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Influence of the Liquid Phase on the Slag Corrosion of Andalusite-Based Refractories

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Influence of liquid phase on the slag corrosion of andalusite-based refractories was studied at 1600°C using the crucible method. Corroded crucibles were either quenched in cold water or allowed to cool in the furnace chamber. Post-mortem microstructural examination of all samples revealed the development of juxtaposed zones with different textures. According to the composition of the slag, the precipitation zone was found to contain one or several monomineral layers which indicated the presence of concentration gradients in the liquid. Extension of the penetration zone was found to be dependent on the viscosity of the interstitial liquid at high temperature.

I. Introduction

High processing temperatures (up to 1650°C), combined with a long holding time of molten steel in the ladle, are in great demand for producing high-quality products. Nevertheless, they are believed to be highly detrimental to high-alumina refractories used as a working lining.^{1,2} In such extreme operating conditions, chemical wear and structural spalling caused by slag penetration severely limit their lifetime in service, so that an improvement of performance is desirable.

Substantial improvements in resistance to corrosion and slag penetration were achieved (particularly for andalusite-based refractories currently used in steel ladles) by reducing porosity, using high-purity raw materials to limit the amount of low-melting phases, and by optimizing secondary-mullite formation. However, in spite of these achievements, corrosion mechanisms in this type of refractories are far from being completely understood. Recently, Lee et al.³ discussed the important role of the liquid phase in slag corrosion of castable refractories and indicated that the composition of local liquid, which may be very different than the bulk slag, is critical. Wear behavior in andalusite-based refractories has not been studied thoroughly. This aspect is addressed in the present study by relating theory, based on application of Gibbs' Phase Rule to the slag-refractory system in which the liquid is locally at equilibrium with the solids, to experimental data of post-mortem analysis.

To overcome crystallization and diffusion phenomena occurring inside the refractory during cooling, laboratory quenching experiments were performed. Microstructure of the andalusite refractory was analyzed before and after corrosion testing in order to clarify the degradation mechanisms. The influence of physicochemical properties of the liquid phase on the resistance to slag corrosion was also studied.

Table I. Chemical composition, density and apparent porosity of the brick tested.

	Composition (wt%)	Density (g/cm ³)	Apparent Porosity (%)
Al ₂ O ₃	64.12		
SiO ₂	33.44		
CaO	0.10		
MgO	0.10	2.64	12.85
Fe ₂ O ₃	0.70		
TiO ₂	0.26		
Na ₂ O	0.08		
K ₂ O	0.25		

II. Experimental procedure

The material investigated in this study is a commercial-grade andalusite refractory brick. Chemical analysis and some physical properties of the brick, as supplied by the manufacturer, are listed in Table I. Powder X-ray diffractometry (XRD, Model N_o PW 1049/10, Philips) showed that the principal constituent element of the brick was mullite (3Al₂O₃•2SiO₂). Laboratory corrosion tests, using the static crucible method, were performed with two model slags (labeled AC and CS) whose nature and chemical composition (Table II) are close to those of ladle slags that are used to produce flat bar steel (Al killed) or steel cords (Si killed). The crucibles, prepared from 10 cm x 10 cm x 60 cm blocks with a 40 mm diameter and 40 mm deep bore, were filled with a fixed amount of slag (40 g), and then fired for six hours at 1600°C in an electric furnace at heating rates of 15°C/min up to 900°C, and 9°C/min up to 1600°C. The model slags were prepared by dry-mixing appropriate proportions of starting powders comprising calcium carbonate (CaCO₃>98%, Alfa Aesar), reactive alumina (CT3000SG, Al₂O₃>99.8%) and silica sand from Fontainebleau (France). After corrosion testing, all crucibles were cross-sectioned perpendicularly to the slag-refractory interface to measure the penetration and corrosion areas. For microstructure examination, 20 mm x 10 mm samples were cut from each corroded crucible, impregnated with resin, polished and carbon-coated using standard ceramographic techniques. A scanning electron microscope JEOL JSM 6400 (SEM) equipped with a Kevex

Table II. Composition of model slags.

	Composition (wt%)	
	Slag AC	Slag CS
CaO	50	55.55
Al ₂ O ₃	50	0
SiO ₂	0	44.45
Al ₂ O ₃ / CaO	1	-
CaO / SiO ₂	-	1.25

Quantum Delta energy-dispersive spectrometer (EDS) was used for the microstructural analysis. Concentrations of major oxides (Al_2O_3 , SiO_2 and CaO) and impurities were obtained from the measured X-ray intensities by calibration with ZAF correction (standardless). To identify the reaction products, several samples cut along the area extending from the residual slag to the base refractory on a ≈ 22 mm length, were characterized by X-ray powder diffraction.

