High-performance Nano-bonded Castables for Petrochemical Applications

E. Prestes, D.T. Gomes, J. Medeiros, J.L.B.C. Veiga, V.C. Pandolfelli

Nowadays, in the refractory market, castables specially designed for fluid catalytic cracking (FCC) units are not common. One aspect that induces this scenario is the difficulty to attain optimized properties in the temperature range compatible with the process conditions. The development of suitable refractory compositions can be achieved by adding nanoscaled particles, which increases the system reactivity, resulting in high mechanical strength values with the temperature increase. Additionally, the use of sintering additives helps the densification at lower temperatures. In this context, colloidal silica bonded castables containing tabular alumina, fused silica or mullite grog and specific sintering additives were designed for riser application. The erosion loss of the developed castables was significantly reduced. Compared with the commercial reference products currently used by the Brazilian petrochemical industry, the nano-bonded material performed better for the main usual properties. Based on this novel technology, a self-flow castable with suitable apparent density and thermal conductivity, high thermal shock resistance and reduced erosion loss was developed for riser application.

1 Introduction

In the petrochemical industry, gasoline and LPG are produced in the fluid catalytic cracking (FCC) unit. Cracking occurs by contact of crude oil with fluidized fine particles of ceramic catalyst [1, 2]. The process profitability is strongly related to a reduced number of FCC maintenance halts. Considering this, the refractory material performance is a key factor to increase the equipment working life. The castables applied in FCC units face various harsh demands, such as: erosion wear, thermal shock spalling and degradation by carbon deposition. Among them, the high erosion resistance is a fundamental requirement [3]. In areas of higher wear rates, such as cyclones, high-alumina products with better erosion resistance (<6 cm^3) are applied. Dense castables, with erosion loss lower than 12 cm^3, are used for the riser lining [4]. Due to the low operation temperature, not above 900 °C, high performance materials are scarce as the available commercial refractory products are usually not specific for this sort of application. One alternative to attain optimized properties at low operation temperatures is the addition of nanometric size particles. This can be carried out replacing the calcium aluminate cement (CAC) by colloidal silica. This nanostructured binder is an aqueous suspension that can be easily added to castables [5]. The high specific surface area provides an increase in the system reactivity, resulting in high mechanical resistance during the refractory firing step [6]. Another possibility is the use of sintering additives which can help densification at low temperatures. The synergism between nanoparticles reactivity and sintering effectiveness allows the development of high-performance nano-bonded antierosive castables. In this context, colloidal silica bonded castables comprising tabular alumina, fused silica or mullite grog and specific sintering additives were designed for riser application.

2 Materials and methods

Refractory castables containing tabular alumina, mullite grog or fused silica were designed based on *Alfred*'s packing model [7]. Tab. 1 shows the characteristics of the developed compositions. A tabular alumina-based castable containing calcium aluminate cement (TA CAC) was compared to a colloidal silica-bonded (TA CS) one. Among the different compositions, the tabular alumina aggregate was selected due to its higher hardness which results in lower erosion loss. The fused silica is a raw material of low apparent density, low thermal conductivity and a very low linear expansion coefficient (0,5 × 10^{-6}/°C), inducing high thermal shock resistance. For these two systems, vibratable castables were designed making

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Tab. 1 Refractory castable characteristics

Raw Material [mass-%]			**Designation**			
			TA CAC	**TA CS**	**FS CS**	**MUL CS**
Packing coefficient (q)			0,26	0,26	0,26	0,24
Aggregate	Tabular alumina (*Almatis*/US)	d ≤6 mm	84,5	86	16	–
	Fused silica (*CE Minerals*/US)	d ≤4,75 mm	–	–	70	–
	Mullite grog (CE Minerals/US)	d ≤6,73 mm	–	–	–	85,5
Matrix	Reactive alumina (Almatis/US)	CL370C and CT3000SG	10	9,5	10	10
	Fumed silica (*Elkem*/NO)	MS971D	2	2	2	2
	Sintering additive (under patent application)	Metallic	–	2	1	2
		Non-metallic	–	0,5	1	0,5
Binder	Colloidal silica (*Eka Chemicals*/SE)	Bindzil 1440	–	7	8,7	–
		Bindzil 50/80	–	–	–	13
	Cement (*Kerneos*/FR)	Secar 71	3,5	–	–	–
Additive	Electrostatic dispersing (*BASF*/DE)		0,2	–	–	0,1
	Gelling agent (98 mass-% MgO, *Magnesita Refratários*/BR)		–	0,01	0,01	0,04
Total water content [mass-%]			4,2	4,2	5,2	6,5

