



Al₂O₃-based binders for corrosion resistance optimization of Al₂O₃–MgAl₂O₄ and Al₂O₃–MgO refractory castables

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Abstract

This work addresses the main aspects related to the use of alternative binders [hydratable (HA) or colloidal alumina (ColAlu)] in castables containing different spinel sources (pre-formed or *in situ* generated), in order to point out: (i) the features that control the corrosion behavior of these materials, and (ii) the key factors to better select a refractory composition. Thermodynamic calculations, corrosion cup-test and SEM analyses were carried out in order to evaluate the slag attack of the designed refractory compositions. According to the attained results, the alumina-based binders (HA or ColAlu) induced a more effective sintering process due to their high specific surface area, improving the physical properties and the binding level of the generated microstructure. The spinel grain size also played an important role in the corrosion behavior of these refractories, as the finer the particles, the greater their dissolution was into the molten liquid, leading to further precipitation of spinel in the solid–liquid interface as a continuous and thick layer. Among the evaluated compositions and considering the presence of silica fume, the most suitable formulation with optimized corrosion resistance was the one with *in situ* spinel generation and HA as a binder.

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1. Introduction

Calcium aluminate cement (CAC) is the most used binder in Al₂O₃–MgO refractory castable formulations due to its ability to give rise to materials with improved green mechanical resistance in a relative short period of time (~24 h) and provide calcium hexaluminate (CA₆) generation after heating [1]. This latter compound is formed by the reactions among the components derived from the cement and alumina sources added to the refractory, resulting in platelet crystals with a high aspect ratio that enhance the overall thermo-mechanical behavior of the designed products [2]. Nevertheless, the volumetric expansion related to the CA₆ formation might induce marked crack generation during the first thermal treatment of high-alumina cement-bonded castables, resulting

in a reduction of the mechanical and slag penetration resistances. Besides that, the molten slag penetration and the wear of such refractories at high temperatures are directly associated with the physical features and location of the CA₆ phase in the microstructure [3,4]. As reported in previous works [5,6], the distribution/scattering and the shape of the calcium hexaluminate grains are affected by the presence of other raw materials (*i.e.*, silica fume) contained in the compositions.

In addition to CAC, another binder, commonly used in systems where the presence of CaO is not desirable [7,8], is the hydratable alumina (HA). Despite some drawbacks (*i.e.*, high thermal spalling/explosion risk during the drying stage of the refractory lining, *etc.*), Al₂O₃–MgO castables (with *in situ* spinel formation) bonded with HA presented higher corrosion resistance when in contact with industrial slags [7,9]. This result was mainly associated to the lower apparent porosity and smaller pore size in the microstructure of these refractories [9]. These features were most likely influenced by the high specific surface area of the hydratable alumina, which induced major

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densification of the material during the sintering process [8], closing some pores and reducing the number of potential channels for further liquid infiltration. Additionally, the higher amount of Al₂O₃ in the HA-containing castable matrix also favored the slag saturation and inhibited the chemical attack of the coarse tabular alumina grains [10].

Over the last decade, a new generation of binders for refractory castables (called “nanostructured”, where colloidal alumina has received some attention) has been commercialized as an alternative to the traditional ones [11,12]. These alumina transition particles with nanometric sizes are dispersed and supplied as aqueous suspensions comprising up to 60 wt% of solids [11], favoring their addition to the refractory mixtures in relative high amounts and without a marked increase of the total water content required for their processing.

Sako and colleagues [13] reported the higher corrosion resistance of pre-formed spinel-containing castables bonded with colloidal alumina when compared to those with CAC or HA. Based on this investigation, a similar corrosion mechanism for formulations with distinct binders was proposed, highlighting the effective CA₆ formation after the slag–refractory interaction due to the high availability of alumina in these materials. The differences in the slag penetration in the evaluated castables were related to the changes in the sintering level, porosity and pore size of the formed microstructure. Nevertheless, regarding the sample's penetration profile, the overall behavior of the HA-containing formulation was better than the one with CAC, whereas similar wearing was observed for both refractories. These results are in agreement with the studies carried out by Braulio et al. [9] and Luz and colleagues [10]; but, in these cases, the use of hydratable alumina in castables with the *in situ* spinel generation resulted in a more significant improvement of the corrosion resistance, when compared to the materials bonded with CAC.

Based on that, the objective of this work is to explain the main aspects related to the use of alternative binders in castables containing different spinel sources (pre-formed or *in situ* generated), in order to point out: (i) the factors that control the corrosion behavior of these materials, and (ii) the fundamentals for an optimized selection of a refractory composition. In this sense, using thermodynamic calculations enabled us to predict the effect of the chemical composition of the matrix fraction and coarse aggregates on the corrosion behavior of the designed refractory castables.

2. Experimental and thermodynamic calculations

2.1. Materials and methods

The corrosion behavior of five castable compositions (shown in Table 1) containing different spinel sources [pre-formed=PF (AR78, 78 wt% of alumina, Almatiss, Germany) and *in situ* generated=IS (addition of dead-burnt MgO, $d < 45 \mu\text{m}$, C/S=0.37, Magnesita Refratários S.A., Brazil)] and 1 wt% of silica fume (971U, Elkem, Norway) were evaluated. Each mixture comprised 6 wt% of calcium aluminate cement (CAC, Secar 71, Kerneos, France) or hydratable

Table 1
Composition of the evaluated refractory castables.

Raw materials (wt%)	PF			IS	
	CAC	HA	ColAlu	CAC	HA
Tabular alumina ($6 \text{ mm} \leq d \leq 0.2 \text{ mm}$)	72	72	78	80	80
Reactive alumina	–	–	–	7	7
Sintered spinel ($d \leq 0.5 \text{ mm}$)	21	21	21	–	–
Sintered magnesia ($d < 45 \mu\text{m}$)	–	–	–	6	6
Silica fume	1	1	1	1	1
CAC	6	–	–	6	–
Hydratable alumina	–	6	–	–	6
Colloidal alumina suspension	–	–	6	–	–
Total water content	4.4	4.6	6.0	4.1	5.3

Table 2
Chemical composition of the evaluated slag.

