CORROSION RESISTANCE
OF HIBONITE BASED LOW CEMENT CASTABLE
AGAINST BIOMASS SLAG

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ABSTRACT

Refractory linings used in incinerators for energy production have to adapt to the energy transition, where fossil fuels tend to be replaced by biomass, exposing the lining to different ranges of chemical compositions. The use of alternative combustibles impacts the life expectancy of the refractory products due to corrosion reactions, whose complexity originates in the variety of the biomass sources. Andalusite, Al_2O_3-Cr, or SiC based refractory products have been heretofore used in incinerators, however refractory containing hibonite ($CaO·6Al_2O_3$) could be an alternative, because of its high refractoriness and high resistance against alkali attack. This work aims to describe and understand the chemical resistance brought by the presence of hexaaluminate of lime in a Low Cement Castable (LCC).

In order to outline the degradation mechanisms induced by biomass, this study focuses on the impact of wood ash and aims to understand the effect of its main oxides, namely CaO, SiO_2 and K_2O on the high temperature corrosion. Therefore, model slags were synthetized to isolate the influence of the different chemical species and enable the comparison with the effects observed by corrosion with the original wood slag. The reaction of hibonite with the model slags were characterized by means of ex-situ XRD performed on the ground refractory powder mixed with the slag. Furthermore, a formulation of LCC was designed with the hibonite raw materials, whose grain size ranges from 0-3 mm, to evaluate the resistance to reactive infiltration of a calcium hexaaluminate based refractory product. The LCC was put in contact with molten slag at high temperature in order to study the dissolution behavior through post-mortem SEM examinations performed on quenched microstructures. Due to its high chemical resistance against different biomass slag compositions, the use of hibonite in the formulation of refractory castables could be a solution to prevent early breakdown of refractory lining, with high performance against the aggressive environment of biomass incinerators.

Keywords: biomass, corrosion, slag, calcium hexaaluminate, alkali, microstructure

INTRODUCTION

During the combustion of biomass to produce energy, the mineral content of the fuel deposits on the incinerator wall through slagging or fouling, leading to corrosion issues of the refractory lining [1]. The energy transition challenges refractory producers, due to the difference of physical and thermal properties between fossil fuels and biomass. Indeed, the inorganic matter of coal is mainly composed of SiO_2 and Al_2O_3 with low variations of the ash composition, while the biomass residues are composed of SiO_2 and CaO with really high amount of K_2O and P_2O_5, which can reach respectively 60 wt.% and 40 wt.% of the ash content, depending on the biomass variety [2]. The combination of high amount of corrosive species and the broad diversity of the mineral composition of the biomass complicate the optimization of refractory material toward an improved corrosion resistance.

To overcome the corrosive attack of alkalis in biomass incinerators, calcium hexaaluminate, with the mineralogical name hibonite, has already shown promising performance in comparison with alumina based refractory products, usually used for this application [3]. In the contact with alkalis, α-alumina reacts to form β-alumina, for instance $K_2O·11Al_2O_3$ in the case of potassium, with a high volume expansion of 26,4%. The calcium hexaaluminate also reacts to form β-alumina, however $CaO·6Al_2O_3$ and $K_2O·11Al_2O_3$ have similar densities and the reaction does not lead to a volume expansion, preventing an explosive spalling and damaging of the refractory product [4].

This work aims at introducing hibonite based refractory raw materials in a Low Cement Castable (LCC) to examine the corrosion mechanisms with molten wood ash at high temperature. Therefore, simplified slag compositions will be prepared as well, to decompose the mechanisms and try to isolate the effect of the main oxides present in the ash, namely CaO, SiO_2 and K_2O. The dissolution of calcium hexaaluminate in CaO-SiO_2 slags was already studied by Vásquez et al., and the main corrosion process was found to be the penetration of the slag through porosity and grain boundaries, coming with the dissolution of the $CaAl_{12}O_{19}$, as well as the formation of calcium dialuminate $CaAl_4O_7$ and gehlenite $Ca_2Al_2SiO_7$[5].

EXPERIMENTAL PROCEDURE

Refractory samples elaboration

For the corrosion test, a Low Cement Castable (LCC) composition was formulated with hibonite based raw materials provided by Almatis, composed of 91wt.% Al_2O_3, 7,6 wt.% CaO and 1,3 wt.% impurities. The aggregates were chosen with a grain size ranging from 0-3mm (82,5 wt.%). The bonding was ensured with calcium aluminate cement (7%) from Kerneos mixed with the same amount of water and deflocculant FS65 (0,15 wt.%) from BASF. Reactive alumina (12,5 wt.%) from Alteo was added as well to react with the cement and further form calcium hexaaluminate. The samples were sintered at 1500°C for 6h with a heating and cooling rate of 2K/min. The technological properties of this castable were not taken into account in this study, which is focusing on the reaction mechanisms.