use of 40 mass-% colloidal silica particle suspension as a binder (Bindzil 1440). Considering the riser application, a self-flow composition coupling high-erosion and thermal shock resistances with low apparent density and reduced thermal conductivity is an innovative solution.

However, it is not possible to simultaneously attain these properties just adding tabular alumina or fused silica as aggregates, due to the high apparent density of the former and the inferior erosion resistance of the latter. An alternative raw material that presents good erosion resistance and low thermal conductivity is mullite. Therefore, this aggregate was selected to be the major constituent of a self-flow composition containing a 50 mass-% colloidal silica particle suspension as a binder (Bindzil 50/80). For all nanobonded castables, the total water content showed in Tab. 1 was derived only from the colloidal suspension. In order to help the setting process, a gelling agent was also added [8]. Two CAC-containing commercial products currently used by the Brazilian petrochemical industry for riser lining were selected to compare with the developed nano-bonded castables (Tab. 2). Reference 1 is a castable based on alumina-silica grog and reference 2 on bauxite one.

The castables were processed in a rheometer especially developed for refractory castables [9]. After shaping, the colloidal silica bonded castables were cured at 50 °C for 24 h in a moisture unsaturated environment (without humidity) [10]. For the CAC-containing one, the curing step was conducted in an acclimatized chamber (*Vötsch* 2020/DE) with relative humidity of 80 % and the drying was carried out at 110 °C for 24 h. The firing step was conduced at 200, 400, 600, 815 and 1000 °C with a heating rate of 3 °C/min and 5 h of dwell time. The apparent density and porosity was measured according to *Archimedes* immersion test (ASTM C 830-88). Mechanical strength was measured based on ASTM C496-90 standard (Splitting Tensile Strength of Cylindrical Concrete Specimens) in *MTS Systems* equipment (model 810, USA) using 40 mm × 40 mm cylindrical samples. The cold erosion resistance was evaluated according to ASTM C 704 standard (1 kg of no. 36-grit silicon carbide to erode 115 mm × 115 mm × 25 mm thick samples, leading to a weight loss that is converted to a volumetric one).

For the thermal shock, samples (150 mm × 25 mm × 25 mm) previously fired (815 °C for 5 h) were heated at 815 °C and then air cooled at room temperature (ΔT = 790 °C). This procedure was repeated up to 8 cycles and the effect of the thermal shock damage was evaluated every two cycles by elastic modulus measurements, according to ASTM C 1198-91 using the resonance bar technique (*Scanelastic* equipment, *ATCP*/BR). Thermal conductivity was measured in a previously fired sample (815 °C/10 h) using the hot wire technique (ASTM C 1113) at 200, 400, 600 and 815 °C temperatures (TCT 426 equipment, *Netzsch*/DE).

3 Results and discussions

3.1 Characteristics of nano-bonded castables containing sintering additives

The consolidation mechanism of colloidal silica-bonded refractory castables is due to the condensation of (Si-OH) groups present on the surface of the nanometric particles. This process is named gelation and leads to the formation of a three-dimensional particles network in the castable matrix, providing mechanical resistance to the material [11]. Nonetheless, Fig. 1 shows that the CS-bonded castable without additives (only CS) do not overcome the bonding strength provided by the usual hydrates (C_2AH_8 and C_3AH_6) in CAC-bonded systems [12]. A remarkable increase in the mechanical strength was de-

Tab. 2 Technical data of the commercial products

Characteristic		**Reference 1**	**Reference 2**
Application method		Vibratable	Self-flow
Chemical analysis [mass-%]	Al_2O_3	45,8	62 min
	SiO_2	49,9	35 max
Apparent density [g/cm³]	815 °C × 5 h	2,32	2,62
Total water content [mass-%]		7,0	6,5