Oxides	Al ₂ O ₃	MgO	CaO	SiO ₂	MnO	FeO _x	P ₂ O ₅	TiO ₂	Cr ₂ O ₃	SO ₃
wt%	1.6	8.5	34.2	8.7	4.1	40.8	1.4	0.4	0.2	0.1

alumina (HA, Alfabond 300, Almatiss, USA). A suspension of colloidal alumina (50 wt% of solids, ColAlu, VP Disp 650 ZXP, Evonik Degussa GmbH, Germany) was only added to the pre-formed spinel-containing castable.

The experimental conditions used in the processing, curing and firing steps for the castable samples' preparation have been reported elsewhere [9,10,13]. The corrosion behavior of these materials was evaluated *via* cup-tests using an iron-rich industrial basic slag (CaO/SiO₂=3.9) as a reactant, whose composition is presented in Table 2. For the pre-formed spinel-containing castables bonded with CAC (PF-CAC), HA (PF-HA) or colloidal alumina (PF-ColAlu), 50 mm × 50 mm cylindrical samples with 20 mm diameter × 25 mm depth internal hole were prepared and evaluated after adding 10 g of slag (powder) [13]. The measurements were carried out at 1500 °C for 2 h in air and the obtained results were previously reported [13]. Additionally, castables based on *in situ* spinel formation and with CAC (IS-CAC) or HA (IS-HA) as binders (previously cured at 50 °C for 24 h, dried at 110 °C for 24 h and fired at 1550 °C for 5 h) were tested at 1550 °C for 2 h in air, using cylindrical samples ($h = 100 \text{ mm}$ and $d = 90 \text{ mm}$) with 50 mm internal diameter and depth hole, after incorporating 150 g of the selected slag.

For both groups of castables, PF and IS, the liquid penetration and the sample wearing were determined by inspecting the cross-section area of the corroded samples. After that, the slag–refractory interface was analyzed *via* SEM (FEI Inspect S50, USA) and EDS techniques.

2.2. Thermodynamic simulations

The phases predicted to be formed during the slag–castable interaction in an equilibrium condition at 1500 °C and 1550 °C were calculated for the designed refractories containing pre-formed or *in situ* spinel generation, according to the method

proposed by Luz and colleagues [10,14] and using the commercial software FactSageTM. The corrosion behavior of the IS-CAC and IS-HA formulations has already been simulated using this methodology, but a different assumption for the matrix components was considered and a previous version of the software was used. Additionally, the results of these calculations [10,14] were compared with the experimental data obtained in different conditions to the ones reported in this work.

The castable corrosion simulation method consisted of: (1) evaluating the contact between the slag and the matrix, after liquid saturation, and (2) analyzing the interaction between the resulting liquid and the aggregates. Although these simulations can overestimate the matrix role in the refractory wearing process, this model describes more accurately the phase transformations when compared to calculations based on the overall components (fine and coarse ones) of the castable formulation [10].

Hence, firstly the reaction of 100 g of slag and 100 g of the castable matrix was simulated and the resulting liquid of each step was successively placed in contact with the original matrix [10,14], until the slag saturation was reached (see Fig. 1). After that, 100 g of the resulting slag (liquid saturated with the matrix components) was used in the simulations involving 100 g of the aggregates and with the same procedure applied in the first part of the calculations.

In order to define the matrix and the aggregate compositions for the thermodynamic studies (Table 3): (a) the particle size of the raw materials in the refractory formulations, considering that the matrix fraction comprised components with $d < 200 \mu\text{m}$ [16], and (b) the content and distribution of phases (CA_6) observed in the microstructure of the castables fired at 1500°C for 5 h (obtained *via* quantitative X-ray diffraction and SEM/EDS analyses), were considered. The phases predicted to be found in the equilibrium condition in the matrix and aggregate fractions were calculated according to the temperature selected for the corrosion tests, 1500°C (PF) or 1550°C (IS), in order to attain a reference of the amount of each phase derived from the interaction of the castable components (without the reaction with the molten slag), before the corrosion process.

Thermodynamic simulations were carried out using FactSage software [version 6.3.1, Thermfact/CRCT (Montreal) and GTT-Technologies (Aachen)], which comprises a series of modules that access and cross link thermodynamic databases and allow for various calculations. For this study, the

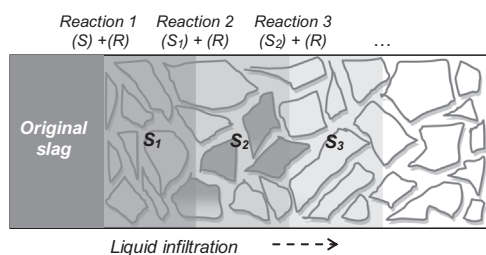


Fig. 1. Sketch of the liquid composition changes and the calculation steps carried out during the liquid+refractory interactions.

Table 3

Composition of the castables' matrix and aggregates used for the thermodynamic calculations.

	Oxides	Content (wt%)				
		PF-CAC	PF-HA	PF-ColAlu	IS-CAC	IS-HA
Matrix	Al_2O_3	31.12	27.88	31.88	29.20	31.00
	CaO	1.76	–	–	0.44	–
	SiO_2	1.00	1.00	1.00	1.00	1.00
	MgO	4.62	4.62	4.62	6.00	6.00
Aggregates	Al_2O_3	60.12	65.12	61.11	62.00	62.00
	CaO	–	–	–	1.32	–
	MgO	1.38	1.38	1.38	–	–

following databases: FactPS, SGTE and FToxid, and the Equilib, Viscosity and Reaction moduli were selected.

3. Results and discussion

3.1. Pre-formed (PF) spinel-containing castables

The main results of the physical characterization and corrosion resistance of the pre-formed spinel containing castables with CAC, HA or ColAlu as binders are summarized in Table 4 [13]. Based on the analysis of the corroded profile of the samples, composition PF-CAC presented the lowest chemical resistance to the attack of the selected slag, whereas the nano-bonded material (PF-ColAlu) showed the best performance.