Two corrosion tests were performed with each slag. In the first test, the crucible was allowed to cool to room temperature in the furnace after a six hour heat treatment, in order to give an indication of the phases crystallizing during cooling. In the second test, the crucible was rapidly immersed in cold water to prevent partial crystallization of the high-temperature liquid during cooling. Global chemical profiles were established by EDS analysis of successive horizontal bands of 1.8 mm thickness from the initial interface on a 20 mm length, thus providing 11 measurement points which are representative of domains containing solids (pre-existing or neo-formed) and remnant slag (liquid at 1600°C). The reported values are the average of four measurements at the same distance in the sample investigated. Composition profiles of the liquid phase at 1600°C were drawn according to two different but complementary methods. The first one consists of interpreting the results from EDS analysis performed on samples cut from the crucibles and allowed to cool, by means of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ (CAS) phase diagram.⁴ This indirect method which does not take into account the secondary oxides of the system and assumes that the liquid is in local equilibrium with the solids. The second method is based on the point analysis of glass between grains in samples issuing from quenched crucibles. In this case, the glass composition is expected to be representative of the composition of the liquid present at 1600°C . Liquid viscosity as a function of depth in the refractory was also estimated from compositional profiles of the liquid phase according to Urbain's model.⁵

III. Results and discussion

(1) Microstructure of the original refractory

The microstructure of the original brick is shown in Fig. 1. Complete mullitization of the andalusite aggregates led to the formation of a composite made of mullite crossed by a capillary network filled with a glass, which acts as a bonding phase. Most of the glass ($\approx 80\%$) remains trapped in the capillaries which are elongated along the c axis.⁶ Point chemical

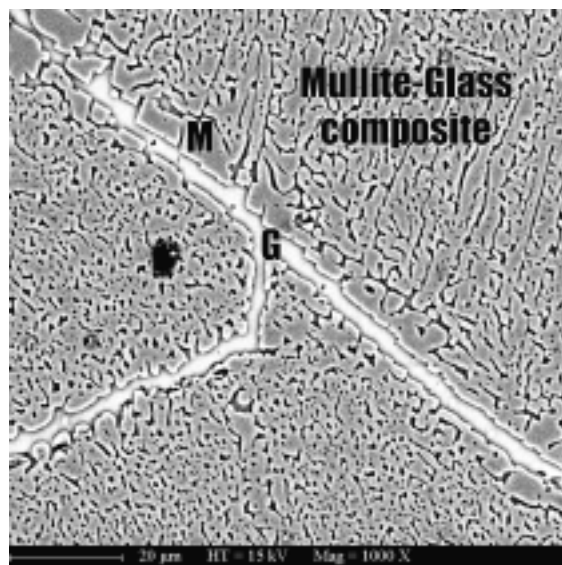


Fig. 1. Backscattered electron micrograph (BEI) of a sample of the original brick showing the mullite-glass composite. The capillaries of glass, with diameters in the micrometer range, form interconnected tubes parallel to the c axis common to the mullite crystals and the parent andalusite grains.

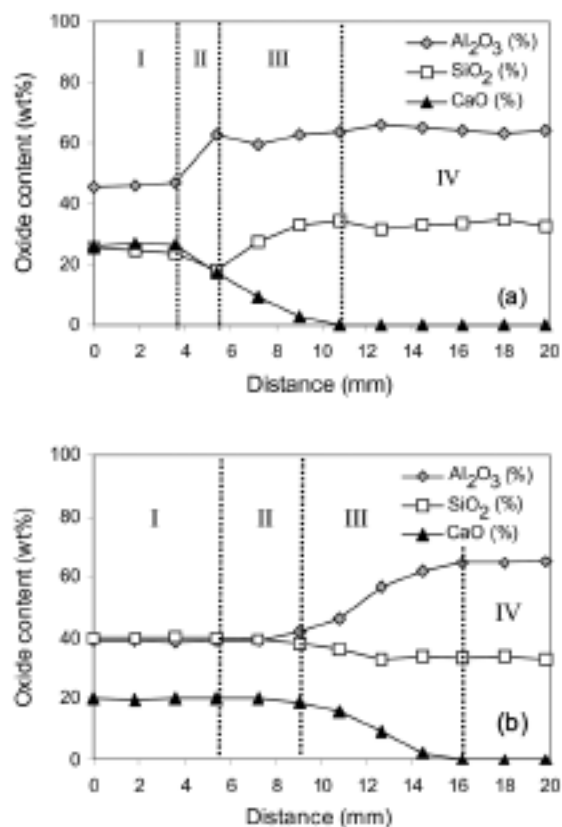


Fig. 2. Chemical profiles of major elements in the cooled crucibles after corrosion at 1600°C by AC (a) and CS (b) slags. (I): slag zone; (II): precipitation zone; (III): penetration zone; (IV): unaffected refractory. Initial slag-refractory interface is located at 0 mm.

analysis revealed that the bonding glass is rich in silica and contains $\approx 80\%$ SiO_2 , $\approx 16\%$ Al_2O_3 , $\approx 1\%$ Fe_2O_3 , $\approx 0.3\%$ TiO_2 , $\approx 0.7\%$ MgO , $\approx 2\%$ K_2O .