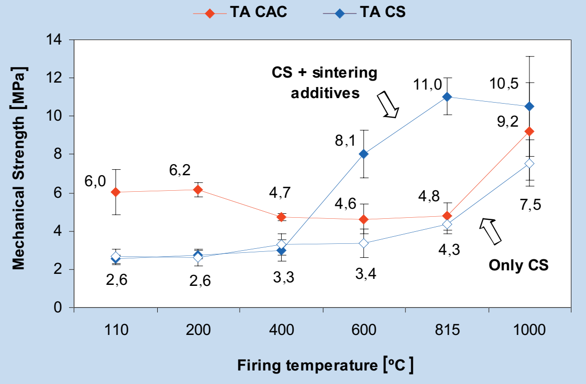

Fig. 1 Mechanical strength of CS and CAC bonded castables versus the temperature

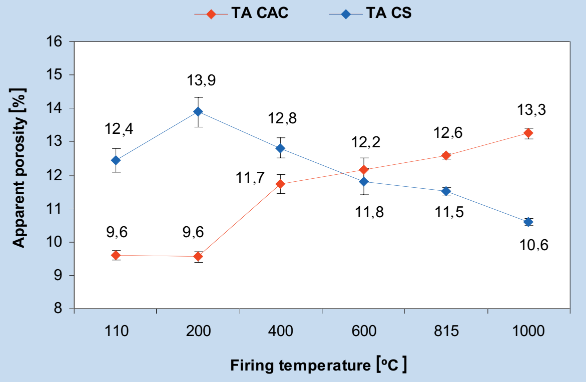

Fig. 2 Apparent porosity of CS and CAC bonded castables versus the temperature

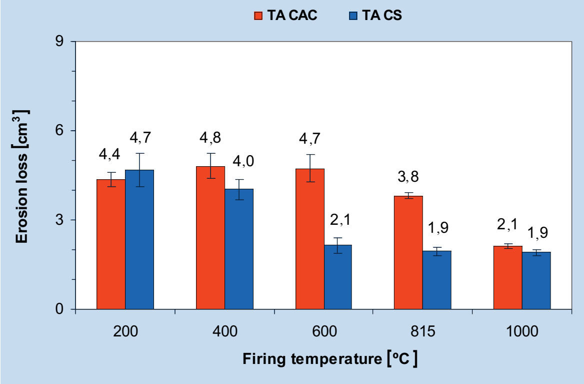

Fig. 3 Erosion loss of CS and CAC bonded castables versus the temperature

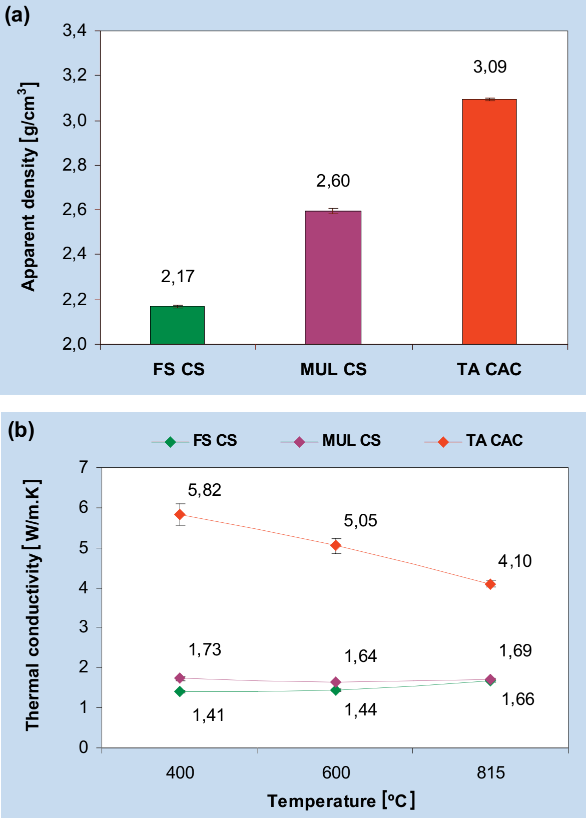

Fig. 4 a–b Apparent density after firing at 815 °C/5 h for different refractory systems (a) and thermal conductivity versus the temperature (b)