Fig. 2 shows the SEM images of the slag–refractory interface after the corrosion cup tests [13], where the chemical reaction of the molten liquid with the coarse tabular alumina (TA) grains is highlighted, as well as the generation of CA_6 phase with a high aspect ratio. A more detailed analysis of the texture of this latter compound also indicated that there are some differences when comparing the calcium hexaluminate grains contained in the three evaluated castables, as described below.

For castable PF-HA, although some damage was observed in the region near the corroded interface, the CA_6 grains showed preferential orientation (forming “clusters”) with higher packing density, and the available pores were mostly filled in by a second phase. It must be pointed out that there was still a high porosity in some areas among the calcium hexaluminate grains, with similar features to the ones detected for PF-CAC, however the overall pore content in the castable bonded with HA was lower. For the samples containing colloidal alumina (Fig. 2, PF-ColAlu), the CA_6 crystals showed a higher level of preferential orientation, coating the border of the tabular alumina aggregates and giving rise to a dense and protective layer (thickness $\sim 80 \mu\text{m}$).

Due to the absence of CA_6 in the fired microstructure (before corrosion) of the PF-HA and PF-ColAlu, Sako and colleagues [13] stated that the calcium hexaluminate generation should be related to the $\text{Al}_2\text{O}_3(\text{l})$ and $\text{CaO}(\text{l})$ reaction, considering the negative ΔG value of this transformation at

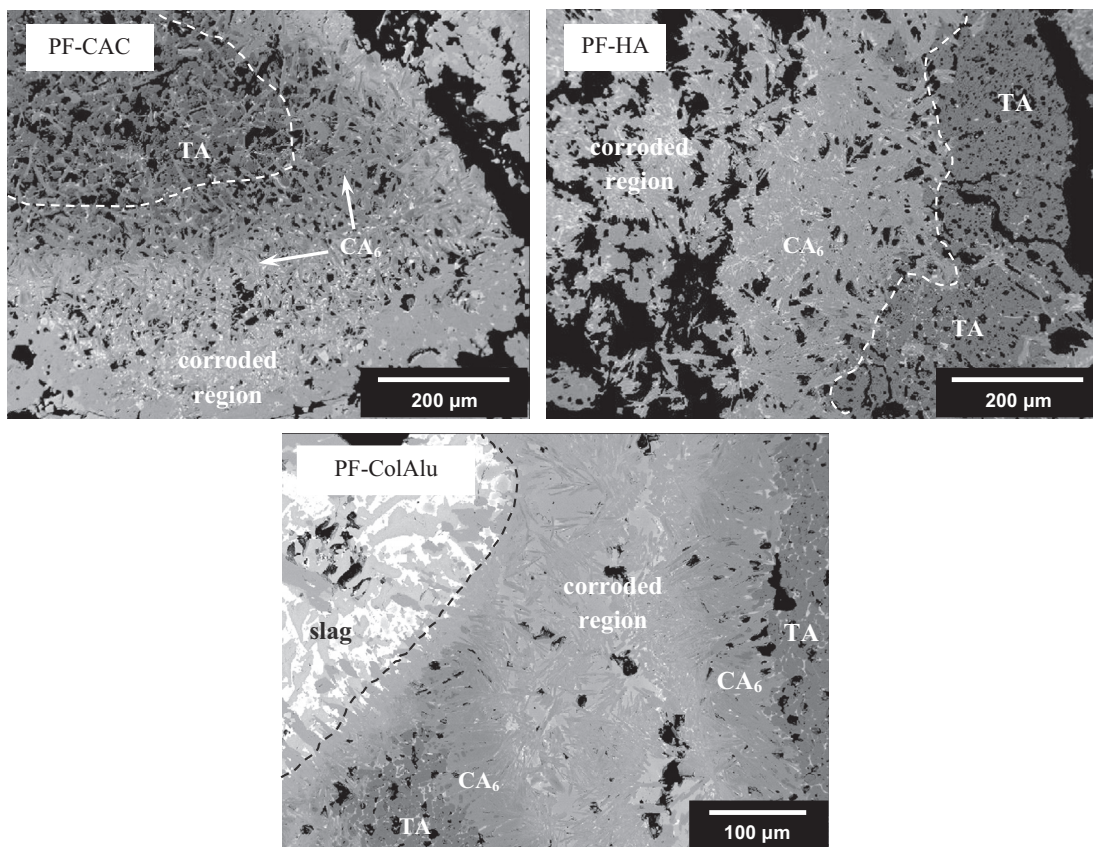


Fig. 2. Micrographs of the corroded zone of the castables by the molten slag (testing temperature=1500 °C) [13].

1500 °C:



According to these authors [13], for the refractory containing CAC, the presence of CA_6 in the matrix region of these samples would not have a significant impact on the overall corrosion behavior of this composition, and the same reaction (Eq. (1)) should take place at high temperatures. Nevertheless, considering the differences in the features of the CA_6 grains described above (see Fig. 2), the reaction mechanism can be the same, but it is expected that the precipitation of this phase should occur under distinct conditions.

The predicted evolution of the phases formed during the slag–matrix contact at 1500 °C (equilibrium condition) as a function of the thermodynamic calculation steps is presented in Fig. 3(a)–(c) for the pre-formed spinel containing castables with different binders. The results indicate that the saturated liquid in the matrix (the most reactive and finer components of the compositions) compounds should not further attack the coarse aggregates, as pointed out in Fig. 3(d) for the PF-HA formulation (no change in the amount of phases was identified in the evaluated condition). However, analyzing the corroded microstructure of the samples (Fig. 2), the interaction of the molten liquid with the coarse alumina grains was observed. Thus, the data obtained *via* thermodynamic simulations highlight the importance of the corrosion of the matrix fraction and the incorporation of these components by the molten liquid, as these transformations should take place at an earlier stage and

further affect the progress of the chemical attack of the coarse grains.