(2) Post-mortem analysis

Detailed SEM examination of the different zones in the corroded crucibles cooled or quenched to room temperature is described below. Regardless of the nature of the corrosive agent used, all the corrosion profiles observed in these crucibles consist of four juxtaposed zones with different textures.^{7,8}

- I: Remnant slag.
- II: Precipitation zone
- III: Penetrated zone
- IV: Unaffected refractory

These four zones are easily distinguishable in all samples. Chemical profiles (Fig. 2) show that residual slags became SiO_2 -rich, which means that initial slag compositions have evolved in the course of corrosion experiments. Current compositions are shown to remain constant along the slag zones whose extent depends on the slag used. Between the slag and the unaffected refractory, composition gradients are also observed. At the slag-refractory interface, several new phases identified as corundum, calcium hexaluminate (CA_6), anorthite (CAS_2) and calcium aluminosilicates (CAS phases) were found to be present in the system. It should be noted that CAS is not a ternary compound in the C-A-S system, so the identified CAS is a mixture of more than one phase.

Adjacent to the unaffected refractory, which shows neither chemical nor microstructural change, the penetrated zone shows a microstructure similar to that observed in the original brick although it is partially permeated by the corrosive slag. The latter invades the matrix by capillary action and

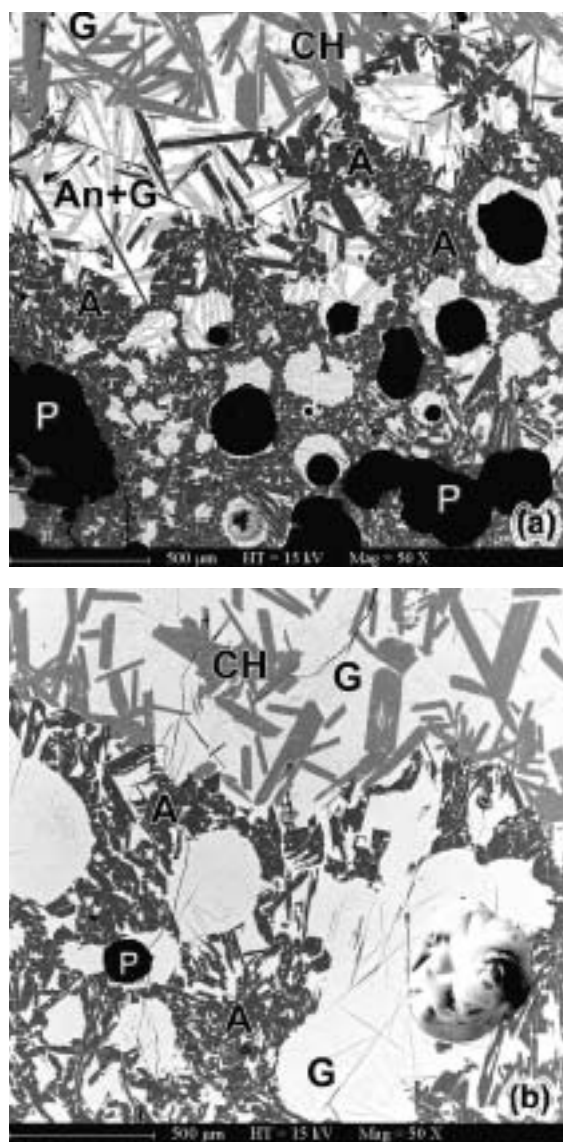


Fig. 3. SEM micrograph of the upper part of the precipitation zone adhering to the slag zone in (a) naturally cooled and (b) quenched crucibles corroded by AC slag. A: Corundum, CH: Calcium hexaluminate, An: Anorthite, P: Pore, G: Glass.

mixes with the pre-existing intergranular liquid. As a consequence, solids dissolve at grain boundaries with a gradual increase in the amount of glass, which seals off the porosity on the hot face allowing chemical changes to take place at the slag-refractory interface rather than further back from the working face. X-ray diffraction analysis in conjunction with SEM observations carried out along the upper part of the precipitation zone adhering to the slag zone (in cooled and quenched crucibles corroded by the AC slag) revealed the presence of various reaction products composed of successive monomineral layers with different thicknesses, separated by an uneven boundary (Fig. 3). In the specimen resulting from cooled crucibles (Fig. 3a), the first layer consists of well-developed calcium hexaluminate plates (20-100 μm thick) randomly oriented in a mixture of glass and anorthite. Because it is not continuous, this barrier has a limited effect on the dissolution of the brick components, and its formation at test temperature may increase the slag viscosity. As a result, the slag could no longer penetrate easily into the pores and grain boundaries, decreasing the corrosion rate. In this case, the corrosion process is termed passive.

Table III. EDS analysis of glass in the slag zone after quenching of the corroded crucibles.