Slag synthesis

The corrosion resistance of hibonite based material was tested against a wood ash slag, whose composition is depicted in Tab. 1, according to X-Ray Fluorescence (XRF) measurements. This slag was compared with two model slags: One binary slag composed of CaO and SiO_2 and a ternary slag with CaO, SiO_2 and K_2O. The targeted compositions are pictured in Tab.2.

Tab. 1: Chemical composition of the wood ash

Denomination	CaO	SiO$_2$	K$_2$O	MgO	P$_2$O5	MnO	SO$_3$	Other oxides
WA	50 wt.%	5 wt.%	17 wt.%	9 wt.%	7 wt.%	5 wt.%	4 wt.%	3 wt.%

Tab. 2: Chemical compositions of the model slags

Denomination	CaO	SiO$_2$	K$_2$O
CS	50 wt.%	50 wt.%	/
CSK	40 wt.%	40 wt.%	20 wt.%

The model slag C4S6 was prepared by mixing limestone (CaCO$_3$) and quartz sand (SiO$_2$) <500µm. The powder mix was first calcined at 1000°C for 12h for decarbonation. The model slag C4S6K was prepared by mixing C4S6 and a commercial powder of potassium carbonate (K$_2$CO$_3$). The K$_2$CO$_3$ containing slag was not decarbonated again, since alkalis carbonates are the typical salts found in incinerators. The composition and homogeneity of the slags were controlled with Scanning Electron Microscope coupled with Energy Dispersive Spectroscopy (SEM-EDS).

The melting temperatures of each slag was determined with hot stage microscopy (Tab. 3) according to the European standard DIN 51730.

Tab. 3: Melting temperature of the slags

Denomination	Melting temperature
WA	1455°C
C4S6	1460°C
C4S6K	1280°C

Phase characterization

Different ex-situ characterization of the corrosion reactions were performed:

- On powders, by mixing hibonite powder with grain size <45µm and slag powder in ratio 85:15
- On hibonite LCC, by heating a parallelepipedic sample of 12,5x25x50 mm^3 of the refractory castable in contact with 5 g of slag

The ex-situ reaction tests were performed at 1550°C for one hour and the samples were quenched in water at room temperature in order to preserve the high temperature microstructure and phase composition. The LCC samples were polished and examine with Scanning Electron Microscope (SEM), while the powders were grounded <63µm to be characterized with X-Ray Diffraction (XRD).

RESULTS AND DISCUSSION
Determination of corrosion mechanisms with model slags

To determine the corrosion products formed by the reaction of hibonite based raw material and slag, the XRD patterns performed on powder mixes were used (Fig. 1). The XRD of the raw material prior to corrosion shows mainly hibonite (CA6) and traces of corundum (A), calcium dialuminate (CA2) and β-alumina (β-A) (Fig. 1a). The β-alumina contained in the raw material is assumed to be formed by the impurities coming from the production process, like Na$_2$O. The corundum and grossite from the refractory powder react further with CaO from the slag to form hibonite (CA6), which remains as the only crystalline phase in the sample (Fig.1b). Trough addition of K$_2$O in the slag, the formation of β-alumina (β-A) is enhanced. Reflexes of calcium dialuminate (CA2) and hexaaluminate (CA6) are visible as well (Fig. 1c).
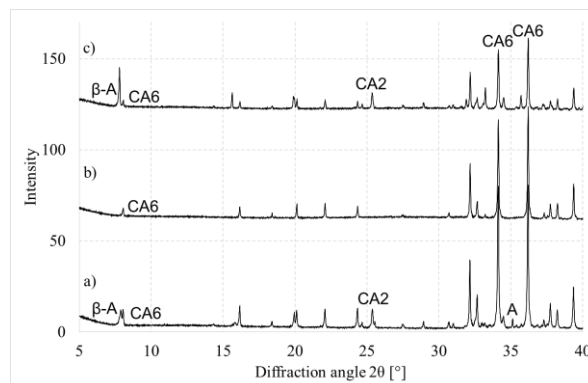

Fig. 1: XRD-patterns of hibonite powder
a) prior to testing
b) after 1h at 1550°C with CS
c) after 1h at 1550°C with CSK

The results testify the formation of beta alumina during the reaction of hibonite with alkali containing slags. To further witness the formation of those phases, the microstructure of the corroded LCC was observed with SEM, and EDX was used to define the chemical composition of the different crystals observed.

