Eka Chemicals*/SW) containing 50 mass-% (Bindzil 50/80) was evaluated. The total amount of colloidal solids was 4 mass-%. The water content for suitable molding was based on an initial 60 % free-flow value and its total amount (free water + suspension water) was of 5,3 mass-% for the colloidal alumina system and 5,0 mass-% for the colloidal silica one. The gelling additive used was a high-purity magnesia source (98 mass-% MgO, *Magnesita Refratários S.A.*/BR). For the CAC-bonded castables, 4,4 mass-% of water was added to attain the same above-mentioned initial free-flow value and 0,2 mass-% of a polycarboxylate dispersant (*BASF*/DE) was added to the castables.

Hot modulus of rupture (HMOR) tests were conducted up to 1400 °C. Prismatic samples (25 mm × 25 mm × 150 mm) were prepared and after processing (1 day curing at 50 °C, 1 day drying at 110 °C and firing at 500, 650, 800, 1000, 1250 or 1400 °C for 5 h), their hot modulus of rupture was evaluated (at the same firing temperature) in HBTS 422 equipment (3-point bending test, *Netzsch*/DE) based on the ASTM C583-8 standard. The erosion resistance was evaluated considering the same firing temperature range used for the HMOR tests (500–1400 °C for 5 h), 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 that is converted to a volumetric one). Concerning the thermal shock tests, the refractories were subjected to various heating and cooling cycles. The samples were placed into a furnace chamber previously heated up to 825 °C or 1025 °C and kept at these temperatures for 15 min. Afterwards, they were taken out of the furnace and cooled in air, leading to thermal gradients of roughly 800 °C or 1000 °C. After 15 min at room temperature, the cycle was repeated. The thermal shock damage was evaluated by the elastic modulus measurements (bar resonance, ASTM C1198 standard) as a function of the thermal cycles (0, 2, 4 and 6). The number of cycles was limited to 6 as the most relevant mechanical damage took place mainly in the initial cycles (<6).

In order to evaluate the formation of transient or permanent liquid and the castables' densification, hot elastic modulus measurements (the heating rate was 2 °C/min, up to 1000 °C) by the bar resonance method (ASTM C1198 standard) were conducted in prismatic samples (25 mm × 25 mm × 150 mm), after previous processing steps (1 day curing at 50 °C and 1 day drying at 110 °C). Finally, as the drying step is a key safety concern during refractory castable applications, thermogravimetrical evaluations on cylindrical samples (40 mm × 40 mm) were carried out up to 800 °C, after 1 day of curing at 50 °C. The test was performed under a heating rate of 20 °C/min, aiming the evaluation of the spalling likelihood. The thermogravimetric device was developed in the authors' research group and used to analyze the mass loss during drying (W) and the drying rate (dW/dt).

3 Results and discussion

FCC units commonly operates at temperatures ranging from 500 °C (reactor zone) to 800 °C (riser), at which cement hydrates are commonly decomposed, leading to a reduction in the castable's mechanical strength. Fig. 1 shows the mechanical results attained for the nano-engineered designed castable (containing colloidal binder and sintering additive – CB+SA) compared to a commercial reference (REF-FCCU). Although at 800 °C, the hot modulus of rupture of the

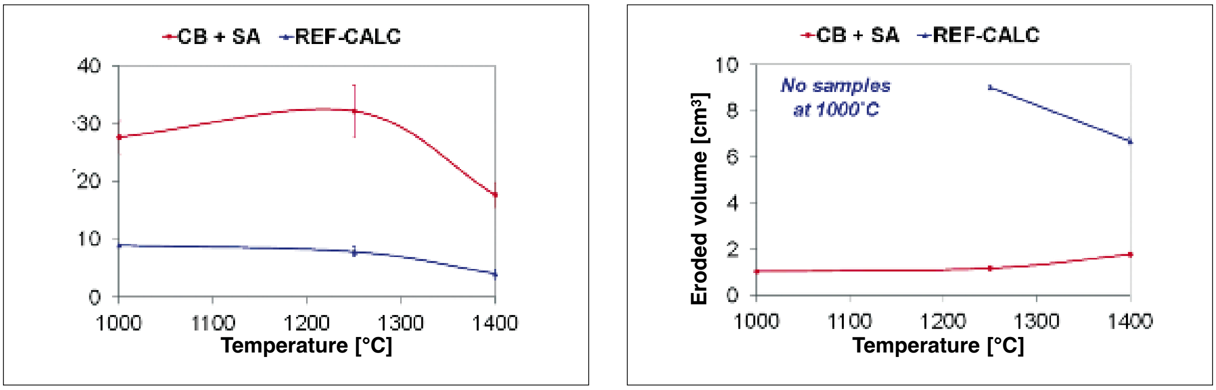

Fig. 2 Hot modulus of rupture (HMOR) and eroded volume as a function of typical alumina calciner temperatures (1000–1400 °C) for the designed composition (CB+SA) and for a commercial reference (REF-CALC)

CB+SA composition was two-fold greater than the one attained for REF-FCCU, its hot mechanical strength was lower at 500 and 650 °C. Considering the technical datasheet information of the reference composition, that indicated 2,3 mass-% of CaO (~7 mass-% of CAC) and 1,7 mass-% of P_2O_5, it was noticed that not only the binder content was much higher (7 mass-% of cement versus 4 mass-% of colloidal binder), but also presented a phosphate bond, which is known to increase the mechanical strength at temperatures of 500–650 °C. Therefore, in order to overcome this drawback detected for CB+SA, only 0,8 mass-% of a phosphate based additive (PA) was added to the CB+SA composition. With this change, the hot mechanical strength levels were higher along the full evaluated temperature range.

