Engineering the Microstructural Parameters of Erosion Resistant High Alumina Castables

V. A. A. Santos, A. P. Luz, D. T. Gomes, V. C. Pandolfelli

Different parameters (i.e., particle size distribution and packing, size and amount of coarse grains, and other features of the resulting microstructure) can affect the erosion resistance of refractory castables. In this sense, this work investigated the performance of high-alumina castable compositions containing: (i) different amounts of calcium aluminate cement (CAC) as binder, (ii) white or brown-fused alumina as coarse grains, (iii) distinct maximum particle size and distribution modulus of the formulations, and (iv) sodium borosilicate (0–5 mass-%) as a sintering additive, during erosion measurements. Besides the determination of the eroded volume of samples fired at distinct temperatures (600–1200 °C), apparent porosity and hot modulus of rupture of the designed formulations were also analysed. The obtained results indicated that the most promising evaluated composition comprised 10 mass-% of CAC as, specimens with lower cement amounts resulted in high eroded volume or even full erosion. No significant changes in the measured eroded volume could be detected for the refractory formulations containing white or brown-fused alumina aggregates and coarse grains with different particle size, as the matrix fraction (fine components) is the main area of the castables to be worn due to the SiC particles' impact. The addition of sodium borosilicate to the castables helped to improve their erosion resistance (due to the generation of a boron-rich liquid phase and its further interaction with the other available oxides), when pre-firing the samples at intermediate temperatures (800 °C, 1000 °C or 1200 °C for 5 h).

1 Introduction

Erosion of refractory materials is one of the main wearing mechanisms that can take place in industrial equipment due to the conveying of solid particles that hit the ceramic lining during service. Despite the complexity of this phenomenon (involving wide range of simultaneous attack angles, particle fragmentation, surface shielding, particle embedding effects, among others), some important advances have been carried out in recent years, resulting in products with enhanced erosion resistance [1–4]. Nevertheless, there is a lack of studies focused on investigating the influence of some specific parameters (particle size distribution, maximum particle size, type of aggregates contained in the compositions, etc.) in the overall performance of refractory castables during the erosion measurements. It is accepted that the adjustment of the particle size distribution (PSD) of refractory formulations can optimise their mechanical and rheological properties [5–8]. Moreover, the erosion resistance of such materials is directly related to mechanical/bonding strength of the castables' matrix fraction, as

the impact of the solid particles tend to: (i) wear out the fine compounds of the structure, (ii) then expose the coarse grains, and (iii) lead to the detachment of these aggregates, which increase the resulting wearing [4, 9–13].

This selective mechanism (where the aggregates stand out from the samples' surface, protecting the matrix fraction) of the refractories is also known as the "shadowing effect". Based on this model, Engman [14] suggested that the erosion resistance of heterogeneous materials should be proportional to the area of exposed matrix (fine components), whereas the wearing of coarse grains was pointed out as negligible. Fig. 1 a illustrates a simplified refractory composition with sparse grain distribution and fixed grain size and distance (2 length units) among them. Moreover, it is considered the presence of circular grains with a radius R and θ (the latter represents the angle between two coarse grains and the material's surface).

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In general, it is accepted that the erosion rate of refractories is given by the somatory of the matrix and aggregates wearing and by the loss of coarse grains. Hence, as the fine components of the microstructure are eroded, the aggregates will stand out and shadow or protect the matrix. When, in a further moment, these coarse grains are detached, the matrix area will be exposed to erosion again [9, 10, 14].

Fig. 1 b shows the relationship between cumulative wearing and wearing depth of the model material (indicated in Fig. 1 a), where different wearing rates can be observed for θ = 0°. Region A (Fig. 1 b) shows a constant rate (slope = 1) as only the refractory matrix should be eroded. B presents a decreasing slope when the coarse grains become more and more exposed to erosion, which protect the fine components. Another constant wearing rate can be detected for C region, as the aggregates act "shadowing" a fixed part of the surface. Region D represents the coarse grain loss (resulting in a vertical slope) and, after that, the wearing cycle starts all over again [14].

Therefore, according to Engman [14], erosion testing of a heterogeneous material may lead to different results depending on the region in which the measurement is taking place. Wiederhorn [9, 11] also stated that the relationship between erosion wearing and impact angle is determined by the size and distance among the largest aggregates contained in the refractory structure (Fig. 2). Considering that only the regions among the aggregates can be eroded by the impact of solid particles, this area suitable for erosion can be calculated by using Eq. 1 [9, 11].

$$A = 2\left(1 - \frac{R}{sen\ \alpha}\right) \qquad \text{(eq. 1)}$$

where, A = total area exposed to erosion (cm^2), R = largest grain size (cm) and α = impact angle. Based on this equation and considering a fixed impact angle, one can infer that the area exposed to erosion can be minimised when increasing the maximum particle size of the aggregates contained in refractory compositions. Thus, some adjustments in the particle size distribution of castable formulations might be a likely alternative to enhance their erosion resistance when in contact with solid particles [11, 12].
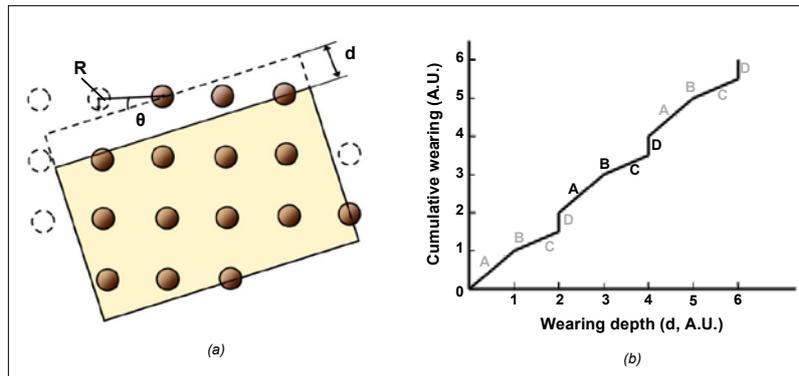

Fig. 1 a–b (a) Bidimensional model representing the initial castables' wearing according to Engman, the original sample surface is shown by the dashed line, the thick line shows the sample shape at the wearing depth d, and (b) cumulative wearing as a function of the wearing depth (d) [14] (A.U. = arbitrary unit)

This work addresses the design and evaluation of the cold erosion resistance of high-alumina refractory castables. Various parameters were analysed, such as: (i) amount of calcium aluminate cement (binder) contained in the matrix fraction, (ii) source of aggregate (white or brown-fused alumina), (iii) the maximum particle size used, (iv) its distribution modulus (q, which defines the coarse and fine components ratio contained in the compositions) of the formulations designed according Andreasen's model, and (v) the addition of sodium borosilicate (0–5 mass-%) as a sintering additive for the castables. Based on the attained results, it was pointed out the importance of a suitable particle size distribution of the compositions and how the components of the refractories' microstructure can affect their overall erosion and mechanical performance.