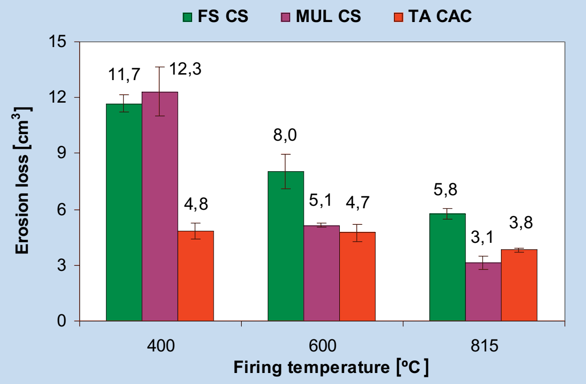

Fig. 5 Erosion loss of fused silica and mullite grog nano-bonded castables compared to CAC-containing tabular alumina

tected in the 600–1000 °C temperature range but still below the CAC performance. The decomposition of hydrates resulted in a mechanical strength decrease up to 600 °C for the CAC-containing castable. Only with the beginning of the ceramic bonding at 1000 °C did the material show improvement in this property.

The incorporation of sintering additives in CS bonded systems changed the mechanical strength profile and led to a very good performance in the temperature range of 600 to 1000 °C. Fig. 2 shows that the apparent porosity results are also influenced by the bonding agent characteristics and the sintering additive presence.

For the CAC-containing castable, the apparent porosity was lower after drying at 110 °C and increased in the range between 200–400 °C due to the water released by hydrate decomposition. A gradual increase in the apparent porosity was observed up to 1000 °C due to the lack of sintering process. When combining colloidal silica and sintering additives (TA CS), the apparent porosity profile was distinct. Almost all water was released at 110 °C, providing a higher initial apparent porosity when compared to the CAC-bonded castable. Nevertheless, for temperatures

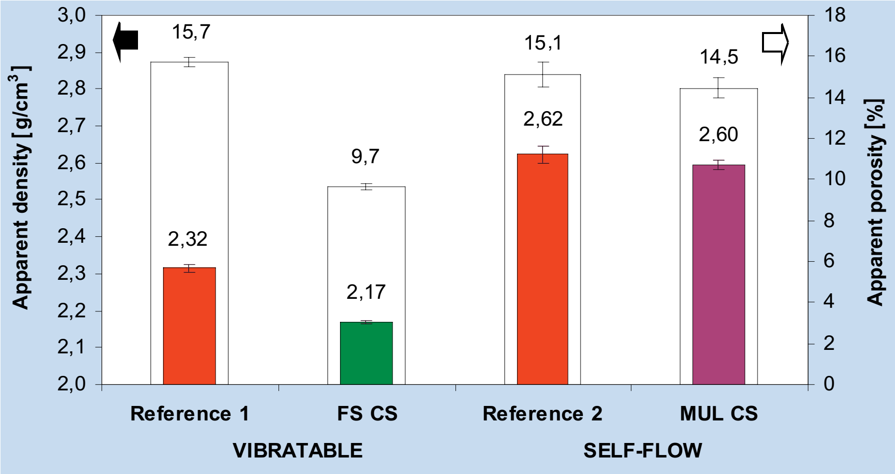

Fig. 6 Apparent density and porosity after firing at 815 °C/5 h of castables for riser

above 600 °C the apparent porosity values decreased due to the sintering additive effect [5]. With no sintering agents, the apparent porosity value would be constant up to 1000 °C. This comparison is valid as the two castables present the same water content and very similar particle size distribution. Fig. 3 shows the cold erosion resistance test values for the CS and CAC bonded castables.