As erosion is the main wearing mechanism for this sort of refractories' application, the eroded volume values obtained for the CB-bonded castable were remarkable: 1–3 cm³ versus 4–4,5 cm³ for REF-FCCU, highlighting that this novel designed composition would reduce the erosion loss, increasing the refractories working life and equipment availability.

Due to these remarkable results for petrochemical application, the CB+SA castable (without phosphate, as it can generate liquid phase at higher temperatures) was fired from 1000 to 1400 °C. Although the typical alumina calciner operational temperature is 1250 °C, this range was selected as in the holding vessel the temperatures are lower (1000 °C) and in the pre-heater and furnace regions it can reach values as high as 1400 °C. Compared to the commercial reference (REF-CALC), the mechanical results (Fig. 2) indicated a potential to increase the refractory calciner's working life: the hot modulus of rupture was at least 3-fold higher in the full selected temperature range, whereas the eroded volume was 7–9 times lower (the 1000 °C temperature was not evaluated for the reference, due to the low amount of samples prepared by the supplier).

The high mechanical performance attained for the colloidal-bonded refractory castable led to a concern regarding its thermal shock behavior, as strong materials, in general, result in catastrophic thermal shock failures owing to its ability to store elastic energy.

Nevertheless, the thermal shock results (T = 800 °C for petrochemical samples fired at 800 °C and T = 1000 °C for alumina calciner samples fired at 1000, 1250 or 1400 °C) showed a different scenario (Tab. 1).

The results shown in Tab. 1 pointed out very high initial elastic modulus (up to ~170 GPa, which are common values for technical ceramics, but not for refractories) and, more relevant than that, almost no decrease in the elastic modulus after 6 thermal cycles. This aspect indicates a high thermal shock resistance. The FCCU or calciner references presented much lower initial elastic modulus values coupled with much higher percentual

Tab. 1 Absolute elastic modulus (initial and after 6 cycles) and percentual elastic modulus loss (after 6 cycles) of the evaluated castables (CB+SA and references)

Samples fired at 800 °C (ΔT = 800 °C)			
	MOE – initial [GPa]	*MOE — final [GPa])*	*Loss [%]*
CB + SA	171,2 ± 5,2	156,0 ± 7,4	–9
REF-FCCU	10,0 ± 0,2	5,9 ± 0,2	–41
Samples fired at 1000 °C (ΔT = 1000 °C)			
	MOE – initial [GPa]	*MOE –final [GPa]*	*Loss [%]*
CB + SA	161,6 ± 2,6	117,6 ± 7,9	–27
REF-CALC	8,7 ± 0,1	6,3 ± 0,2	–28
Samples fired at 1250 °C (ΔT = 1000 °C)			
	MOE – initial [GPa]	*MOE – final [GPa]*	*Loss [%]*
CB + SA	103,9 ± 1,5	96,0 ± 3,6	–8
REF-CALC	9,0 ± 0,3	6,5 ± 0,3	–28
Samples fired at 1400 °C (ΔT = 1000 °C)			
	MOE – initial [GPa]	*MOE – final [GPa]*	*Loss [%]*
CB + SA	69,5 ± 3,3	67,1 ± 4,6	–3
REF-CALC	20,7 ± 1,2	16,7 ± 1,3	–19