2 Experimental

The influence of different parameters on the erosion resistance of refractory castables were investigated in this work. Initially, six formulations based on the Andreasen's model [5, 15] (q = 0,21, Eq. 2) were designed to infer the role of the binder content on the compositions' performance. Tab. 1 shows the details of the evaluated castables, which were comprised by brown-fused alumina aggregates (D <4,75 mm, Elfusa/BR), fine aluminas (A17NE and CT3000SG, Almatis/DE) and calcium aluminate cement (CAC, Secar 71, Kerneos,/FR).

$$\frac{CPFT}{100} = \left(\frac{D}{D_{\max}}\right)^q \qquad (2)$$

where, CPFT is the cumulative percent finer than D, D is the particle size, $D_{\max}$ is the largest particle size and q is the distribution modulus [5, 15].

After adding 0,1 mass-% of the dispersant Castament FS60 (BASF/DE) to the compositions, they were dry-homogenised for 1 min and mixed for an additional 3 min in a rheometer [16]. The required water amount and attained free-flow (ASTM C860) are presented in Tab. 1. After that, prismatic samples (115 mm × 115 mm × 25 mm or 150 mm × 25 mm × 25 mm) were cast under vibration, cured at 50 °C for 24 h in an acclimatized chamber (Vötsch 202/DE) with relative humidity ~80 %, dried at 110 °C for another 24 h and fired at 600 °C or 1200 °C for 5 h.

The cold erosion resistance of the fired samples was measured according to ASTM C704 and using a NBR 13185 apparatus
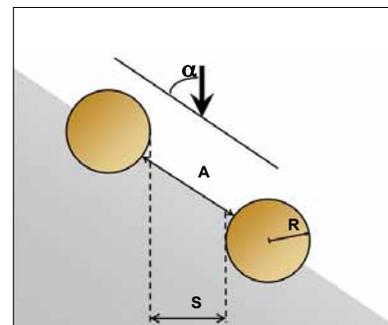

Fig. 2 Geometric representation of Wiederhorn's interpretation of the erosion wearing mechanism. By decreasing the impact angle (α) and increasing the coarse particles' radius (R), a lower matrix area (A) should be exposed to erosion; S represents the A line projection [9]

Tab. 1 General information of the designed castables' formulations containing 2–30 mass-% of Calcium Aluminate Cement (CAC)

Raw Material		Composition [mass-%]					
		2 CAC	5 CAC	10 CAC	15 CAC	20 CAC	30 CAC
Brown-fused alumina	MR <4,75 mm	62	62	62	59	55	51
	MR 200F	5	5	5	5	5	1
Fine aluminas	A17NE	25	22	19	17	17	15
	CT3000SG	6	6	4	4	3	3
Calcium aluminate cement	Secar 71	2	5	10	15	20	30
Water content [mass-%]		4,6	4,6	4,6	5,2	5,8	6,7
Measured free-flow [%]		40	55	50	45	60	60

Tab. 2 High-alumina castables' formulations containing different maximum particle size (D_{max})

Raw Material		Composition [mass-%]		
		D2,8	D4,75	D8,0
Brown-fused alumina	MR <8,0 mm	–	–	62
	MR <4,75 mm	–	62	–
	MR <2,8 mm	65	–	–
	MR 200F	2	5	5
Fine aluminas	A17NE	19	19	19
	CT3000SG	4	4	4
Calcium aluminate cement	Secar 71	10	10	10
Water content [mass-%]		5,8	4,6	4,8
Measured free-flow [%]		30	50	50

Tab. 3 Formulations designed according to the Andreasen's model and presenting distinct distribution modulus (q)

Raw Material		Composition [mass-%]		
		q0,21	q0,26	q0,31
Brown-fused alumina	MR <4,75 mm	62	67	71
	MR 200F	5	4	4
Fine aluminas	A17NE	19	16	14
	CT3000SG	4	3	1
Calcium aluminate cement	Secar 71	10	10	10
Water content [mass-%]		4,6	5,0	4,9
Measured free-flow [%]		50	40	15

(Solotest, Brazil). In this equipment, SiC erosive particles (1 kg of no. 36-grit SiC to erode specimens of 115 mm × 115 mm × 25 mm) are conveyed by air flux and hit the castable's surface placed at 90° regarding the particles flow. The material loss was expressed in terms of eroded volume (ΔV), using the following expression:

$$\Delta V = \frac{M_i - M_f}{M_{ea}} \qquad \text{(eq. 3)}$$

where, ΔV is the material volumetric loss after the test (cm³), M_i and M_f (g) are, respectively, the initial and final mass and M_{ea} is the specific apparent gravity (g/cm³) of the sample.

Additionally, apparent porosity (ASTM C380-00, using kerosene as the immersion liquid) and hot modulus of rupture (HMOR) measurements (ASTM C583) of the fired specimens were also analysed. The latter test was carried out at 600 °C and 1200 °C

in HBTS 422 equipment (3-point bending device, Netzsch/DE).

A second aspect that could affect the erosion resistance behaviour of the analysed castable, is the type of aggregate incorporated into the mixture. In this sense, instead of brown-fused alumina, an additional composition containing 10 mass-% of CAC were prepared but replacing the former aggregates by white-fused Al_2O_3 ones (D <4,75 mm, Elfusa/BR). The cold erosion measurements were carried out for samples obtained after drying (110 °C/24 h) and pre-firing (200 °C, 400 °C, 600 °C, 800 °C and 1500 °C for 5 h) steps.

The optimisation of the particle size distribution of the refractories can also be a suitable alternative to improve their erosion resistance. Based on previous studies [9, 12, 14], the erosion behaviour of castables (due to the impact of solid particles) is related to the higher wearing trend of the matrix fraction (fine components), which further exposes and favours the detachment of the coarse particles of the microstructure. Consequently, it is important to select suitable raw materials with proper particle size and adjusted packing, in order to reduce the number of pores and flaws contained in the resulting microstructure.