Based on Fig. 3(a)–(c), the corrosion of the matrix fraction leads to the dissolution of the castables' components, except for castable PF-CAC, as in this case the spinel content did not decrease for the first liquid–solid interaction [first calculation step, Fig. 3(a)]. After reaching the saturation of the molten slag for some ions (such as Ca^{+2} , Al^{+3} and Mg^{+2}), the precipitation of solid phases (the same compounds contained in the fired refractories) occurred in different intensities, leading to the generation of distinct contents for each evaluated system. The following sequence of phases is expected to be observed in the slag–refractory interface: spinel, CA_2 , CA_6 and Al_2O_3 as corundum.

Furthermore, the number of interaction steps can also indicate the chemical attack likelihood of the matrix components and this information can be used to define which formulation would have the highest corrosion resistance [10]. Whereas the PF-CAC castable required 19 calculation steps to reach the liquid saturation, the formulations containing binders based on alumina (HA or ColAlu) only needed 6 of them. This result is in tune with the higher penetration index obtained experimentally for the CAC-containing samples (Table 4).

Considering that the three evaluated refractories contained 1 wt% of silica fume, the ratio of molten liquid and solid phases expected to be attained at high temperatures during the attack of the matrix of the formulations should be similar. Nevertheless, the total amount of formed slag (after fulfilling

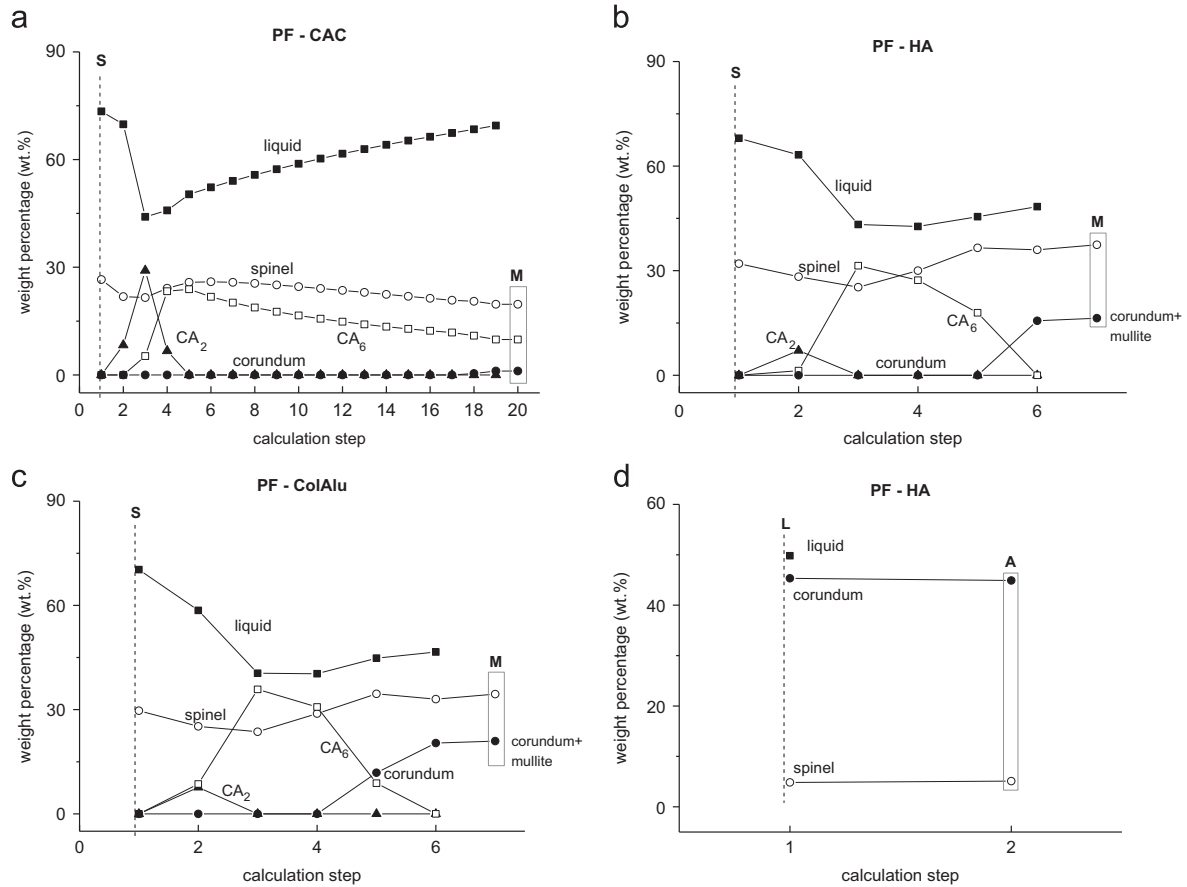


Fig. 3. Predicted phase evolution at 1500 °C as a function of the calculation steps for the interaction of: (a)–(c) matrix–slag and (d) aggregates–slag.

Table 4

Apparent porosity, average pore size and parameters of the corrosion behavior of the castables based on pre-formed spinel and containing different binders [13].

	AP (%) ^a	D ₅₀ (μm) ^b	Penetration index (%)	Wearing index (%)
PF-CAC	20 ± 0.5	20	34.0 ± 1.1	14.8 ± 0.8
PF-HA	17 ± 0.4	12	22.9 ± 0.9	13.2 ± 0.9
PF-ColAlu	12 ± 0.7	7	6.9 ± 0.5	0

^aAP: apparent porosity.

^bD₅₀: average pore size; measured *via* the analyses of SEM images.

all required calculation steps to reach the saturation of this phase) was markedly higher for the PF-CAC composition (Table 5) and only a few differences were obtained for the other two castables.

The values of the viscosity (η) of the liquid phase predicted to be formed in an equilibrium condition as a function of the calculation step for castables PF-CAC, PF-HA and PF-ColAlu are presented in Fig. 4. As observed, minimum changes were detected in the results obtained for PF-HA and PF-ColAlu, whereas a more fluid liquid should be formed during the corrosion of PF-CAC samples. Not only the amount of this

Table 5

Total content of CA₂, CA₆ and liquid generated during the matrix–slag interaction.

Mass (g)	PF-CAC	PF-HA	PF-ColAlu
Liquid	2786.42	657.49	623.32
CA ₂	114.48	16.70	18.31
CA ₆	616.61	171.92	183.53

molten phase, but also its lower viscosity must favor a more effective penetration and wearing of the composition containing CAC (as confirmed in the experimental corrosion tests).