	Composition (wt%)	
	Slag AC	Slag CS
Al ₂ O ₃	48	41
SiO ₂	25	39
CaO	26	19
TiO ₂	1	1
Fe ₂ O ₃	<1	<1

Alteration of the refractory microstructure can be explained by dissolution-precipitation processes inside a liquid phase. Liquid slag penetrated the andalusite brick pores and grain boundaries and reacted with the bonding glass (which is liquid at 1600°C) to yield a local liquid enriched in CaO that can react with mullite to form corundum. Dissolution of mullite is greater because of the presence of secondary oxides in raw materials which provide high amount of melt. The process is influenced by the solubility of mullite in the slag.⁸ The calcium aluminates (CA, CA₂), formed during heating, reacted with corundum to form CA₆. Further into the crucible, a second layer (1.5-2 mm in depth) is a connection of faceted tabular crystals of corundum forming roughly three-dimensional structures inside which lamellar crystals of CAS₂, glass and pores (black areas connected or not) can be observed. In this region, CAS is present and likely consists of remnant glass and CAS₂, which is representative of the liquid composition at 1600°C. The morphology of corundum crystals observed near the slag-refractory interface showed evidence of rapid crystallization. Consequently, the formation of corundum crystals is not involved in the corrosion process. Discriminating between corundum formed during corrosion and that formed during cooling proved difficult. However, it may be considered that acicular crystals probably formed during cooling while tabular grains of corundum, which form 3D-cellular structures, resulted from slag corrosion at 1600°C.

The only reaction products that were detected in the quenched crucible after corrosion by AC slag are CA₆ and corundum (Fig. 3b). The homogeneity of the quenched liquid phase (glass) allowed an accurate EDS analysis. The rapid drop in temperature, which avoids CAS and CAS₂ formation, makes the composition of glass obtained at room temperature representative of that of the liquid present at 1600°C. The general sequence of corrosion products, from the slag zone to the refractory were CA₆ → corundum → mullite. From these experimental data, it can be noticed that crystallization of CAS₂ occurs subsequently to that of corundum whatever its facies. With CaO-SiO₂ slag, the microstructure of the modified domain (Fig. 4) near the slag-refractory interface shows that for cooled crucibles, the only crystalline phases present are corundum and CAS₂. These phases were formed during cooling as would be predicted using the C-A-S ternary phase diagram. The corrosion area (defined here as regions of refractory completely replaced by slag) as can be seen in Fig. 2b, is more extensive in the crucibles corroded with CS slag than with AC slag. This may be explained from the formation of a greater amount of liquid phase in the case of CS slag. Such a high liquid concentration indicates that at 1600°C, the andalusite brick became entirely liquid-bonded and would consequently be extremely susceptible to slag corrosion. However, potential for more reaction products to be present is lower in the case of CS slag. Indeed, the precipitation zone, which is comparatively wider with CS slag, is composed of only one type of reaction product as it is corundum crystals with different shapes. In quenched crucibles (Fig. 3b), these crystals are embedded in a homogeneous matrix formed of glass the composition of which is representative of that of the liquid existing at 1600°C. For CS slag, the general sequence of corrosion products, from the slag zone to the refractory, was corundum → mullite.

At the wavy slag-refractory interface (Fig. 4b), the main phases were corundum, glass and mullite. The typical microstructure of mullitized