A further step of this study consisted in evaluating the change of the maximum particle size (D_{max}) of the brown-fused alumina aggregates contained in the self-flowing (q = 0,21, Andreasen's model) castable formulations. Tab. 2 highlights the analysed compositions, which presented D_{max} = 2,8 mm, 4,75 mm or 8,0 mm and 10 mass-% of CAC as binder.

Besides that, aiming to vary the proportion of coarse and fine particles' fraction contained in the refractories, a q = 0,21 (with higher amount of fine components), q = 0,26 (which can present adjustable rheological behaviour depending on the added water content during its preparation) and a q = 0,31 (with higher amount of coarse particles) were designed and tested (Tab. 3). The cold erosion and apparent porosity performance of the new formulations showed in Tabs. 2–3 were evaluated after pre-firing the samples at 600 °C, 800 °C, 1000 °C and 1200 °C for 5 h.

The use of a sintering additive to induce faster densification of the refractory microstructure and its effect on the samples' erosion resist-

ance were investigated in the last stage of this work. As indicated in Tab. 4, 0–5 mass-% of sodium borosilicate powder (d <45 μm, Magnesita Refratários S.A./BR) were added to the formulations containing 10 mass-% of CAC. The cold erosion, apparent porosity and HMOR measurements were carried out for the samples pre-fired at 600 °C, 800°C, 1000 °C and 1200 °C for 5 h.

3 Results and discussion

3.1 Role of different parameters on the castables' erosion resistance

3.1.1 Binder content

Keeping in mind that the matrix region should be the first area of the refractory microstructure to be eroded due to the impact of solid particles, it was decided to analyse the role of the binder additive content (2–30 mass-% of CAC) in the erosion performance of the high-alumina castables. By increasing the calcium aluminate cement amount added to the mixtures, it is expected that the higher binding strength of the fine components of the matrix fraction could induce lower wearing of the samples. Fig. 3 a–b show the cold eroded volume and apparent porosity of the designed
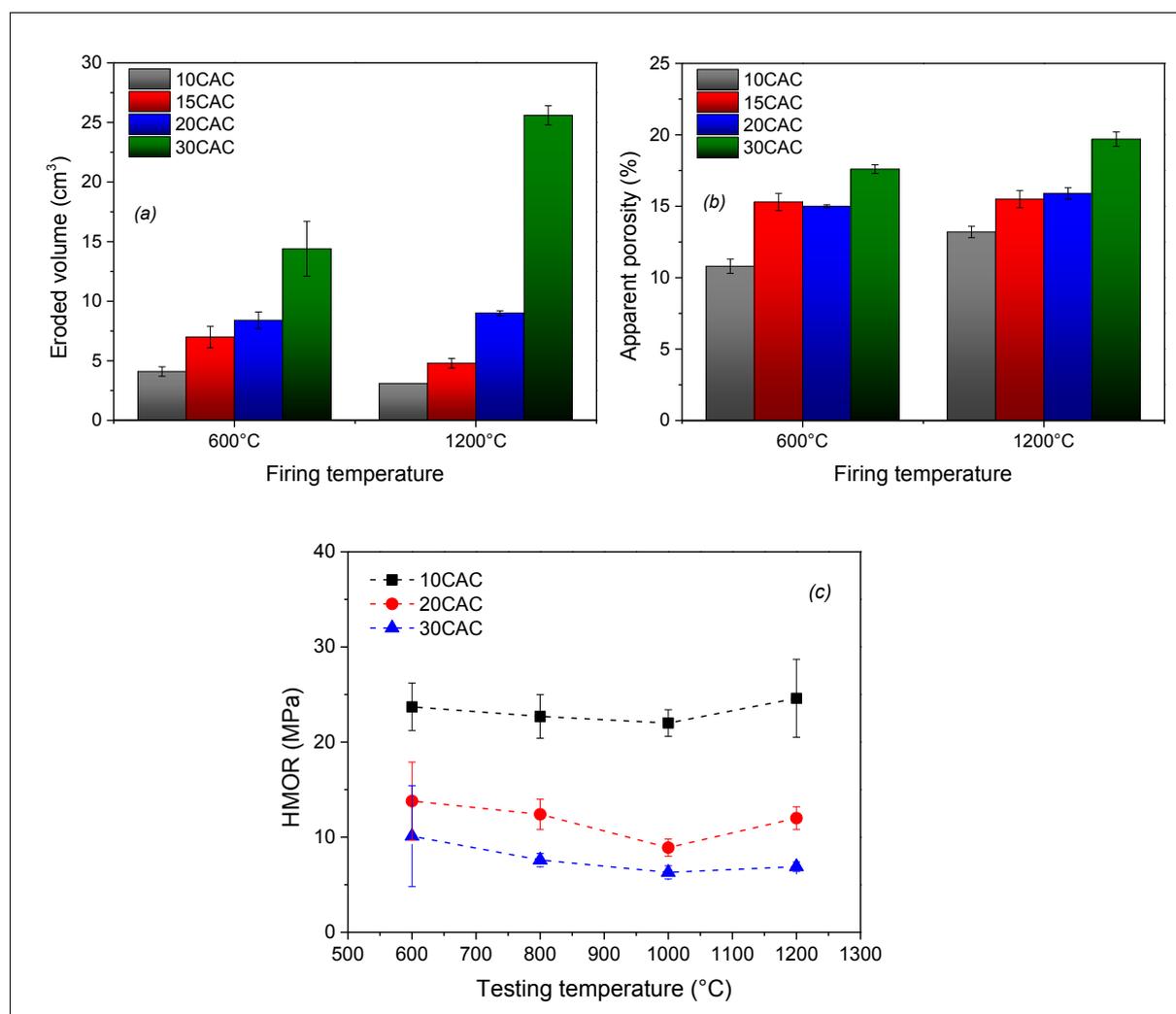
Tab. 4 Evaluated castables containing 0–5 mass-% of a sintering agent (sodium borosilicate)

Raw Material		Composition [mass-%]			
		0BS	1BS	3BS	5BS
Brown-fused alumina	MR <4,75 mm	62	62	62	62
	MR 200F	5	5	5	5
Fine aluminas	A17NE	19	18	16	14
	CT3000SG	4	4	4	4
Calcium aluminate cement	Secar 71	10	10	10	10
Sodium borosilicate	BS	–	1	3	5