Additionally, Table 5 presents the total content of the CA₂ and CA₆ phases estimated to be formed during the matrix attack of the castables at 1500 °C. In general, the highest amount of calcium aluminate phases was obtained for the system containing CAC as a binder. A previous investigation carried out by the authors [15], reported that a greater CA₆ content is expected to be generated in the corroded PF-CAC samples, due to the dissolution of CaO (found mainly as CA₆ grains in the fired matrix structure) and further incorporation of this phase in the molten liquid. This aspect explains the differences in the corrosion performance of PF-CAC and the other two castables evaluated in this work.

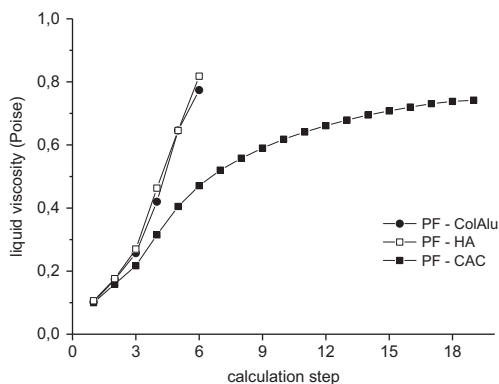


Fig. 4. Calculated viscosity of the molten liquid formed during the slag–matrix interaction at 1500 °C.

Comparing the resulting CA_2 content derived from the matrix corrosion process of the evaluated pre-formed spinel-containing castables, the total amount of this phase was very low for PF-HA and PF-ColAlu (~ 16 – 18 g, whereas PF-CAC ~ 114 g, Table 5). This different behavior is attributed to the higher availability of fine alumina particles and the absence of CaO in these castables, which favors the precipitation of aluminates with a reduced CaO/ Al_2O_3 ratio (such as calcium hexaluminate over the calcium dialuminate) at 1500 °C.

As highlighted in Fig. 3, all fine alumina particles of the castables' matrix are expected to be dissolved and incorporated by the molten slag in the first liquid–solid contact. With the progress of the slag–refractory interaction, the liquid phase will become saturated by this component, inhibiting a further attack of the castable and allowing the identification of remnant corundum in the final calculation steps. This is the reason why no chemical corrosion of the tabular alumina grains is predicted to take place in the thermodynamic calculations, when considering the reaction of the saturated slag with the coarse aggregates of the compositions. Furthermore, an earlier detection of the corundum phase in the matrix–slag interaction indicates that the evaluated formulation should present higher corrosion resistance [10]. Based on the results showed in Fig. 3, Al_2O_3 was identified at the calculation step, number 4 for PF-ColAlu (whereas PF-HA=5 and PF-CAC=17), which corroborates with the improved corrosion resistance performance of this composition.

Hence, the main differences in the corrosion behavior of the designed castables are mainly related to the amount of fine CaO and Al_2O_3 available in their matrix fraction, where: (i) the dissolution of the CA_6 grains contained in PF-CAC gives rise to higher content of a liquid phase with lower viscosity at high temperature (1500 °C), compared to the one found in the alumina-bonded systems (PF-HA and PF-ColAlu); (ii) the greater amount of fine alumina particles (which can readily react with the molten slag) in the colloidal alumina-bonded composition led to an earlier saturation of the liquid, minimizing the chemical corrosion of this refractory. On the other hand, the precipitation of calcium aluminate layers at the liquid–solid interface should also be affected by the spinel dissolution (which takes place mainly in PF-HA and PF-ColAlu), as this transformation will

decrease the CaO concentration in the molten slag due to a dilution effect. The protective action of these dense layers (preventing liquid infiltration) depends on their continuity and thickness [16]. According to the theoretical calculations, castable PF-CAC should present a more significant formation of CA_2 and CA_6 after it interacts with the molten liquid at high temperature. However, when considering this latter phase, its generation is associated to expressive volumetric changes that can lead to damage (cracks and flaws) in the solid structure, giving rise to new paths for slag penetration. Thus, this negative effect identified for the CAC-bonded composition (as shown in Fig. 2), induced a higher liquid penetration and wearing of these samples.

Other aspects related to the CA_6 generation in this sort of castables have been discussed elsewhere [15], where it was pointed out that the crystallization of this phase usually takes place with a high driving force (due to chemical factors mentioned above), most likely at temperatures lower than 1500 °C and in the presence of a viscous liquid phase.

Despite the lower amount of CA_6 predicted to be formed in PF-HA samples (compared to PF-CAC), the precipitation conditions of these crystals during the slag attack seem to be similar to the ones verified for the CAC-containing composition. On the other hand, a dense calcium hexaluminate layer presenting oriented crystals, low porosity and no cracks and flaws were observed in the corroded castable PF-ColAlu (with calculated amount of CA_6 similar to the PF-HA one, Table 5), which indicates that other physico-chemical aspects might also play a role in the corrosion behavior of this refractory. As reported by Sako and colleagues [13], physical properties, such as the lower pore size and apparent porosity of the fired PF-ColAlu samples (as a consequence of a more significant sintering of the microstructure due to the addition of the nanoparticles [13]) when compared to PF-CAC and PF-HA (Table 2), better explain the lowest penetration index attained for this former refractory. Thus, the reduced slag penetration and dissolution of the nano-bonded castable during the corrosion tests inhibited further wearing of the samples. Consequently, the CA_6 crystallization might have taken place in a more controlled manner, at higher temperatures and in the presence of a liquid phase with lower viscosity than the one found in the other evaluated formulations.

In summary, the physical properties reported by Sako et al. [13] as well as the differences in the chemical composition of the designed matrices (whose effects were suitably evaluated by the thermodynamic calculations) can explain the improved corrosion resistance of the alumina-bonded compositions (PF-HA and PF-ColAlu) when in contact with basic slag.