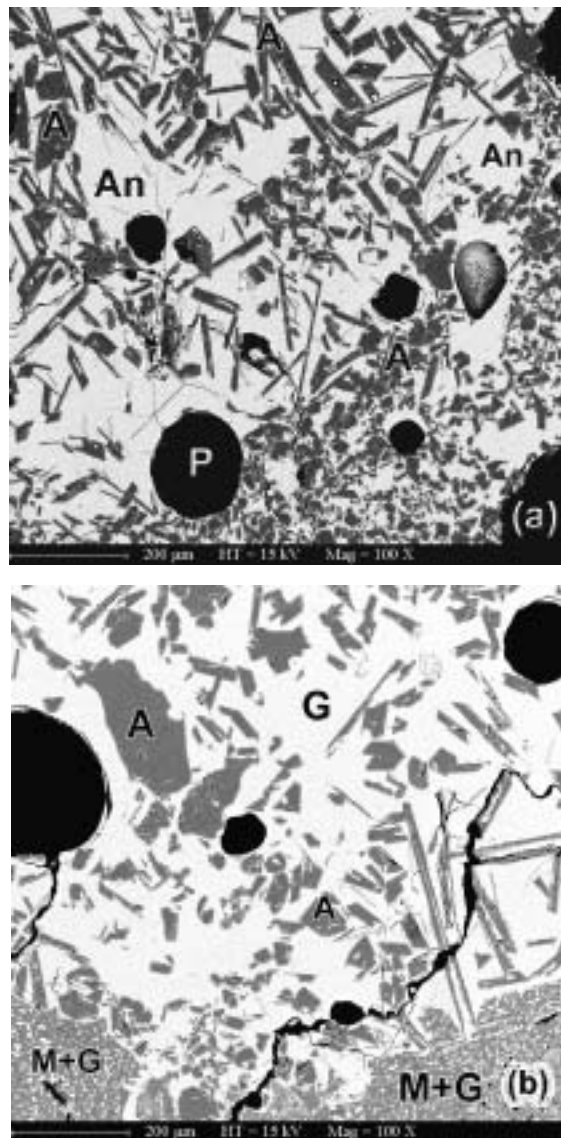


Fig. 4. SEM micrograph of the lower part of the precipitation zone adhering to the penetrated refractory in (a) naturally cooled and (b) quenched crucibles corroded by CS slag. A: corundum, G: glass, An: anorthite, M: mullite, P: Pore. Note that microcracks observed on micrograph (b) arose during rapid quenching.

andalusite, modified in the immediate vicinity of the interface, is gradually preserved in the penetrated area, where an enlargement of grain boundaries invaded by glass can be noticed.

Figure 5 shows the microstructure of the slag zone in the bricks that were allowed to cool after 6 h heating at 1600°C. With Al_2O_3 -CaO slag, SEM observations showed that the main phases consisted of lathlike crystals of calcium hexaluminate dispersed in a matrix of various calcium aluminosilicates and glass formed from the remnant liquid (having a locally varying composition). The morphology of the dendrites is typical of a phase that has crystallized from the high-temperature liquid during cooling.¹⁰ With CaO-SiO₂ slag, tabular crystals of corundum (~2 mm length and 2-10 μm thick) with no preferential orientation were identified throughout the remaining slag area. Higher-magnification SEM of the matrix indicates it contains anorthite with a small amount of glass appearing as small white areas.

In the case of quenched crucibles, the slag zone consists only of a glassy phase with a uniform composition which is expected to be representative of that of the liquid phase present at 1600°C. Semi-quantitative EDS data

obtained for glass composition in this zone with each slag are given in Table III. The absence of crystalline phases throughout the slag zone in cooled crucibles, confirmed by XRD analysis, suggests that CA_6 , corundum, CAS and CAS_2 are formed during cooling.

Some important conclusions can now be drawn. Data of microstructural examination described above show that a succession of monomineral layers will be observed for all types of calcium aluminosilicate slags as long as their initial composition is close to $C/(A+S)\approx 1$. The sequence of corrosion product formation is consistent with the C-A-S phase diagram. However, it must be noted that because a limited amount of slag was present, variation of the slag composition during laboratory testing may have removed the outermost layers such as calcium dialuminate (CA_2). This was not observed in the specimen taken from the crucibles corroded by the AC slag.

(3) Estimation of composition profiles

The chemical composition of the liquid phase at 1600°C, as a function of the distance to the initial slag-refractory interface, may be determined by a combination of EDS analysis data and local-equilibrium rules applied to CaO- Al_2O_3 -SiO₂ ternary phase diagram.

Composition profiles established by means of this approach are given in Fig. 6. Along the unaffected zone, which is wider with AC slag, contents of major elements are constant ($\text{Al}_2\text{O}_3 \approx 18\text{wt}\%$, $\text{SiO}_2 \approx 82\text{wt}\%$), which means that the composition of the interstitial liquid inside the original refractory was homogeneous at 1600°C and quite different from that of the liquid slag. On the other hand, the evolution of the initial composition of the slag towards silica-rich contents indicates that exchange reactions between slag and refractory occur throughout the corrosion test. Across the modified area, the liquid composition presents gradients of concentration connecting the composition of the interstitial liquid in the brick to that of the slag. The most impressive fact which can be seen clearly in Fig. 6 is that regardless of the nature and composition of the slag used, the liquid composition is nearly constant at the interface separating the precipitation zone and penetration zone.

Composition profiles were also established from point analysis of glass in samples originated from quenched crucibles (Fig. 7). The data gained by this method are in good agreement with those obtained by the approach using the CaO- Al_2O_3 -SiO₂ system. However, concentration gradients in the precipitation zone are more shallow with CS slag while more pronounced with AC slag. There also, a “buffer composition” of the liquid phase ($\text{CaO} \approx 20\text{wt}\%$, $\text{Al}_2\text{O}_3 \approx 40\%$, $\text{SiO}_2 \approx 40\text{wt}\%$) can be noticed at the interface between the penetration and precipitation zones.