Fig. 3 a–c (a) Eroded volume, (b) apparent porosity, and (c) Hot Modulus of Rupture (HMOR) of alumina-based castables containing different amounts of calcium aluminate cement (CAC, 2–30 mass-%). The samples were pre-fired at the same testing temperature for 5 h before the HMOR measurements
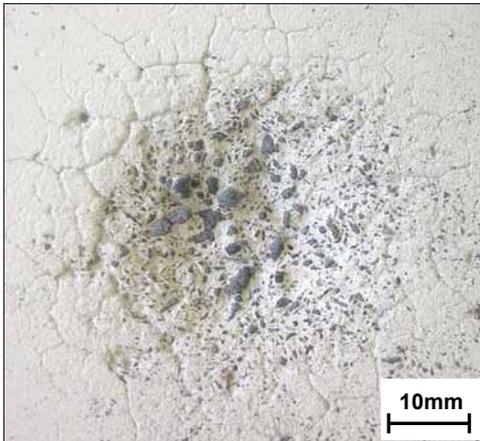
Fig. 4 Eroded sample of the castable containing 30 mass-% of CAC (binder). Crack formation as well as matrix erosion can be observed in the presented image

castables after firing at 600 °C or 1200 °C for 5 h using a heating rate of 1 °C/min. The samples containing 2 mass-% of CAC (2 CAC) and fired at 600 °C/5 h was fully eroded after the erosion tests and, for this reason, the data regarding this composition is not presented in Fig. 3. Such performance is associated with the insufficient binding effect derived from the reduced CAC content of this castable. Another aspect to be highlighted is the cement hydrates' decomposition that should take place during the first heating of the samples in the temperature range of 180–360 °C [17, 18]. After these phase transformations, further sintering and densification (with the formation of ceramics bonds) could only take

place above ~1100 °C [1]. Thus, the evaluation of castables pre-fired at 600 °C was chosen to contemplate a condition that can be found in some industrial processes (i.e., fluid catalytic cracking units, where the service temperature is lower than 815 °C [19]) and, at the same time, the CAC-containing microstructure would still be in a metastable state, as additional reactions are still expected to take place with the temperature increase.

5 CAC specimens also presented high erosion values (~9,1 ± 0,5 cm³) after firing at 600 °C/5 h and they were not evaluated for erosion, apparent porosity and HMOR in the following steps.

When testing the prepared samples after firing at 600 °C or 1200 °C for 5 h, the CAC content increase from 10–30 mass-% in the formulations led to lower erosion resistance values (Fig. 3 a). Although the higher amount of binder can induce greater binding effect among coarse and fine components, resulting in a more cohesive microstructure, a drawback observed during the preparation of the compositions with 15–30 mass-% of CAC was the higher water demand required for obtaining mixtures with suitable flowability behaviour. As pointed out in Tab. 1, for instance, a total of 6,7 mass-% (instead of 4,6 mass-% for 10 CAC) of distilled water was used during the processing step of 30 CAC composition. Consequently, after the decomposition of the hydrated phases during the thermal treatment at 600 °C/5 h, higher apparent porosity results could be obtained for the

15 CAC, 20 CAC and 30 CAC castables (Fig. 3 b). Even when firing the samples at 1200 °C (allowing the beginning of the sintering process of the refractory microstructure), the same trend detected for the materials pre-fired at 600 °C was still observed.

Moreover, all compositions were comprised approximately by 40 vol.-% of fine components (matrix fraction) and, with the CAC content increase in the formulations, other raw materials had to be replaced by the cement. Such changes also help to increase the deviation of the calculated particle size distribution curves of the 15–30 mass-% of CAC formulations with the theoretical one predicted by the Andreasen's model (q = 0,21, D_{max} = 4,75 mm). Therefore, the presence of flaws and pores in the CAC-rich (15–30 mass-%) compositions (derived from packing issues and higher water demand) favoured a more pronounced wearing of these specimens when in contact with SiC particles. For instance, Fig. 4 shows a photo of a 30 CAC sample pre-fired at 1200 °C/5 h after the erosion test, which points out the matrix wearing and crack formation on the castable's surface. When analysing the results presented in Fig. 3 a and 3 b, the best erosion resistance and lower apparent porosity values was detected for the 10 CAC formulation, which resulted in suitable binding among the matrix components and lower flaws content in the resulting microstructure.

The hot modulus of rupture of the 10 CAC, 20 CAC and 30 CAC castables measured at 600, 800, 1000 and 1200 °C also highlighted the improved performance of the composition containing 10 mass-% of CAC (Fig. 3 c). Thus, this amount of binder was selected to be used in the following tests of this work.

3.1.2 Source of aggregates (white or brown-fused alumina)

The comparison of two castable compositions containing 10 mass-% of calcium aluminate cement (CAC) and white or brown-fused alumina aggregates were carried out for samples obtained after drying at 110 °C/24 h and firing at 200 °C, 400 °C, 600 °C, 800 °C and 1500 °C for 5 h. Fig. 5 shows the eroded volume measured for the prepared castables with distinct coarse grains.
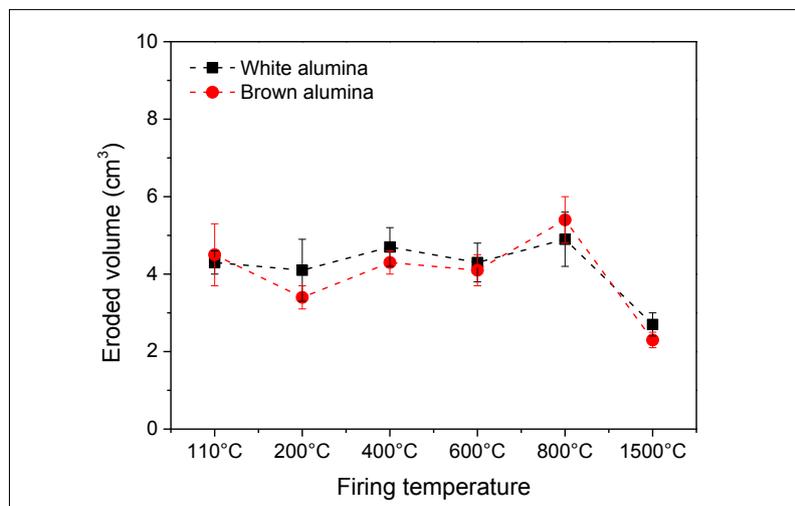