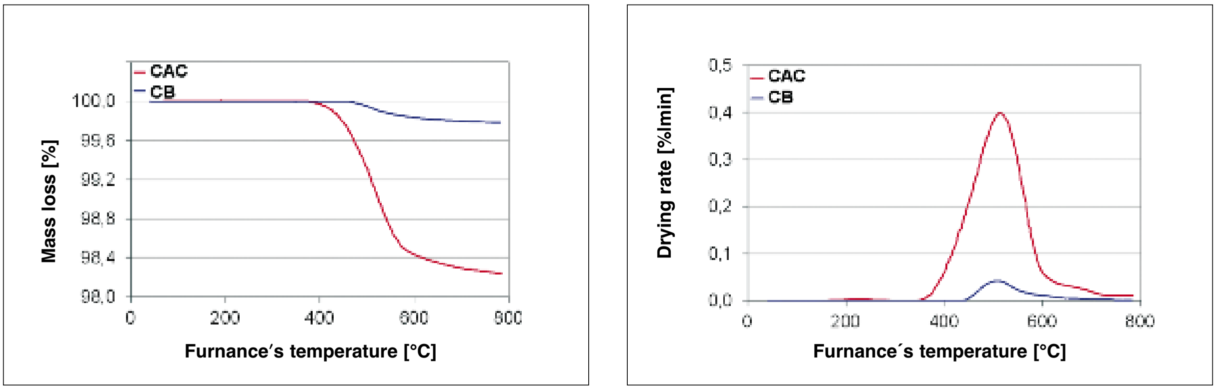

Fig. 3 **Drying behavior of cement-bonded (CAC) or colloidal-bonded (CB) refractory castables up to 800 °C, after 1 day of drying at 50 °C**

elastic modulus loss. The high thermomechanical performance attained (erosion, hot mechanical and thermal shock resistances) in a wide temperature range (from 500–1400 °C) pointed out that this novel refractory design is a multi-applicable and flexible solution for these two important operational units.

Taking these results into account, one must wonder whether calcium aluminate cement-bonded castables containing the boron-based sintering additive would also lead to a similar performance, without the need of adding colloidal binders, which require some attention during initial processing steps (mixing and setting time) as they are aqueous suspensions containing reactive particles and also dispersion additives that can affect the castable's stability.

Nevertheless, two drawbacks that restricts this combination (CAC+SA) can be highlighted: (i) the mass loss during drying is higher for cement-bonded castables (Fig. 3), indicating the need of better control during this processing step and also lower heating rates (longer time for repairing and, consequently, additional impact of the lost income) and (ii) the formation of a permanent liquid phase, that spoils the hot mechanical properties (drop in the hot modulus of rupture at temperatures above 1000 °C) and can result in an unexpected production halt (overheating of the steel shell due to the refractory layer wearing) and further lost income. In Fig. 4 the HMOR of castables containing only cement (CAC) or colloidal binders (CB) and also these binders with sintering additive (CAC+SA or CB+SA) highlights that only the combination of colloidal binder and sintering additive (CB+SA) could result in reliable and constant values of hot mechanical strength throught the full temperature range. The elastic modulus (MOE) evaluation indicates that CB+SA show a more effective sintering (MOE increase at lower temperatures than CAC+SA) and no drop in the MOE up to 1000 °C (transient liquid formation), whereas CAC+SA presents a reduction in the MOE at 900 °C (permanent liquid), which is in tune with the HMOR values. These results indicate that the refractories performance in use can be improved, ensuring safety and longer working life.

4 Conclusions

The simultaneous addition of a colloidal binder and sintering additive proved to be an outstanding novel route to design high-performance refractory castables for FCC petrochemical units and alumina calciners. Conversely to calcium aluminate cement, which displays a high sintering temperature and can lead to permanent liquid formation, colloidal binders coupled with sintering additives can provide low densification temperature by generating a transient liquid that does not spoil the castables' hot properties. Remarkable results for thermal shock, erosion and hot mechanical strength were attained. This new material can be classified as a multi-applicable full temperature range refractory castable, with very promising perspectives for application in petrochemical and aluminum industries.

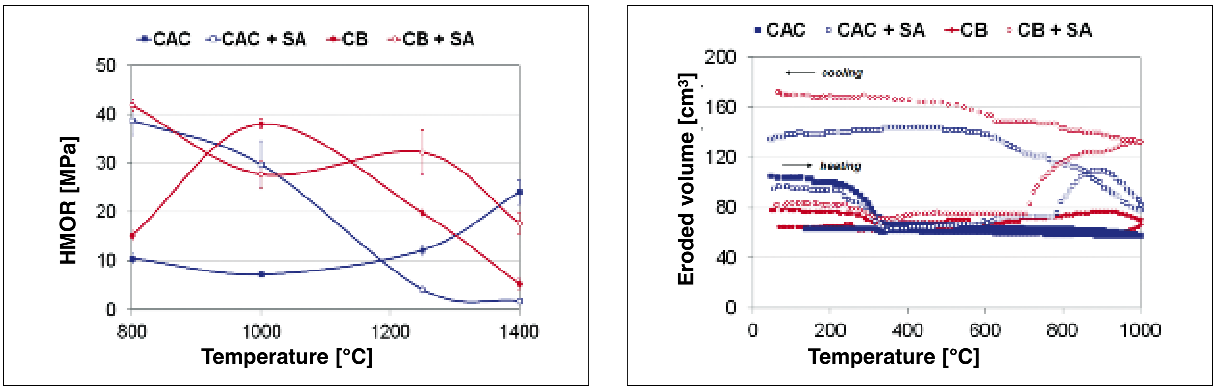

Fig. 4 **HMOR as a function of testing temperature (800–1400 °C) and elastic modulus evaluation up to 1000 °C for castables containing only cement (CAC) or only colloidal binder (CB) or bonded with these binders and containing sintering additive (CAC+SA or CB+SA)**

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