(4) Estimation of viscosity profiles

The viscosity profiles, estimated by means of Urbain’s model from compositional profiles established through a direct analysis of glass integrating all the elements of the slag-refractory system, are given in Fig. 8. The profiles obtained by this method are consistent with those drawn up from CAS diagram. As previously observed, the liquid viscosity is constant along the slag zone (1 Pa·s for AC slag and 3 Pa·s for CS slag) as well as in the unaffected refractory. From the refractory to the slag, a considerable decrease in the liquid viscosity is observed. As a consequence, the liquid becomes more fluid near the corrosion front and easily infiltrates into the grain boundaries leading to an intensification of the corrosion processes. However, an explanation for the lack of deep slag penetration of andalusite bricks lies in the fact that a high amount of viscous glass forms and stops slag penetration beyond the slag-refractory interface. It can also be noticed that when using either slag, liquid viscosities are practically identical (≈ 3.9 Pa·s with AC and ≈ 4.1 Pa·s with CS slag) at the interface between the precipitation and penetration zones.

(5) Theoretical approach

In a solid-liquid system, chemical exchanges occur through the liquid phase. Depending on its local composition, the liquid dissolves the solid

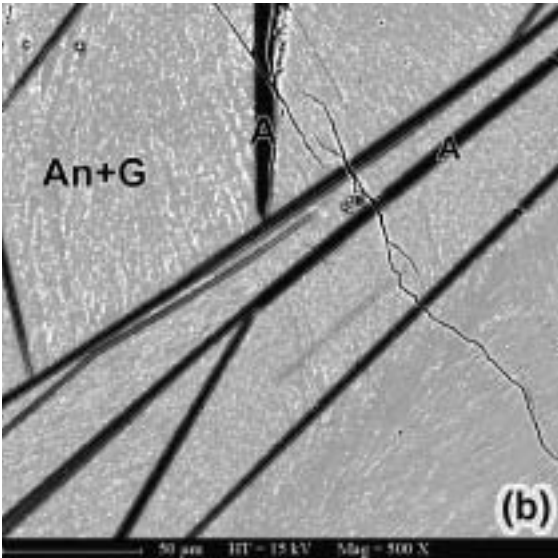
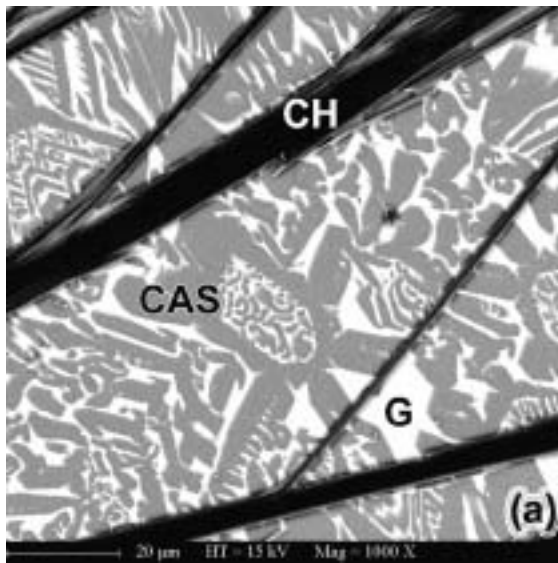


Fig. 5. BEI micrograph of the slag zone in corroded andalusite crucibles left to cool down naturally in the furnace. (a): Al_2O_3 -CaO slag ($A/C=1$); (b): CaO- SiO_2 slag ($C/S=1.25$). On micrograph (a): bright intergranular phase is residual glass (G), light grey dendrites are calcium aluminosilicates (CAS), and black phase is calcium hexaluminate (CH). On micrograph (b): black bars are corundum (A) randomly embedded in a matrix containing anorthite An (grey phase) and glass G (lighter grey areas).

phases which are not in equilibrium with it, and precipitates new phases after it becomes saturated. When solid-liquid reactions (dissolution, precipitation) are faster than chemical-transport, equilibrium motion and Gibbs rule may be locally applied to the system.

To simplify, we take as example the attack of a $3/2$ mullitized andalusite-based refractory by an Al_2O_3 -CaO model slag. The high-temperature liquid is assumed to contain only Al_2O_3 , CaO and SiO_2 . It is also assumed that concentrations of constituents are equal to their activities. The international notation was used to represent the species state: $\langle c \rangle$ means “in the solid state” and $[c]$ “dissolved in a liquid phase”. In the unaffected refractory, the liquid must be saturated with mullite, the saturation of which is defined by the equilibrium constant K_M of the reaction:

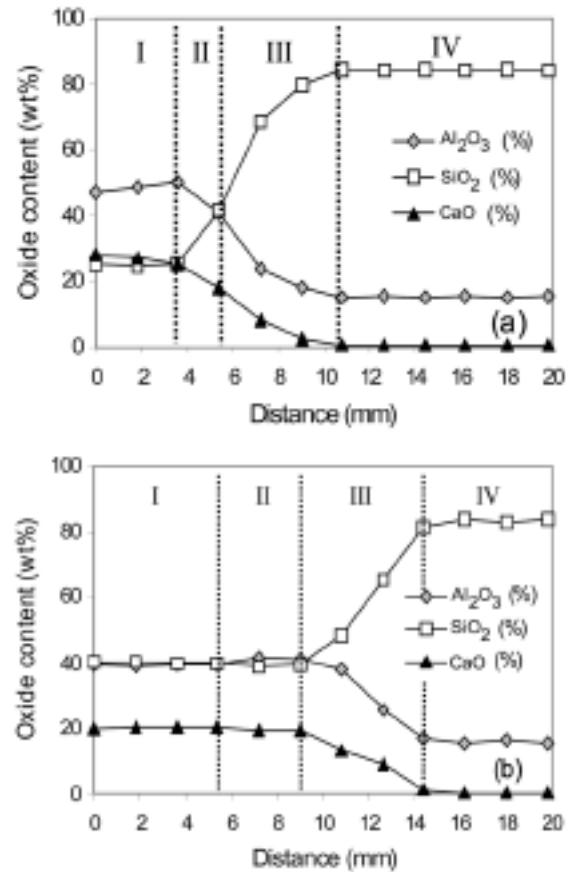
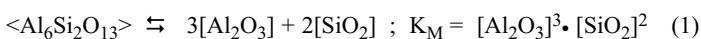
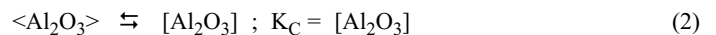


Fig. 6. Compositional profiles of liquid phases at 1600°C established from CAS diagram for the two slags AC (a) and CS (b). (I): slag zone; (II): precipitation zone; (III): penetration zone; (IV): unaffected zone. Note that $\text{CaO} + \text{Al}_2\text{O}_3 + \text{SiO}_2 = 100$ wt%, consistent with the CAS phase diagram.

At this depth, CaO did not infiltrate. Al_2O_3 and SiO_2 are then the sole constituents of the liquid. As $[\text{Al}_2\text{O}_3] + [\text{SiO}_2] = 1$, alumina and silica contents are fixed throughout the unaffected refractory. The liquid composition is then constant because the number of degrees of freedom is 0. However, in the penetration zone in which CaO infiltrates the interstitial liquid, Al_2O_3 and SiO_2 contents decrease. As a consequence, the liquid composition will not be in equilibrium with mullite which gradually dissolve until it totally disappears at the boundary separating the zones of penetration and precipitation. At the boundary, two mineral phases coexist: residual mullite and neofomed corundum from the precipitation zone. The liquid thus has to be simultaneously in equilibrium with corundum and mullite. The corundum saturation is expressed by the reaction constant expressed as follows:



When liquid is simultaneously in equilibrium with corundum and mullite (C/M equilibrium), Al_2O_3 and SiO_2 contents are both constant:

$$[\text{Al}_2\text{O}_3]_{C/M} = K_C \quad \text{and} \quad [\text{SiO}_2]_{C/M} = (K_M/K_C^3)^{1/2}$$

As the liquid contains only three species, concentration of CaO can be determined by means of the following equation:

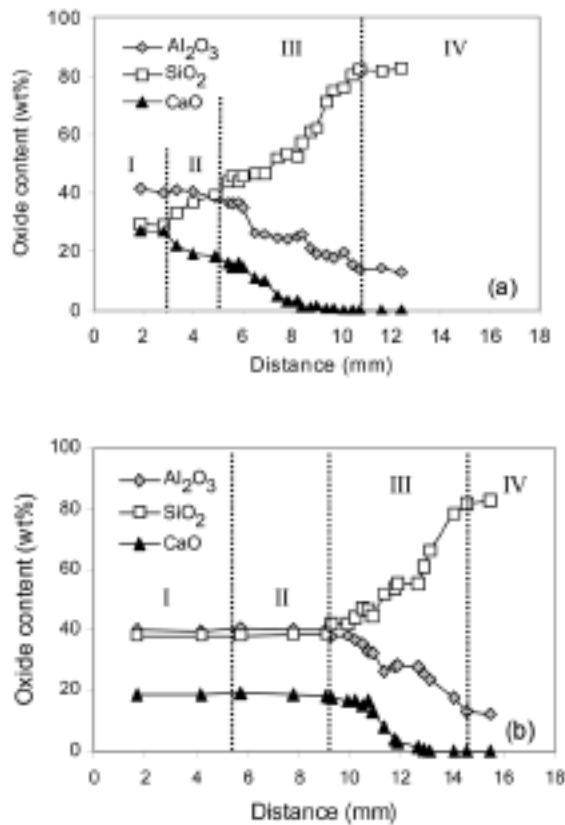
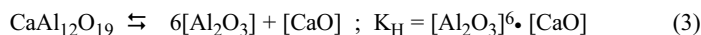


Fig. 7. Compositional profiles of liquid phases at 1600°C established from direct analysis of glass in quenched crucibles after corrosion by AC (a) and CS (b) slags. (I) slag zone; (II): precipitation zone; (III): penetration zone; (IV): unaffected zone. Note that $\text{CaO} + \text{Al}_2\text{O}_3 + \text{SiO}_2 < 100 \text{ wt}\%$ considering the presence of secondary oxides in the quenched liquid phase (glass).

