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Degradation of aluminosilicate refractories: An integrated approach

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ABSTRACT

The aim of this work is to track neogenic minerals and microstructures in degraded aluminosilicate refractories. Six samples are used to represent the low, moderate and high alumina bricks and low-cement castables as working linings. In addition, a steelmaking converter slag is used as the attacking agent/medium. The samples are characterized using XRD, XRF, polarized light microscopy, cathodoluminescence, X-ray micro-computed tomography (3D- μ XCT) and SEM microscopy attached with EDAX. Non-refractory neogenic anorthite and augite appear as synthetic doleritic texture in the attacked matrix. As well, neogenic hercynite spinel is formed together with pseudobrookite as precipitates on the corundum and anorthite, respectively. The pore size distribution is affected differentially in the attacked areas. Such effects are related to the slag aggressiveness, the shape of pores and the microstructure of the samples before the attack. The ANOVA-Post Hoc analyses showed that castable materials can replace the bricks with no change in the properties of the slag attack resistance.

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1. Introduction

Refractories are those ceramic materials used to line industrial high temperature kilns to protect them from thermal, mechanical and chemical corrosions that can occur separately or together [1–3]. Traditional aluminosilicate refractories are of widespread use, especially in the iron and steel making industry which uses ~70% of all refractories [4,5].

The aluminosilicate refractory linings are classified based on shape into shaped bricks or blocks and un-shaped monolithics or castable linings. The manufacture of both linings is mainly based on refractory kaolinitic clays. In addition, calcined Al_2O_3 -rich materials, such as sillimanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) and gibbsite [$\text{Al}(\text{OH})_3$], are added to the calcined kaolinitic clays to raise their alumina content [6–8].

There are three main groups of aluminosilicate bricks: fire-clay (25–45 wt.% Al_2O_3), aluminous fireclay (45–65 wt.% Al_2O_3) and high alumina (>72 wt.% Al_2O_3). The latter group is subdivided into three subgroups: mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) and

corundum (Al_2O_3) with Al_2O_3 contents of 72–80 wt.%, 80–90 wt.% and >90 wt.%, respectively [8,9]. The aluminosilicate castables are classified based on the content of high alumina cement (HAC) as a mineral grain matrix. There are four types of aluminosilicate castables: the conventional castables (CC) (10–25 wt.% HAC); low-cement castables (LCC) (5–8 wt.% HAC); ultra-low cement castables (ULCC) (1–4 wt.% HAC) and No-cement castables (NCC) (0 wt.% HAC). ULCC and NCC castables have been addressed by several authors [8,10–16].

Compared to rigid-shaped bricks, the castables are more economical and easier to use. The castables have: (a) low production cost; (b) high installation efficiency; (c) high safety; (d) low material consumption; (e) conformance to geometrically complex shapes and (f) overcome geometrical disorder among the brick linings joints that appear with long use in furnaces [17–22].

The main major constituents in aluminosilicate bricks and castables are alumina (Al_2O_3) and silica (SiO_2), with traces of other oxides. The contents of TiO_2 , Fe_2O_3 , CaO , MgO , P_2O_5 and alkali oxides are mainly derived from the raw kaolinites and bauxite together with HAC. These minor oxides affect the refractory linings performance [23,24]. The latter oxides are considered as total impurity oxides (TIO) and act as fluxing material for the major Al_2O_3 and SiO_2 components. Therefore, the various types of the alumi-