3.2. *In situ* (IS) spinel-containing castables

A previous paper by the authors [10] presented some thermodynamic simulations and corrosion data for the IS-CAC and IS-HA castables. However, in this work: (i) results of samples with different dimensions are reported, (ii) a higher amount and a different slag was used during the cup tests, (iii)

a different matrix composition and (iv) an updated version of FactSageTM software were used for the actual calculations.

Table 6 shows the physical properties (pore size and apparent porosity attained before the corrosion tests=fired refractories) and penetration index calculated for the corroded samples of the castables with *in situ* spinel formation and bonded with CAC or HA. The wearing of these materials was not determined due to the presence of remnant slag in the samples' cup. Fig. 5 also presents images of the cross-section area of the corroded refractories. As observed for the pre-formed spinel-containing castables, the formulation with HA showed improved corrosion resistance when compared to the CAC-bonded one.

Fig. 5 presents the micrographs of the slag–refractory interface for the IS-CAC and IS-HA samples. CA₆ grains with a high aspect ratio were identified in both refractories at the border of the coarse particles of tabular alumina (TA). The

formed calcium hexaluminate layer was denser (pointing out greater protection to infiltration in the grains) in the IS-HA refractory. Besides that, the alumina-bonded system also showed a continuous region, close to the CA₆ layer, comprised by spinel (spi) with Mn and Fe in solid solution [~ 2 wt% and 11 wt% (data obtained *via* EDS analyses), respectively]. The features (continuity, thickness, *etc.*) of this spinel region depend on the MgO content in the liquid phase [17] and its generation in the slag–refractory interface may protect the solid from a further chemical attack, as some ions (such as Fe⁺², Fe⁺³ and others) should be incorporated into the spinel structure [18].

Comparing to the pre-formed spinel containing castables bonded with CAC or HA, the crystallization of CA₆ seemed to be carried out in a more controlled way in the compositions with *in situ* spinel formation (Fig. 6). Calcium hexaluminate grains are mainly generated at the border of the tabular alumina aggregates during the pre-firing step of the IS-CAC samples and only a minor content of this phase is located in the matrix fraction of this refractory [4]. Therefore, in this case, the incorporation of CaO to the molten liquid during the slag–matrix interaction is limited, resulting in the precipitation of CA₆ with a similar feature as the one observed in the corroded refractory bonded with HA (IS-HA, which did not contain CaO in its matrix).

The predicted phase evolution as a function of the calculation steps for the slag–matrix contact for castables IS-CAC and IS-HA is plotted in Fig. 7. Few changes were detected when

Table 6

Apparent porosity, pore size and parameters of the corrosion behavior of the castables based on *in situ* spinel formation and containing different binders.

	AP (%) ^a	D ₅₀ (μm) ^b	D _{min} (μm) ^b	Penetration index (%)
IS-CAC	23.0 ± 0.9	2.0	0.8	11.4 ± 0.1
IS-HA	18.0 ± 0.7	1.7	0.3	5.2 ± 0.2

^aAP: apparent porosity.

^bD₅₀ and D_{min}: average and minimum pore size; measurements carried out *via* Hg porosimetry.

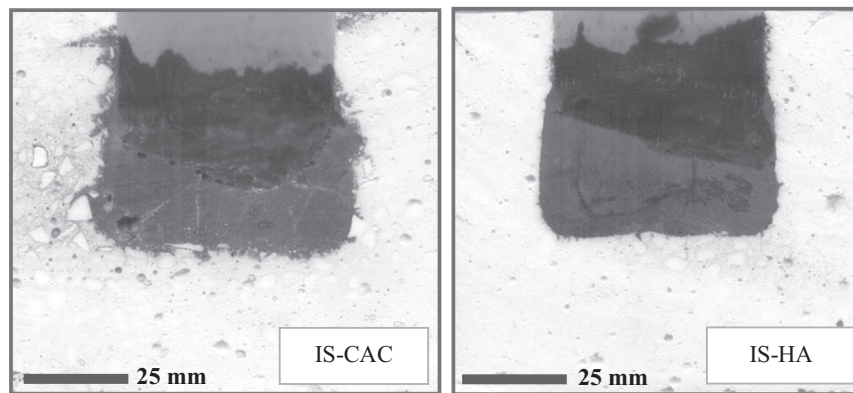


Fig. 5. Images of the cross-section area of the *in situ* spinel-containing castables after the corrosion cup-tests at 1550 °C for 2 h.

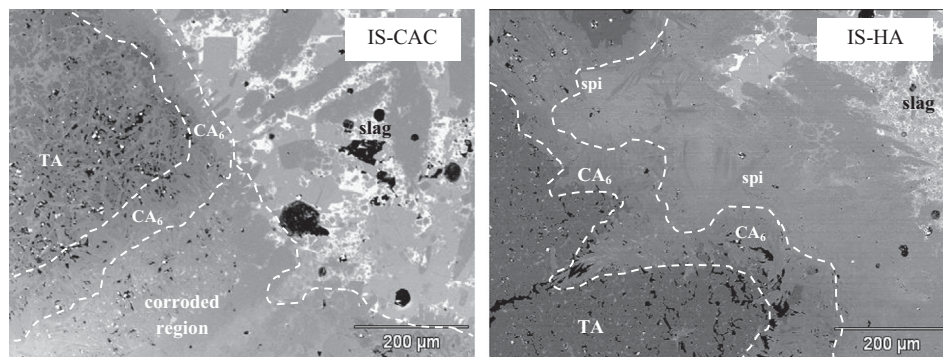


Fig. 6. Micrographs of the corroded zone of the *in situ* spinel-containing castables. Corrosion tests were carried out at 1550 °C for 2 h.