The microstructural examination revealed the complete diffusion of the slag elements CS and CSK through the LCC samples, since SiO$_2$ and respectively SiO$_2$ and K$_2$O were measured on the side of the sample which was not in contact with the slag (Tab.4). No interface remain between the slags and the refractory samples.

Tab. 4: Composition of the LCC measured with EDX 10mm from the slag interface in a surface of 5mmx1mm.

[Wt.%]	Al$_2$O$_3$	SiO$_2$	K$_2$O	CaO
with CS	78,78	8,17	-	12,46
with CSK	83,29	3,86	0,74	12,11

During the corrosion of the LCC sample with CS slag, the calcium hexaaluminate (CA6) and corundum grains could be observed in the corroded microstructure, surrounded by a liquid phase (Fig.1).
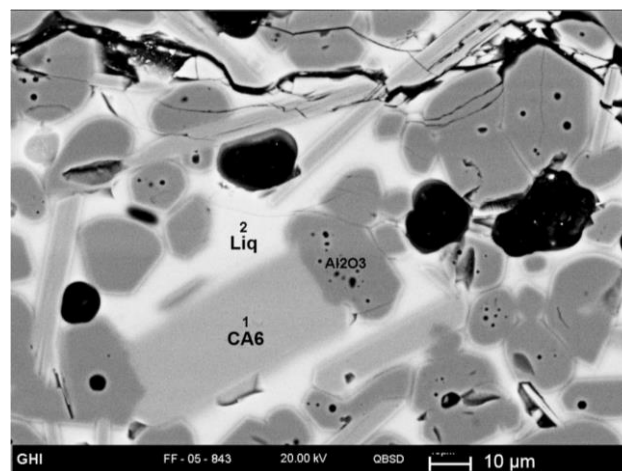

Fig. 2: Micrograph of the hibonite rich castable after being in contact with the slag CS at 1550°C for 1h

After corrosion with CSK, calcium dialuminate (CA2) could be observed, surrounded by hibonite grains (CA6) and liquid phase (Fig.3).
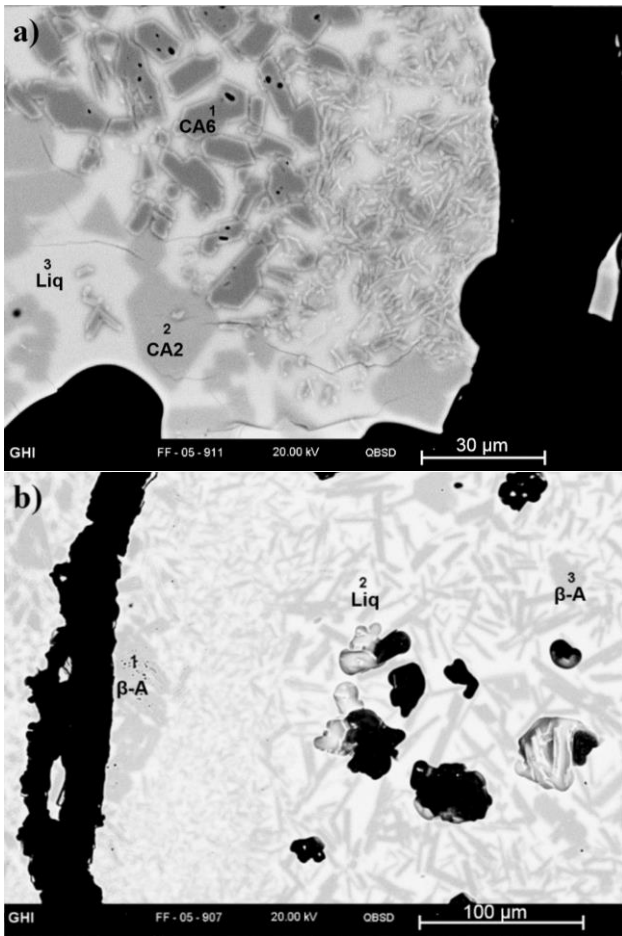

Fig. 3: Micrographs of the hibonite rich LCC after being in contact with the slag CSK at 1550°C for 1h

In the case of the alkali containing slag, the contact of hibonite with K_2O leads to the formation of $K_2O \cdot 11Al_2O_3$, which can be difficult to determine as corrosion product with XRD, due to the presence of $Na_2O \cdot 11Al_2O_3$ with the same crystal structure in the raw material. However the EDX measurement allowed to observe the $K_2O \cdot 11Al_2O_3$ crystals in the microstructure (Fig. 3b). Through this reaction CaO from the calcium hexaaluminate is released in the liquid phase, where precipitation of calcium dialuminate was observed (Fig. 3a).