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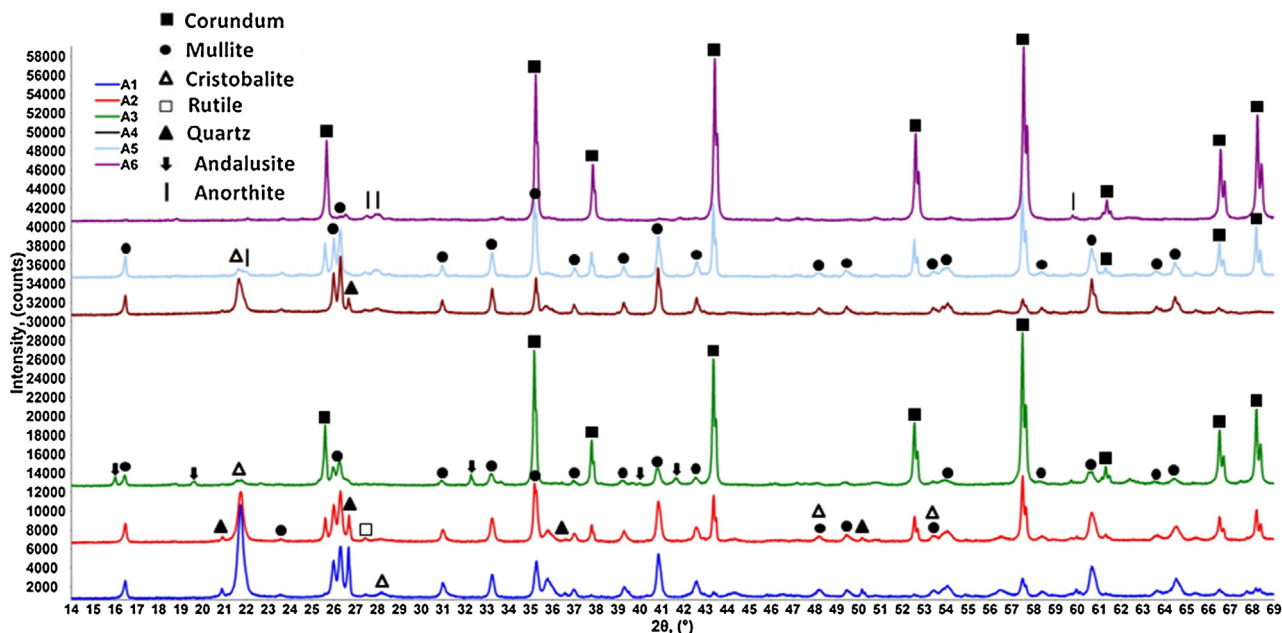


Fig. 1. XRD charts of the investigated bricks and castables samples.

Table 1
 Calcined based chemical composition of all studied samples and liquid phase contents of the castables. M: mullite; C: corundum; Cr: cristobalite; Q: quartz; An: anorthite; R: rutile; And: andalusite; Al-Ti: Al-titanate; Al-Ph: Al-phosphate.

Sample	Calculated mineral composition using Rietveld, (wt.%)									Chemical composition on calcined base, (wt.%)										Liquid content, (wt.%)			
	M	C	Cr	Q	An	R	And	Al-Ti	Al-Ph	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO	A/S molar ratio	1300 °C	1400 °C	1500 °C
A1	59.7	1.5	31.9	6.6	0.0	0.3	0.0	0.0	0.0	56.2	36.8	1.9	2.0	0.4	0.3	0.1	0.3	2.2	7.1	0.4	n.d.	n.d.	n.d.
A2	55.9	21.6	16.7	3.4	0.6	0.8	4.8	0.0	1.0	40.2	51.0	2.6	2.8	0.7	0.2	0.1	0.4	2.2	8.9	0.8	n.d.	n.d.	n.d.
A3	27.7	60.5	0.9	0.5	0.0	0.3	0.0	0.0	1.7	18.1	71.4	2.9	2.4	0.2	0.1	0.0	0.3	4.7	10.5	2.3	n.d.	n.d.	n.d.
A4	74.3	0.9	18.5	2.0	3.8	0.5	0.0	0.0	0.0	53.0	38.1	2.6	1.6	4.1	0.1	0.2	0.1	0.1	8.8	0.4	18.4	20.6	28.8
A5	53.2	34.4	3.4	0.4	7.9	0.6	0.0	0.0	0.0	36.2	55.9	2.9	1.7	2.4	0.2	0.2	0.3	0.2	8.0	0.9	16.3	17.1	19.7
A6	2.0	86.3	0.0	0.0	8.1	0.6	0.0	3.1	0.0	18.8	71.3	3.8	2.1	2.3	0.3	0.2	0.7	0.5	10.0	2.2	14.6	16.4	17.6
Slag	n.d.*	5.8	0.5	0.1	37.6	37.4	1.4	0.0	0.0	6.5	n.d.	n.d.	n.d.	n.d.	n.d.								