Fig. 5 Eroded volume of castable compositions containing 10 mass-% of CAC and different aggregates (white or brown-fused alumina)
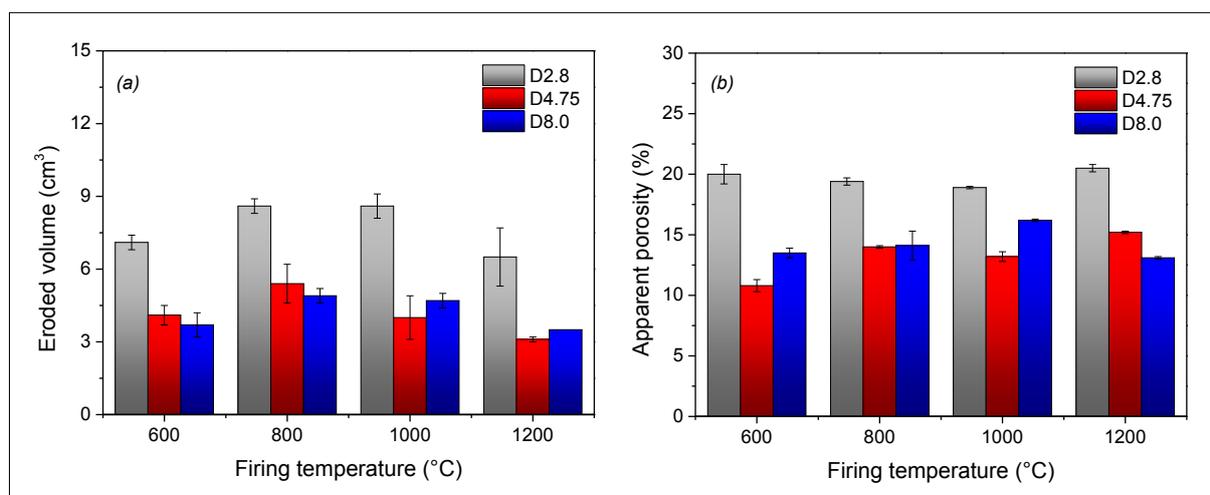
Fig. 6 a–b (a) Eroded volume and (b) apparent porosity of alumina-based castables containing 10 mass-% of CAC and different maximum particle size (D_{max} = 2,8 mm, 4,75 mm or 8,0 mm, respectively)

Despite the different apparent porosity level of the coarse alumina grains (white = 7,0 % and brown = 2,5 %), the overall pores content of the both castable samples were very similar ~6,8–6,9 % after firing at 1500 °C/5 h. As previously mentioned, the matrix wearing tends to expose the aggregates and induce their detachment of the refractory surface. However, as the fine components of the two evaluated compositions were the same, no major changes of the overall erosion resistance could be observed for the castables prepared with brown or white-fused alumina (Fig. 5).

3.1.3 Largest particle size (D_{max} = 2,8 mm, 4,75 mm or 8,0 mm) of the aggregates

In order to analyse the role of the aggregate size of the compositions on the erosion resistance of the castables, three formulations based on brown-fused alumina with different D_{max} (2,8 mm, 4,75 mm or 8,0 mm) and containing 10 mass-% of calcium aluminate cement (Tab. 2) were evaluated after a pre-firing step of the samples at 600 °C, 800 °C, 1000 °C and 1200 °C for 5 h.

Fig. 6 shows the eroded volume of the prepared refractories for each evaluated condition. As the composition with the lowest D_{max} (D2,8) presented higher surface area, it was required larger water content during its mixing to attain the desired flowability level (Tab. 2). Consequently, D2,8 specimens showed lower erosion resistance after drying and firing steps in the 600–1200 °C

range (Fig. 6 a), due to the greater amount of flaws and pores (Fig. 6 b) formed in the resulting microstructure (which is associated with the free-water release, cement hydrates decomposition and sintering reactions).

On the other hand, few changes in the eroded volume of the D4,75 and D8,0 castables could be observed in Fig. 6 a, as all attained data seem to be in a similar range when comparing the calculated deviation values. Regarding the apparent porosity results (Fig. 6 b), 4,8 mass-% instead of 4,6 mass-% of water was used during the preparation of the D8,0 and D4,75 samples, respectively. This small difference might be responsible for the slightly higher pores content of the refractory containing larger aggregates. Furthermore, the "shadow effect" of the coarser grains should be more significant in the D4,75 and D8,0 compositions, which most likely also favoured the better performance of these refractories when compared to D2,8.

3.1.4 Distribution modulus (q) of the formulations based on Andreasen's model

Due to the good performance of D4,75 composition (as presented above), it was decided to keep the largest particle size as 4,75 mm for the following designed formulations, but their coarse and fine components ratio was changed. In order to do that, the distribution modulus (q, Eq. 1) in the Andreasen's packing model was modified to values equivalent to 0,21 (com-

monly used for obtaining a self-flowing mix with higher amount of fine materials), 0,26 (multifunctional composition, as it can present adjustable rheological behaviour depending on the added water content during its preparation) and 0,31 (for vibratable formulation, presenting higher amount of coarse particles) [5, 15]. More details of these formulations can be found in Tab. 3.