As found in the literature [5], it could be observed that the infiltration of hibonite with $CaO-SiO_2$ slag occurs mainly through the open porosity and the grain boundaries. It was also noticed that the remaining corundum and calcium dialuminate of the raw materials together with calcia from the slag tend to form further calcium hexaaluminate.

Comparison of the corrosion mechanisms with molten wood ash

To compare the phases formed during reaction with molten wood ash and model slags, the XRD performed on the corroded hibonite rich LCC were used (Fig. 4). After sintering, the LCC exhibit approximatively the same mineralogical composition as the hibonite raw material with mainly calcium hexaaluminate, rest of calcium dialuminate and β-alumina, but no corundum was detected (Fig. 3a). After corrosion with CS, calcium hexaaluminate (CA6) and corundum (A) are remaining (Fig. 4c), in agreement with the microstructural examination (Fig. 1). After corrosion with CSK, the LCC is composed of mainly calcium

hexaaluminate (CA6) and dialuminate (CA2) (Fig. 3d). Reflexes of β-alumina were found, however with lower intensities as for the powder reaction (Fig.1c).
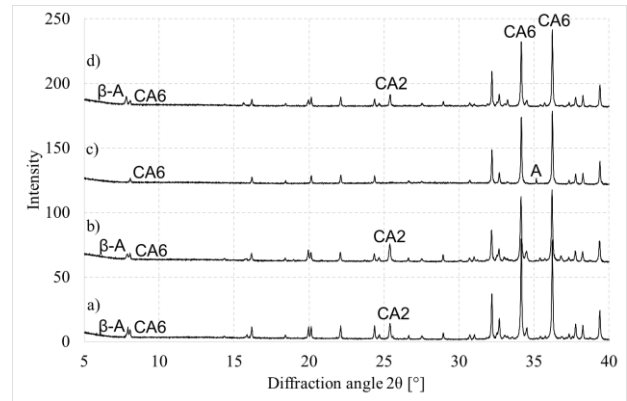

Fig. 4: XRD-patterns of hibonite rich LCC
a) prior to testing
b) after 1h at 1550°C with WA
c) after 1h at 1550°C with CS
d) after 1h at 1550°C with CSK

The phases found after corrosion with the molten wood ash are qualitatively similar to the phase composition of the LCC prior to corrosion and to the LCC after corrosion with CSK, with major presence of hibonite (CA6) and grossite (CA2) with low amounts of β-alumina (Fig. 3a). However, the SEM examination of the corroded LCC sample revealed a high differentiation in the microstructure and the corrosion mechanisms (Fig. 5).
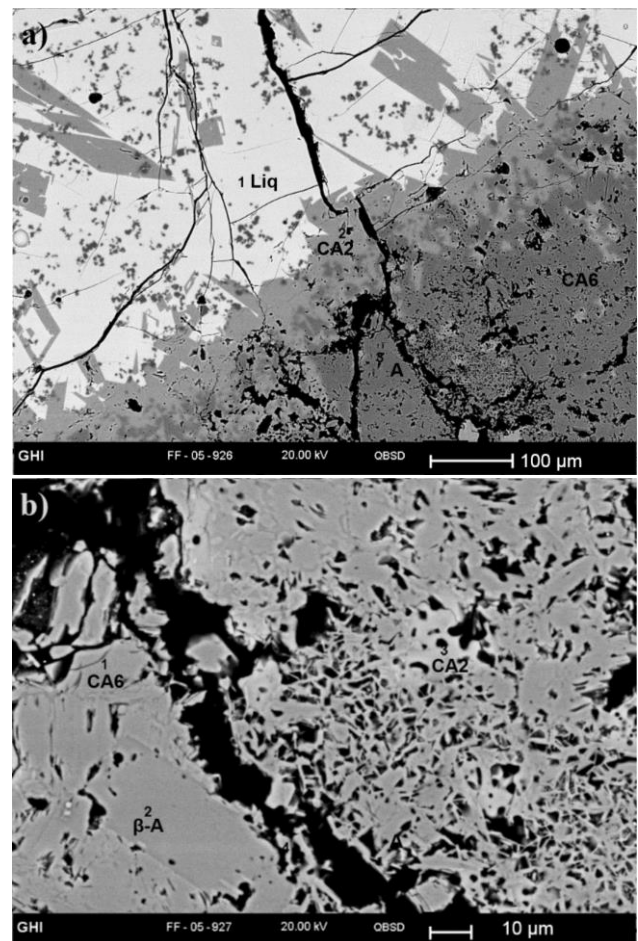