*n.d.: not-determined.

Table 2
 Chemical composition of measured points by EDAX. (1) mullite grain; (2) mullite in the groundmass; (3) corundum grain; (4) corundum in the groundmass; (5) anorthite; (6) rutile; (7) glassy phase; (8) Al-titanate; (9) corundum; (10) Ti-rich iron oxide; (11) anorthite; (12) augite; (13) Fe-rich titanium oxide (pseudobrookite); (14) anorthite; (15) hercynite; (16) corundum; (17) hercynite; (18) hercynite; (a) ferroan hibonite-5 h; (b) SFCAM; (c) SFCAM; (d) gehlenite; (e) gehlenite; (f) spinel; (g) spinel.

Element	Elemental concentration of points measured by EDAX, (wt.%)																								
	Non-attacked areas									1:1 Slag/refractory mixes						Slag-attacked areas									
	1	2	3	4	5	6	7	8	9	a	b	c	d	e	f	g	10	11	12	13	14	15	16	17	18
O	26.8	51.2	38.1	40.4	41.3	37.6	45.2	40.5	41.9	49.8	68.2	72.4	69.1	71.8	54.6	68.3	32.7	36.8	41.1	38.2	46.3	40.4	48.2	35.2	36.3
Si	15.9	22.3	n.d.	7.0	23.7	0.9	32.6	0.4	0.5	0.6	0.3	1.5	2.3	3.8	n.d.	n.d.	2.0	20.7	8.5	0.9	17.3	1.5	n.d.	1.1	0.6
Al	45.2	23.6	61.9	44.7	14.0	0.9	10.4	28.6	55.3	37.7	22.1	9.3	15.7	9.8	18.8	14.4	5.4	22.9	7.0	4.2	19.6	30.1	51.8	29.5	16.0
Fe	3.0	0.6	n.d.	1.2	2.4	2.7	1.2	4.6	0.8	5.5	3.6	8.5	2.8	1.4	14.5	8.6	47.3	1.5	2.6	24.9	0.9	14.5	n.d.	19.5	31.1
Ca	2.8	0.4	n.d.	1.8	10.5	0.6	6.3	0.0	0.1	4.8	4.3	5.8	9.4	13.2	0.3	0.2	1.2	18.1	4.5	0.5	14.9	4.6	n.d.	5.4	5.5
Mg	0.9	n.d.	n.d.	n.d.	0.7	n.d.	0.6	0.3	0.5	0.7	0.5	0.6	0.3	n.d.	6.3	5.2	0.8	n.d.	6.5	1.4	n.d.	2.1	n.d.	1.9	3.0
Mn	*n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	0.2	0.0	0.4	0.3	1.1	0.2	n.d.	5.1	3.2	2.1	n.d.	15.2	1.5	n.d.	1.2	n.d.	1.5	7.5
P	1.1	n.d.	n.d.	n.d.	0.5	n.d.	0.5	0.2	0.6	n.d.	0.3	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12.4	n.d.	n.d.	0.5	n.d.	0.4	n.d.
Na	n.d.	n.d.	n.d.	n.d.	0.7	n.d.	0.8	0.2	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.4	1.6	n.d.	1.0	n.d.	n.d.
K	0.8	n.d.	n.d.	0.7	2.2	0.2	0.4	0.0	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.0	0.4	0.3	0.1	n.d.	0.1	n.d.
S	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ti	3.1	1.8	n.d.	4.1	4.0	55.5	2.2	24.9	0.2	0.5	0.5	0.3	0.3	n.d.	n.d.	n.d.	8.4	n.d.	0.4	26.5	0.5	3.5	n.d.	4.6	n.d.
Zr	n.d.	n.d.	n.d.	n.d.	n.d.	1.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.4	n.d.	n.d.	n.d.	n.d.	n.d.
F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
V	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

*n.d.: not-determined.

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