Considering the working temperatures in an FCC unit riser (400 to 815 °C), the performance attained with the nano-bonded castable was better than the CAC ones. The excellent erosion resistance values show that the development of antierosive castables with optimized properties at low temperatures can be attained by combining colloidal silica and sintering additives. For the riser application, the target is the development of a material that associates high thermal shock and high erosion resistance with low apparent density and reduced thermal conductivity. For this purpose, the same designed system tested for the tabular alumina castable (TA CS) was applied substituting the aggregates for fused silica (FS CS) or mullite grog (MUL CS). Fig. 4a and 4b, respectively, shows the difference among the compositions for apparent density and thermal conductivity when compared to the tabular alumina CAC bonded castable.

Mullite grog is an interesting aggregate for the design of riser castables as it couples a medium apparent density with thermal conductivity values much lower than the high alumina material. Fig. 5 shows the erosion loss of the fused silica and mullite grog nano-bonded castables compared to the CAC containing tabular alumina after thermal treatment at different temperatures.

Nano-bonded systems showed a great erosion resistance improvement, from 12 cm^3 after firing at 400 °C to less than 6 cm^3 at 815 °C. The mullite grog based castable provided the same performance of the tabular alumina CAC-containing in the range of

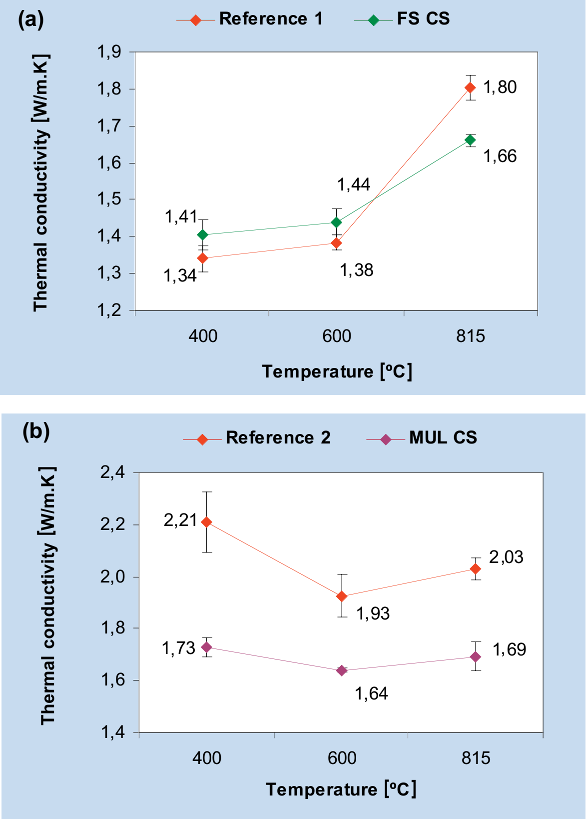

Fig. 7 a–b Thermal conductivity of vibratable (a) and self-flow (b) castables for riser application

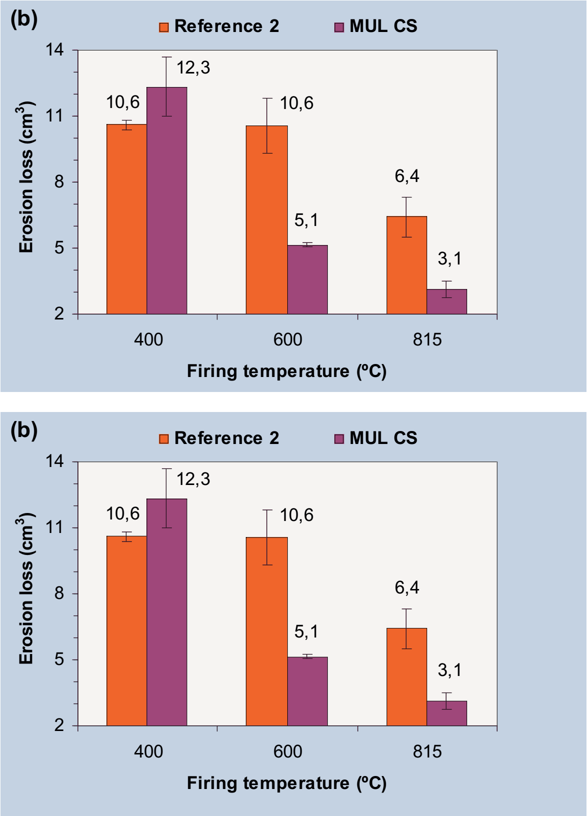

Fig. 8 a–b Erosion loss of vibratable (a) and self-flow (b) castables for riser application