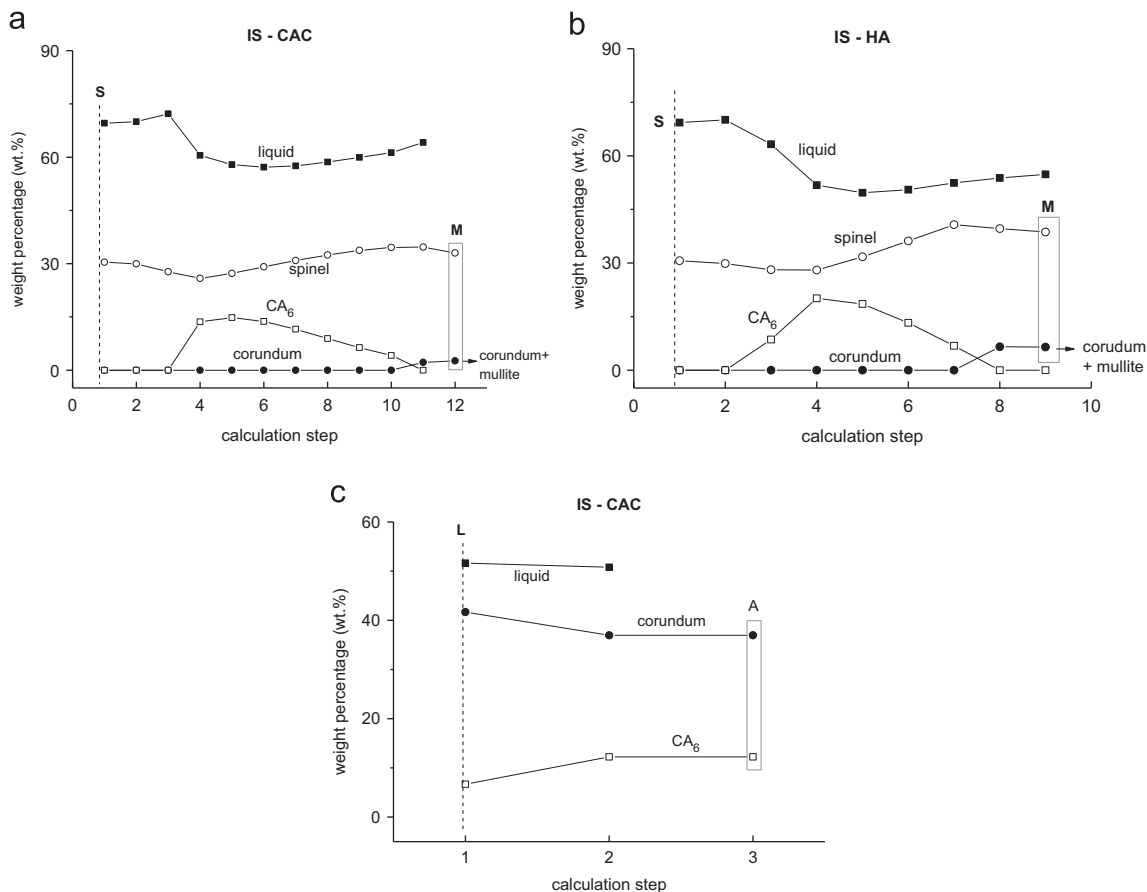


Fig. 7. Chemical composition predicted to be formed in an equilibrium condition as a function of the thermodynamic calculation steps during the interaction: (a),(b) slag–matrix and (c) slag–aggregates.

comparing the attained results. However, the number of simulation steps required to reach the slag saturation was lower for the hydratable alumina-bonded system, which is in tune with the experimental results (lower penetration index, see Table 6). After the initial dissolution of the fine components of the castables, spinel and CA₆ should be generated in both compositions due to the saturation of the molten liquid by the ions that comprise these phases. These compounds were identified by SEM/EDS analyses of the corroded interface of the samples (Fig. 6). The liquid amount expected to be found after the initial slag–matrix contact at 1550 °C is similar for both evaluated systems, but a higher consumption of this phase, followed by the precipitation of the above mentioned compounds should be observed for IS-HA (Fig. 7b).

The viscosity of the resultant slag as a function of the calculation step is presented in Fig. 8. The values of this property were lower for the liquid contained in the IS-CAC samples, which can partially explain the higher slag penetration in this refractory.

Due to the higher amount of alumina in the matrix of the IS-HA castables, the thermodynamic simulations do not predict the chemical attack of the tabular alumina aggregates of this formulation. However, in a practical condition, the reaction between the molten liquid and coarse particles starts before the slag saturation by the fine components. Furthermore, for the

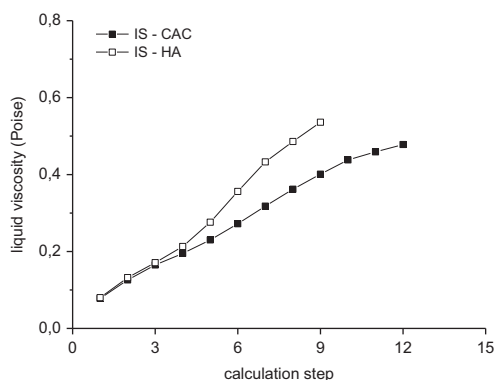


Fig. 8. Estimated viscosity of the molten liquid generated at 1550 °C during the slag–matrix interaction.

IS-CAC refractory, the alumina aggregates should present a limited reaction with the liquid phase, as only two calculation steps were required to attain the equilibrium condition of the system (Fig. 7c). The total content of spinel, CA₆ and liquid generated during the chemical interaction of slag–matrix of the designed castables is reported in Table 7.

Without taking into consideration the higher temperature used in the corrosion evaluation of the *in situ* spinel containing compositions (1550 °C instead of 1500 °C), the lower CaO

Table 7

Total content predicted for spinel, CA₆ and liquid phase formation derived from the castables' matrix interaction with the molten slag at 1550 °C.

Mass (g)	IS-CAC	IS-AH
Liquid	1728.60	1184.69
Spinel	843.14	874.14
CA ₆	192.83	174.63

content in the IS-CAC matrix led to a reduced generation of CA₆ (~193 g) when compared to the one estimated for PF-CAC (~616 g).

The differences in the CA₆ and spinel amounts predicted for IS-CAC and IS-HA are small (< 10%) and a continuous MgAl₂O₄ layer was mainly generated in the alumina-bonded samples due to the precipitation of this phase from the molten slag. However, the thermodynamic data are not able to explain the spinel formation close to the aggregates' particles and the liquid penetration observed for these refractories.