The different matrix-aggregate ratios of the tested castables resulted in distinct erosion resistance, as pointed out in Fig. 7 a. The main observed trend indicated that the lower the aggregates content (<q), the lower the eroded volume of the castables will be in all evaluated condition (after firing the samples in the 600–1200 °C range). Keeping in mind that the fine components of the matrix should be the first fraction of the refractory structure to be eroded by the SiC particles, one may ask "why did the castable with higher matrix content presented better performance in the evaluated tests?" In fact, the presence of larger amount of aggregates in the q0,26 and q0,31 compositions play an important role in the overall packing of the samples. As highlighted in Fig. 8, the non-organised arrangement of fine particles at the region close to a much larger aggregate may result in uneven packing and gaps after thermal treatment. This so-called "wall effect" would be responsible for generating a thick porous zone (also known as interfacial transition zone – ITZ) closer to the coarse grain surface, which could be at least as big as the size of the largest matrix particles [20–23].
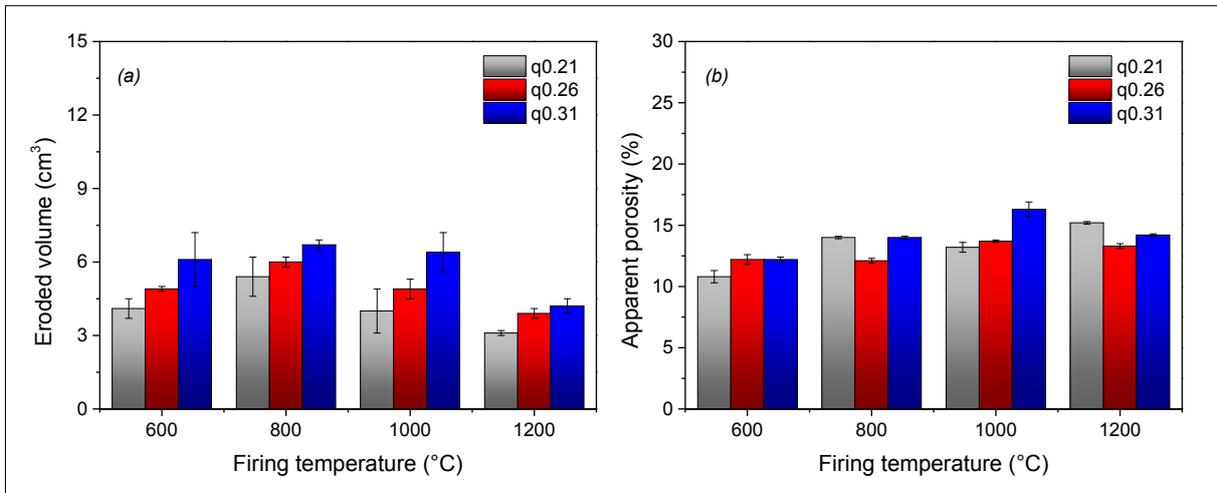
Fig. 7 a—b (a) Eroded volume, and (b) apparent porosity of alumina-based castables containing 10 mass-% of CAC and different Alfred's packing coefficient (q = 0,21, 0,26 or 0,31)
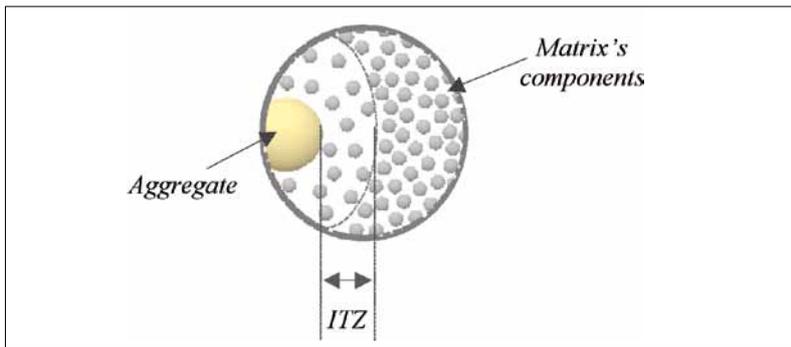

Fig. 8 Sketch of the interfacial transition zone (ITZ) near the aggregate's surface, which corresponds to an area with lower packing density in the refractory structure [23]

The distribution modulus (q) increase leads to castables with higher aggregates content (Tab. 3) and favours the formation of thicker ITZ at the coarse-fine components interfaces. Consequently, the overall apparent porosity level of the q 0,31 samples was,
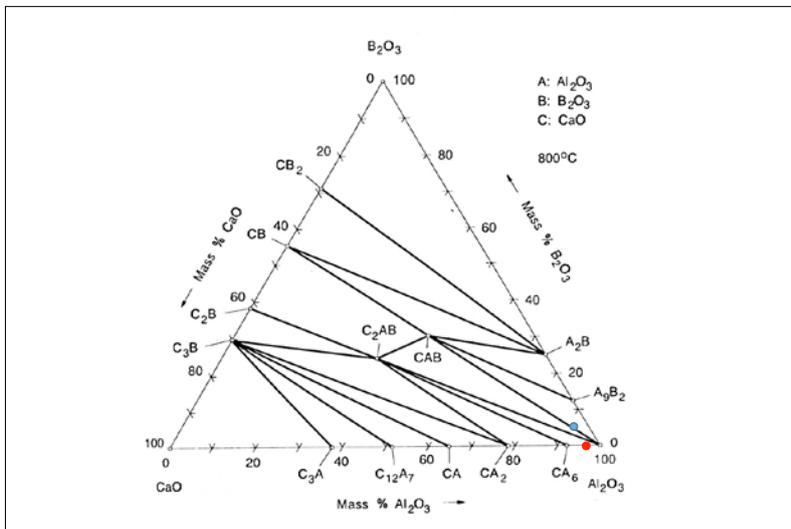
in general, the highest one when compared to the other evaluated materials (Fig. 7 b). Moreover, despite the reduced spaces among the largest aggregates contained in the q0,31 structure (which should enhance the erosion resistance of the castable), this "wall-effect" might be affecting in a greater extent the erosion and mechanical performance of such systems.

3.1.5 Addition of a sintering additive (sodium borosilicate) to the compositions

Aiming to find an alternative to induce faster sintering of CAC-bonded compositions and, therefore, optimise the erosion resistance of such refractories at intermediate temperature (600–1200 °C), 4 new formulations comprising 0–5 mass-% of sodium borosilicate (sintering agent, Tab. 4) were analysed.

According to previous studies [1, 19, 24], the addition of sodium borosilicate to high-alumina castables induce the formation of a B-rich liquid phase during the samples' firing treatment (above 650 °C), which should then speed up the reaction with Al_2O_3 and CaO (derived from CAC) in the matrix fraction of the compositions. The interaction of such oxides can lead to the formation of two ternary compounds $CaO \cdot Al_2O_3 \cdot B_2O_3$ (CAB) and $2CaO \cdot Al_2O_3 \cdot B_2O_3$ (C_2AB, Fig. 9), but they should melt incongruently at 1015 °C and 800 °C, respectively, giving rise to solid and liquid phases (eq. 4–5) [25, 26]. The reaction of Al_2O_3, CaO, SiO_2 and Na_2O (provided by the sintering agent)

Fig. 9 Isothermal section of the Al_2O_3–B_2O_3–CaO system at 800 °C [27]. Red and blue circles represent the 0BS and 5BS castables, respectively

in the refractories matrix fraction might also favour the generation of compounds with low melting point.

$$CaO \cdot Al_2O_3 \cdot B_2O_3 \rightarrow 9\,Al_2O_3 \cdot B_2O_3 + liquid \quad (eq.\ 4)$$