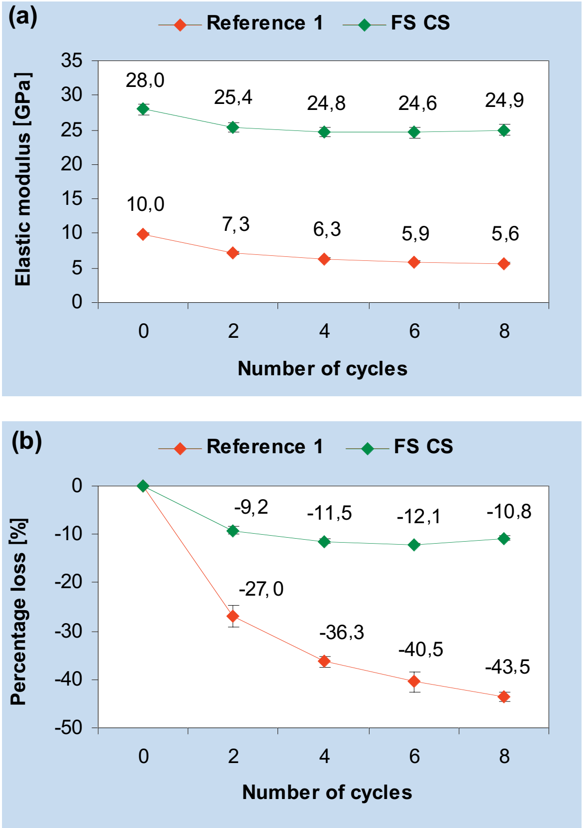

Fig. 9 a–b Absolute elastic modulus (a) and the percentage loss (b) for the vibratable castables versus the thermal shock cycles number (Δ T = 790 °C).

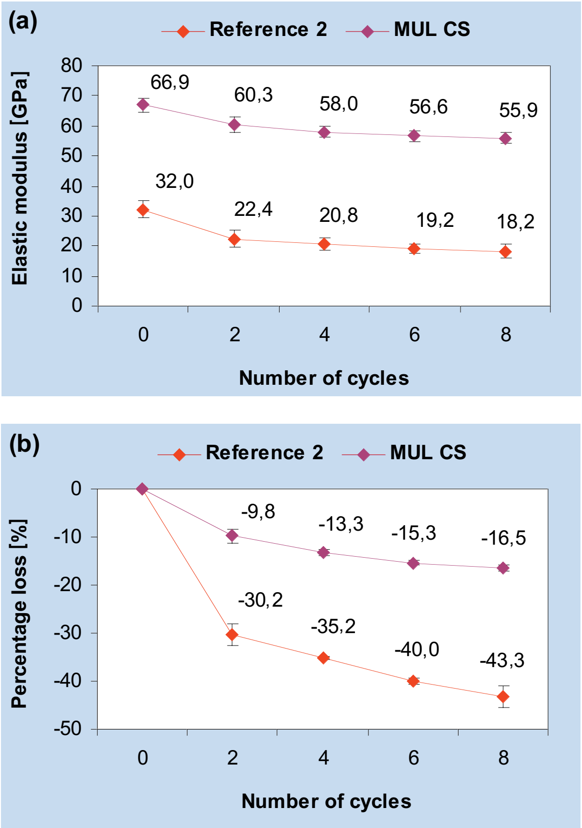

Fig. 10 a–b Absolute elastic modulus (a) and the percentage loss (b) for the self-flow castables versus the thermal shock cycles number (Δ T = 790 °C)

600 to 815 °C. The erosion loss requirement of the Brazilian petrochemical industry is 12 cm^3 or less for the castables with apparent density up to 2,4 g/cm^3 (castables for riser) and 6 cm^3 for the ones with apparent density higher than 2,6 g/cm^3 (cyclones application), after firing at 815 °C. Considering these specifications, it could be attested that the fused silica castable fulfilled the erosion target (<12 cm^3) and that the mullite containing material is a self-flow product with the same erosion resistance of high-alumina CAC-containing castable, after firing at 600 °C. In this context, this nano-bonded system stands as an innovative solution.