Previous works by the authors [9,10] pointed out the reduced pore size and open porosity of the hydratable alumina-bonded samples (Table 6). Additionally, Braulio et al. [8] reported that IS-HA and IS-CAC refractories showed spinel grains with different sizes (< 10 μm and > 20 μm, respectively, particle size estimated by the evaluation of the SEM images) after their pre-firing treatment at 1500 °C for 5 h. Due to the presence of finer MgAl₂O₄ grains in this former composition, the dissolution of this phase into the molten liquid should take place at an earlier stage, increasing the local concentration of Mg⁺² and Al⁺³, favoring the slag saturation in these components and giving rise to the re-precipitation of a continuous layer of spinel [17], as detected in Fig. 6. This fact induced the higher corrosion resistance of the IS-HA castable. On the other hand, the pre-formed spinel-containing refractories (PF-CAC and PF-HA) did not present spinel with such different granulometry, leading to a less significant improvement of the corrosion behavior of these materials when compared to IS-HA.

3.3. Selecting an optimized system with improved corrosion resistance

Based on the comparison of the designed MgO–Al₂O₃ and MgAl₂O₄–Al₂O₃ castables with distinct binder agents, some important aspects can be defined to improve the corrosion resistance of these systems when in contact with a basic slag.

It is clear that the pore size and apparent porosity of the refractory structure affect the liquid penetration behavior at high temperatures. Considering that the alumina-based binders (hydratable alumina or colloidal alumina) induce a more effective sintering process due to their high specific surface area, the selected colloidal suspension can improve the physical properties and the binding level of the generated microstructure, increasing the corrosion resistance of the matrix fraction.

The spinel grain size is another aspect that defines the corrosion behavior of these refractories: the finer the particles, the easier their dissolution into the molten liquid will be,

leading to further precipitation of spinel in the solid–liquid interface as a continuous and thick layer. This is the reason why some authors [19] stated that *in situ* spinel-containing refractories are more resistant to the slag attack than the compositions presenting coarser pre-formed spinel particles. For MgO–Al₂O₃ castables, using hydratable alumina is a good alternative to induce the generation of spinel with a reduced size, which usually results in the formation of a well defined protective layer of this phase at the liquid–solid interface during the corrosion process and inhibits further attack of the refractories.

According to the chemical composition of the evaluated refractory systems, the thermodynamic simulations of the slag–castable interactions indicated that the CA₆ presence in the matrix fraction of these formulations negatively affected their corrosion resistance, due to the earlier saturation of the molten liquid in Ca⁺² and a further precipitation of a high amount of this calcium aluminate phase (*via* CaO_(l) and Al₂O_{3(l)} reaction), resulting in crack formation and, consequently, in higher slag penetration in the samples. A suitable route to minimizing this effect is based on replacing calcium aluminate cement by the alumina-based binders, as presented in this work. Besides that, other alternatives to reduce or eliminate the CaO content in the matrix fraction of CAC-bonded compositions consist of: (i) withdrawing silica fume of the mixtures, as in the absence of this oxide, the CA₆ generation (derived from the reaction of cement components and fine alumina of the refractories) should take place mainly at the border of the coarse tabular alumina particles during the pre-firing treatment of the samples [15], or (ii) adding silica fume only to Al₂O₃–MgO formulations (*in situ* spinel-containing refractories). Therefore, based on the obtained results, the most suitable castables (containing silica fume) to better withstand the molten slag attack at high temperatures would be the ones with *in situ* spinel generation and alumina-based binders.

Although this work only evaluated refractories containing microsilica, it is well known that this additive gives rise to high contents of liquid phase during the corrosion of the samples, favoring their wearing. Moreover, according to the thermodynamic calculations, a greater amount of liquid with lower viscosity, should be found in the CAC-containing formulations. Aiming to avoid the use of silica in Al₂O₃–MgO formulations, the addition of mineralizing agents (*i.e.*, boron-based compounds, titania, *etc.* [20,21]) can also be a suitable option, as they speed up spinel formation at lower temperatures, generating a fine and well scattered phase in the resultant dense structure. Some promising preliminary data indicate that this can be another route that should be better investigated in combination with alternative binders, in order to develop castables with enhanced corrosion resistance.

4. Conclusions

The use of alumina-based binders (hydratable alumina and colloidal alumina), instead of the traditional calcium aluminate cement, in Al₂O₃–MgO (*in situ* spinel formation) and Al₂O₃–MgAl₂O₄ (containing pre-formed spinel) castable formulations

proved to be an efficient way to reduce their corrosion wearing when in contact with a molten basic industrial slag. Furthermore, a more significant improvement of the corrosion resistance was observed for the *in situ* spinel system.

By applying the thermodynamic calculations (based on an initial interaction of the liquid with the refractories' matrix components, followed by a further reaction of the resultant slag with the coarse aggregates), the main chemical composition aspects of the systems could be identified, which play an important role in the corrosion behavior of the castables. Based on this, the CaO content in the matrix fraction (derived from the CA₆ grains formed during the samples' pre-firing step at 1500 °C for 5 h) has a major impact on the refractories wearing. The absence of this compound, as well as the higher concentration of Al₂O₃ in the compositions bonded with HA and Col-Alu are the main aspects that lead to the improved corrosion resistance of these castables when in contact with the selected slag.

In addition to the samples' physical properties (pore size and apparent porosity), the particle size of the spinel grains contained in the refractories also affected their resultant corrosion behavior. For instance, for the MgO–Al₂O₃ castable, the use of hydratable alumina proved to be a good alternative to induce the generation of spinel with a reduced grain size, which resulted in the formation of a well defined protective layer of this phase at the liquid–solid interface during the corrosion process and inhibited further attack of the refractory.

Among the evaluated compositions and considering the presence of silica fume, the most suitable formulation with optimized corrosion resistance is the one with *in situ* spinel generation and HA as a binder. The use of colloidal alumina in this refractory system should also result in castables with improved chemical resistance, as long as the sintering process does not negatively affect the particle size of the formed *in situ* spinel grains. The replacement of microsilica (whose presence can increase the castables' wearing) can be carried out by adding mineralizing agents.

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