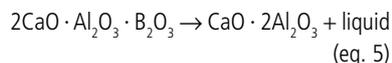$$2CaO \cdot Al_2O_3 \cdot B_2O_3 \rightarrow CaO \cdot 2Al_2O_3 + liquid \quad (eq.\ 5)$$
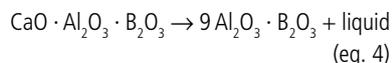
Fig. 10 shows the eroded volume, apparent porosity and hot modulus of rupture of boron-containing castables after pre-firing the samples at 600 °C, 800 °C, 1000 °C and 1200 °C for 5 h. As expected, the action of the selected sintering additive could be identified above 600 °C, resulting in higher erosion resistance (Fig. 10 a) for the BS-containing materials when compared to the reference composition (0 BS). Such performance is associated with the formation of ternary phases (CAB and C_2AB) as well as metastable aluminium borates [$AlBO_3$,

Al_2BO_4 and $Al_5(BO_3)O_6$] in the fired microstructure of the samples exposed to the 600–1000 °C temperature range [25, 28]. As the erosion measurements were carried out at room temperature, no further change in the obtained eroded volume could be observed when treating the 1 BS, 3 BS and 5 BS castables at 1200 °C for 5 h, which should induce the generation of liquid phase in the structure of these at high temperature. The apparent porosity values (Fig. 10 b) of the BS-containing samples were in tune with their erosion behaviour, because a drop of the pores content was followed by the increase of the erosion resistance after firing such materials between 800–1200 °C for 5 h. Nevertheless, the drawback related to the use of a boron-containing additive is the liquid formation in the castables' samples during the hot mechanical measurements. Thus, the decomposition of the intermediate compounds (aluminium borates and ternary phases) affected the refractoriness

and HMOR values of the 5 BS compositions at 1000 °C and 1200 °C (Fig. 10 c).

Based on the obtained results, the use of sodium borosilicate can be a suitable additive to improve the erosion resistance of the calcium aluminate cement-bonded refractory castables at intermediate temperatures, where such materials usually present higher porosity levels (derived from the decomposition of the CAC hydrates). However, due to the boron-rich liquid phase formation at high temperatures (>800 °C), it is required to select the proper amount and sort of sintering additive for each refractory system to prevent some drawbacks to its thermomechanical behaviour.

4 Conclusions

This study evaluated various parameters that can influence the erosion resistance of refractory castables. Based on the obtained results, the following aspects can be pointed out:
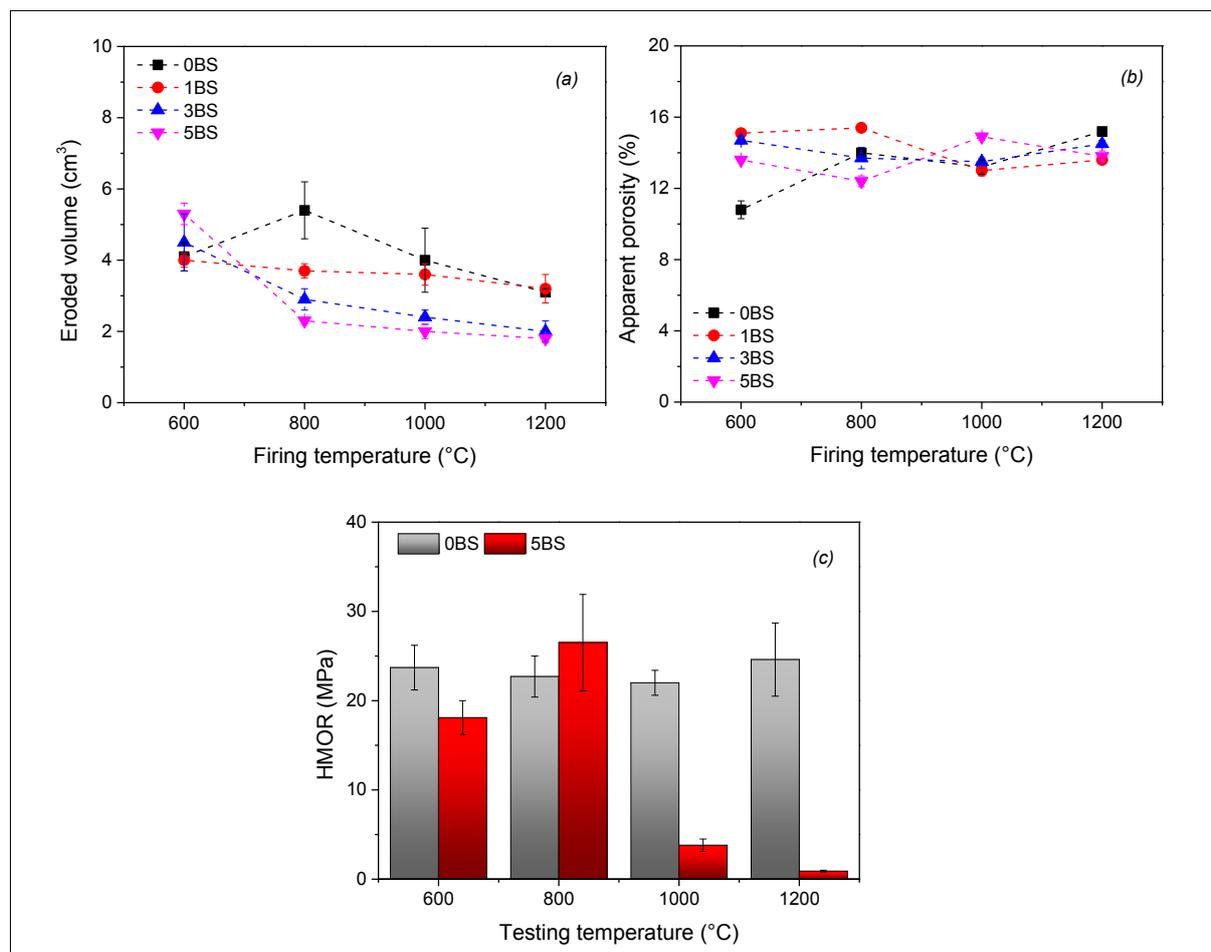

Fig. 10 a–c (a) Eroded volume, (b) apparent porosity, and (c) Hot Modulus of Rupture (HMOR) of brown-fused alumina-based castables containing 10 mass-% of CAC and different amounts of sodium borosilicate (BS, 0–5 mass-%)

• By increasing the binder (CAC) content of the designed compositions, it was required the use of larger amounts of water during their mixing step to obtain suitable free-flow levels. Consequently, the specimens of the formulations with CAC content higher than 15 mass-% presented more pores and flaws in their structure due to the cement hydrates decomposition during the pre-firing treatments (600 °C and 1200 °C for 5 h) before the cold erosion measurements. The most promising composition comprised 10 mass-% of the selected binder and, specimens with lower CAC amounts resulted in high eroded volume or even full erosion, whereas greater cement contents (15–30 mass-%) also led to materials with lower erosion resistance.