Fig. 5: Micrographs of the hibonite rich LCC after being in contact with the slag WA at 1550°C for 1h

During the corrosion with wood ash, the elements of the slag could be measured with EDX up to 2 mm from the interface, respectively 3 mm for K_2O which has diffused the deepest in the refractory sample. The interface between slag and refractory is strongly pronounced (Fig. 5a), and a layer of 100 µm composed of grossite (CA2) is formed at this interface, preventing further reaction. The slag area above the interface is mostly composed of liquid phase, whose composition is compared with the liquid phases found in the samples corroded with model slags (Fig. 6)
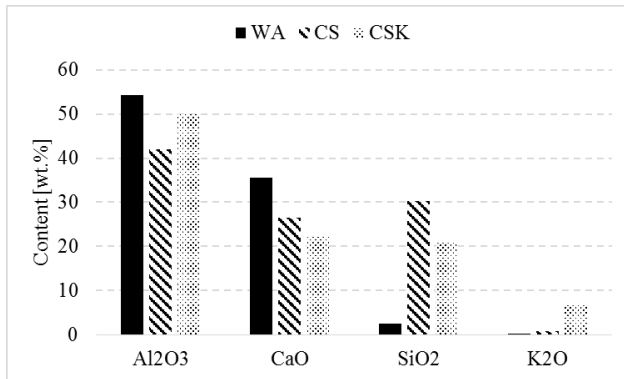

Fig. 6: Composition of the intergranular amorphous phase

The amorphous phase found after corrosion with wood ash showed a high content of Al_2O_3 of 55 wt.%, while the of Al_2O_3 content of the ash is <1 wt.%. The matrix was locally dissolved and enriched the liquid phase with Al_2O_3, which reacted with the high amount of CaO contained in the slag to precipitate grossite (CA2) at the interface (Fig. 5a). The strong amount of Al_2O_3 in the liquid phase was observed as well with the model slags, confirming the partial dissolution of hibonite. The ratio between CaO and SiO_2 is approximatively the same in the liquid phase as the one in the slag, of 10 for the wood ash and of 1 for the model slags, confirming that the precipitation of calcium dialuminate occurs through the CaO from the refractory previously dissolved in the slag. Potassium could be observed beyond the reaction layer, where β-alumina crystals were found surrounded by hexaaluminate and dialuminate of calcium. The EDX measurements of the β-alumina composition revealed high impurities contents (Tab. 5).

Tab. 5: Composition of ß-alumina crystals measured with EDX, respectively from Fig. 3b and Fig. 5b

[Wt.%]	Na_2O	MgO	Al_2O_3	K_2O	CaO	MnO
with CSK	-	-	90,58	8,27	0,79	-
with WA	0,76	2,34	89,79	5,10	1,58	0,42

CONCLUSION

The comparison between a binary and ternary model slag was efficient to determine the effect of the K_2O in the corrosion of hibonite based material. The corrosion with $CaO-SiO_2$ slag leads to the further formation of hibonite as revealed with the XRD, parallel to the dissolution of the matrix as seen with SEM-EDX. By adding K_2O to the slag, the main mechanisms are the dissolution of the matrix and the formation of β-alumina, supplementing the liquid phase in CaO. The hibonite grains are then surrounded by a CaO-rich liquid phase and their dissolution leads to the precipitation of grossite crystals. No explosive spalling of the LCC samples corroded with the ternary slag was observed, confirming that the β-alumina formation with hibonite as reagent does not come with a volume expansion.

Whereas the same mineralogical composition could be observed in the LCC after corrosion with the ternary model slag

and the wood ash, the SEM revealed distinct corroded microstructures. For the ternary $CaO-SiO_2-K_2O$ slag, as well as for the molten wood ash, the dissolution and reaction of hibonite leads to the precipitation of grossite from the melt- However, the model slag infiltrates the whole refractory sample, due to its low viscosity, and the precipitation of calcium dialuminate is occuring locally in the intergranular liquid phase. During corrosion with molten wood ash, the grossite precipitates at the interface between slag and refractory, lowering the diffusion kinetics and preventing further infiltration of the slag.

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