$$[\text{CaO}]_{C/M} = 1 - ([\text{Al}_2\text{O}_3]_{C/M} + [\text{SiO}_2]_{C/M})$$

It thus appears clearly that the contents of the three constituents of the liquid are fixed at the interface between the zones of precipitation and penetration. This result is consistent with data obtained from composition profiles previously established (either by direct analysis of glass or using $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ diagram), that revealed the existence of a constant composition at this interface regardless of the nature of the slag. In the precipitation zone, a first monomineral layer containing corundum formed during corrosion at 1600°C is observed. Equilibrium of liquid with corundum is defined by the reaction (2) mentioned above. It follows that Al_2O_3 content is fixed in this zone ($[\text{Al}_2\text{O}_3]_C = K_C$), and concentrations of CaO and SiO_2 must inversely vary because their sum has to remain constant. It must be noted that corundum is really stable only near the surface of the refractory where it precipitates, while far from the corrosion front, it dissolves to maintain a constant Al_2O_3 content in the liquid and thus to make up for the increase in the CaO content.

At the interface between layers of corundum and CA_6 , the liquid must be saturated with these two phases, so corresponding to equilibrium between reaction (1) and the reaction expressed below:



this implies that concentrations of CaO and Al_2O_3 are defined as follows at this interface:

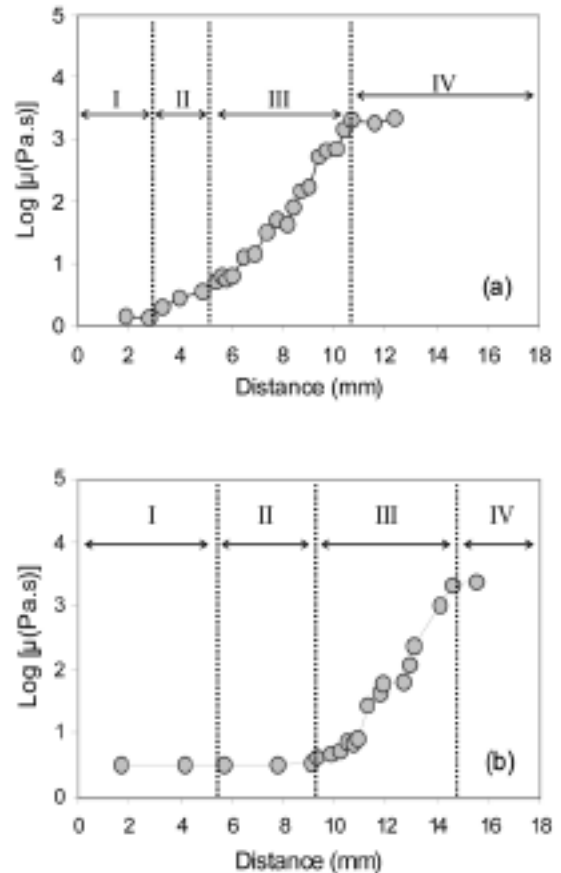


Fig. 8. Viscosity profiles of the liquid phase at 1600°C established from point analysis of glass in quenched crucibles after corrosion by AC (a) and CS (b) slags. (I): slag zone; (II): precipitation zone; (III): penetration zone; (IV): unaffected zone.

$$[\text{Al}_2\text{O}_3]_{C/H} = K_C \quad \text{and} \quad [\text{CaO}]_{C/H} = K_H / K_C^6$$

As $[\text{Al}_2\text{O}_3] + [\text{CaO}] + [\text{SiO}_2] = 1$, the SiO_2 concentration is also determined at the interface. Further, along the CA_6 layer, concentrations of Al_2O_3 , CaO and SiO_2 are variable up to the slag zone where they become constant.

IV. Conclusion

The unaffected zone of an andalusite-based brick mainly contains coarse grains of mullitized andalusite, bonded by a porous matrix made of mullite and silica-rich glass. In all static crucible tests, the corrosion profiles observed display the same succession of zones whose textures are different: unaffected refractory → penetrated zone → precipitation zone → remaining-slag zone. Furthermore, according to the slag composition, the precipitation zone may contain one or several monomineral layers. This vertical zonation will be observed for all types of CAS slags

It was also noticed that the resistance to slag corrosion of andalusite-based refractories is governed by the evolution of the liquid-slag composition at service temperature: the higher the SiO_2 content, the lower the dissolution rate of mullite.

On the other hand, experimental data related to the liquid phase, gained either from the point analysis of glass in quenched crucibles or using the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system based on local equilibrium criteria, indicate that at 1600°C:

- concentration gradients, which are the driving force of corrosion

processes at high temperature, exist and link the composition of interstitial liquid in the unaffected refractory to that of the slag, and

- at the interface between the penetration zone and precipitation zone, the composition of the liquid is constant regardless of type and composition of the slag used.

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