• As the matrix fraction (fine components) is the main area of the castables to be worn due to the SiC particles' impact during the erosion tests, no significant changes in the measured eroded volume could be detected for the refractory formulations containing white or brown-fused alumina aggregates and coarse grains with different particle size (D_{max} = 2,8 mm, 4,75 mm or 8,0 mm).

• By keeping the largest particle size of the castables as 4,75 mm and then changing their matrix-aggregate ratio (Andreasen's distribution modulus, q = 0,21, 0,26 or 0,31), it was verified that the best erosion resistance was attained for the mixture with higher content of fine particles (q = 0,21). Such behaviour is related to the so called "wall effect", where a thick porous zone (also known as interfacial transition zone – ITZ) were likely formed closer to the coarse grain surface of the refractories that contained higher amount of aggregates (i.e., q = 0,26 and 0,31).

• The addition of a sintering agent (sodium borosilicate) to the evaluated compositions helped to improve their erosion resistance (due to the generation of a boron-rich liquid phase and its further interaction with the other available oxides), when pre-firing the samples at intermediate temperatures (800 °C, 1000 °C or 1200 °C for 5 h). However, care must be taken when using such additive, as the liquid formation in such materials affected the hot mechanical properties of the alumina-based castables above 800 °C.

5 Acknowledgements

References

[1] Luz, A.P.; et al.: High-alumina boron-containing refractory castables. Int. J. Appl. Ceram. Technol. (2014). doi:10.1111/ijac.12310

[2] Braulio, M.A.L.; et al.: Nano-bonded wide temperature range designed refractory castables. J. Amer. Ceram. Soc. **95** (2012) 1100–1104. doi:10.1111/j.1551-2916.2011.05053.x

[3] Luz, A.P.; et al.: Monoaluminum phosphate-bonded refractory castables for petrochemical application. Ceram. Int. **42** (2016) 8331–8337. doi:10.1016/j.ceramint.2016.02.047

[4] Wiederhorn, S.; Roberts, D.E.: A technique to investigate high temperature erosion of refractories. Ceram. Bull. **55** (1976) 185–189

[5] Myhre, B.; Hundere, A.M.: The use of particle size distribution in the development of refractory castables. Proc. of XXV Alafar Congr., San Carlos de Bariloche, Argentina, 1996, 1–4

[6] Myhre, B.: The effect of particle size distribution on flow of refractory castables. Proc. of 30th Ann. Refract.. Symp., St Louis, USA, 1994, 1–17

[7] Studart, A.R.; et al.: High-alumina multifunctional refractory castables. Amer. Ceram. Soc. Bull. **80** (2001) 34–40

[8] Ismael, M.R.; Salomão, R.; Pandolfelli, V.C.: Colloidal silica bonded refractory castables: optimization of the particle size distribution. Refractory Appl. News. **13** (2008) 10–15

[9] Wiederhorn, S.: Erosion of castable refractories. Refract. Appl. **2** (1997) 2–6

[10] Ritter, J.E.; Rosenfeld, L.; Jakus, K.: Erosion and strength degradation in alumina. Wear **111** (1986) 335–346

[11] Wiederhorn, S.; Hockey, B.J.: Effect of material parameters on the erosion resistance of brittle materials. J. Mater. Sci. (1983) 766–780

[12] Crowley, M.S.: The influence of particle size on the erosion resistance of refractory concretes. Amer. Ceram. Soc. Bull. **48** (1969) 707–710

[13] Prestes, E.; et al.: Hot-erosion of nano-bonded refractory castables for petrochemical industries. Ceram. Int. **39** (2013) 2611–2617

[14] Engman, U.: Erosion testing of refractories – a new testing procedure Wear **186–187** (1995) 215–223

[15] Luz, A.P.; Pandolfelli, V.C.; Braulio, M.A.L.: Particle size distribution and packing desing. Refractory Castable Engineering. Baden-Baden 2015, 91–155

[16] Pileggi, R.G.; et al.: Novel rheometer for refractory castables. Amer. Ceram. Soc. Bull. **79** (2000) 54–58

[17] Luz, A.P.; Borba, N.Z.; Pandolfelli, V.C.: Mechanical strength and hydrate products evolution of calcium aluminate cement for endodontic applications. Ceramica **60** (2014) 192–198. doi:10.1590/S0366-69132014000200005 (In Portuguese)

[18] Lee, W.E.; et al.: Castable refractory concretes. Int. Mater. Rev. **46** (2001) 145–167. doi:10.1179/095066001101528439

[19] Luz, A.P.; et al.: Mullite-based refractory castable engineering for the petrochemical industry. Ceram. Int. **39** (2013) 9063–9070. doi:10.1016/j.ceramint.2013.05.001

[20] Scrivener, K.L.; Nemati, K.M.: The percolation of pore space in the cement paste/aggregate interfacial zone of concrete. Cem. Concr. Res. **26** (1996) 35–40

[21] Roy, D.M.; Scheetz, B.E.; Silbee, M.R.: Processing of optimised cements and concretes via particle packing. MRS Bull. **18** (1993) 45–49.

[22] Luz, A.P.; Braulio, M.A.L.; Pandolfelli, V.C.: Refractory Castable Engineering. Baden-Baden 2015, 91–149

[23] Oliveira, I.R.; et al.: Dispersion and particles packing – principles and applications in ceramics processing. Fazendo Arte Editorial, São Paulo, 2000, 119–137 (in Portuguese)

[24] Maizo, I.D.G.; et al.: Boron sources as sintering additives for alumina-based refractory castables. Ceram. Int. **43** (2017) 10207–10216. doi:10.1016/j.ceramint.2017.05.047

[25] Swamy, V.; Jung, I.H.; Decterov, S.A.: Thermodynamic modeling of the Al_2O_3–B_2O_3–SiO_2 system. J. Non. Cryst. Solids. **355** (2009) 1679–1686. doi:10.1016/j.jnoncrysol.2009.06.036

[26] Schafer, U.L.; Kuzel, H.I.: Neues Jahrbuch für Mineralogie, Monatshefte, **4–5** (1967) 131

[27] V.D. Eisenhüttenleute, Slag Atlas, 2nd Ed., Düsseldorf 1995, 99

[28] Gielisse, P.J.; Foster, W.R.: The system Al_2O_3–B_2O_3. Nature **195** (1962) 69–70