3.2 Performance evaluation of nano-bonded castables and CAC-containing commercial products

The reference riser castables for the Brazilian petrochemical industry were presented in Tab. 2. The vibratable one is a 45 mass-% alumina-silica grog and the self-flow castable is a bauxite based material. Fig. 6 shows a comparison (apparent density and porosity) between the materials, according to the application technique.

Regarding the vibratable castables, the use of fused silica aggregate provided an inferior apparent density than reference 1 and lower porosity due to the reduced water content (7,0 mass-% for the commercial product and 5,2 mass-% for the nano-bonded one). Reference 2 and MUL CS self-flow castables were processed with the same water content (6,5 mass-%) and presented similar apparent density and porosity. Fig. 7 presents the thermal conductivity of these castables.

The vibratable castables showed very similar behaviorur. Therefore, the lower apparent density of the fused silica based material was an advantage. Although the same apparent density for the self-flow castables could be observed in Fig. 6, the thermal conductivity of the mullite grog nano-bonded material was much lower compared to reference 2. Fig. 8 shows the erosion loss results for the castables.

Nano-bonded systems showed a high erosion resistance improvement by increasing the firing temperature, pointing out the main technological advantage of these colloidal silica and sintering additives containing compositions. As seen in Fig. 6, fused silica aggregate is a raw material of lower apparent density than the alumina-silica grog used in reference 1 castable and, even so, it did not result in higher erosion loss. The mullite-based castable presented the best erosion resistance performance after firing at 815 °C when compared to the references and the fused silica composition. Associating this result with its lower thermal conductivity, it can be concluded that this self-flow composition is more suitable than reference 2.

One important property which is not usually considered in the castables evaluation for riser application is the thermal shock resistance. Fig. 9–10 show, respectively, the absolute elastic modulus and the percentage loss versus the thermal shock cycles for the vibratable and self-flow castables.

Tab. 3 Comparative performance of castables for riser

Requirement	Vibratable Castable		Self-flow Castable	
	FS CS	Reference 1	MUL CS	Reference 2
Low apparent density	•		•	•
Reduced thermal conductivity	•	•	•	
High-erosion resistance	•		•	
Low damage by thermal shock	•		•	

The commercial products (reference 1 and 2) presented the worst performance, considering the low absolute elastic modulus and the high percentage loss. The refractory microstructure cracking due to cycling temperature variations can lead to spalling and increase the refractory lining susceptibility to carbon deposition, for example. The better initial properties of the developed nano-bonded castables make them the best choice to increase the FCC unit profitability and reduce the maintenance halts. The performance of the different products based on the main requirements for riser application was summarized in Tab. 3.

Nano-bonded materials met the requirements for riser applications as the castables were designed considering the suitable aggregate selection, the riser application conditions and by combining the addition of colloidal silica and sintering additives, which allowed for optimized properties at lower temperatures. As a result, a high-performance self-flow riser castable for FCC unit could be developed.

4 Conclusions

The replacement of CAC by colloidal silica as a binding agent and the use of sintering additives in castable compositions allowed for great erosion resistance improvement with the firing temperature. Based on this novel technology, two castables (fused silica and mullite grog) were developed and compared with the best commercial products currently used by the Brazilian petrochemical industry. The results showed a better performance of the nano-bonded materials for the main usual properties. The mullite grog self-flow castable with the same erosion resistance of high-alumina CAC-containing castable in the range of 600 to 815 °C is an innovative solution for the FCC unit riser application. This material associates an intermediate apparent density value; between the tabular alumina and fused silica ones; with low thermal conductivity and high thermal shock resistance. The better properties of the developed nano-bonded castables make them the best choice to increase the FCC unit profitability and reduce the maintenance halts.

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