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Mullite-based refractory castable engineering for the petrochemical industry

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Abstract

Refractory castables used in fluid catalytic converter (FCC) risers should present suitable particle erosion and thermal shock resistances at temperatures below 900 °C. Considering that calcium aluminate cement (CAC)-bonded refractories usually start their densification above 1200 °C, the use of sintering additives to induce faster densification is a promising technological alternative. Therefore, this work addresses the evaluation of mullite-based castables containing a boron-based sintering additive and CAC and/or hydratable alumina as the binder sources. Hot elastic modulus, cyclical thermal shock, hot modulus of rupture and cold erosion resistance measurements were carried out to evaluate the compositions. According to the attained results, adding 1.5 wt% of the evaluated sintering additive to the designed castables led to a remarkable increase of the hot modulus of rupture (maximum of 40.4 MPa at 800 °C for the CAC-containing refractory) and high erosion resistance (1.5–2.9 cm^3) after pre-firing at 800 °C for 5 h. Moreover, the combination of CAC and hydratable alumina gave rise to an improved refractory (M–2CAC–2HA–S) showing a transient liquid formation at an increased temperature, high thermal shock resistance (no E decay after 8 thermal cycles, $\Delta T = 800$ °C) and high mechanical strength at 800 °C and 1000 °C.

Keywords: D. Mullite; Binder; Refractory castables; Sintering additive

1. Introduction

The growing demand for refractory castables with designed properties has brought about continuous technological development involving the simultaneous understanding of particle size distribution, the use of additives (inducing better dispersion of particles in aqueous medium [1,2], speeding up the compositions' densification [3,4], etc.) and the binders' performance [5–8].

Refractory castables applied in risers for petrochemical fluid catalytic converters (FCC, Fig. 1) are commonly exposed to temperature fluctuations and mainly to high speed catalyzer particles [9]. Therefore, thermal shock and particle erosion resistances are some of the main requirements for this application. Additionally, these castables should present optimized properties around 800 °C but, depending on the working conditions, some regions of the refractory lining can reach peaks of temperature close to 1200 °C. Hence, as most commercial cement-bonded castables show densification only at temperatures above 1200 °C, a different composition approach should be designed to match the refractory's performance requirements for the petrochemical industries [3].

Considering the increasing interest in the development of refractories presenting optimized hot mechanical strength in the range of 800–1200 °C, as well as the necessity for using less dense compositions due to the risers´ geometry (the height/diameter ratio usually ranges between 30 and 50 times [9]), there is a continuous motivation for the design of novel castable formulations to better fulfill those needs, maintaining high erosion and thermal shock resistances.

In order to attain refractories with enhanced properties at high temperatures, calcia-free binders [i.e., hydratable alumina (HA), colloidal silica and colloidal alumina] containing castables have been developed [3,10,11]. For densification at temperatures close to 800 °C, previous studies [3,4] pointed out that an interesting alternative based on using sintering

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additives led to liquid formation and, consequently, faster densification of refractories containing CAC or colloidal binders (silica or alumina). Nevertheless, selecting these additives should be tailored, as a liquid phase can result in refractoriness drawbacks. High alumina and mullite compositions containing calcium aluminate cement and 2 wt% of a boron-based sintering additive, for instance, presented remarkable hot mechanical strength, thermal shock and erosion resistances at 800 °C. Nevertheless, above this temperature, the presence of a liquid phase resulted in a significant decrease of the hot modulus of rupture of those materials [4].

Various studies have shown that HA bonded castables present high refractoriness. However, similar to CAC, it does not provide good mechanical strengths at temperatures below 1200 °C [11–14]. Based on these aspects, the aim of this work was to evaluate mullite refractory castables designed for petrochemical applications containing a boron-based sintering additive and CAC and/or hydratable alumina (HA) as the binder sources. Hot elastic modulus tests (using the bar resonance method) were carried out in order to follow the phase transformations in dried (110 °C for 24 h) and fired (1000 °C for 5 h) samples with and without a holding time of 5 h at 1000 °C. Furthermore, apparent porosity, hot modulus of rupture, erosion resistance and XRD quantitative analysis of the crystalline phases contained in the samples were also performed for a better understanding of the refractories' behavior.

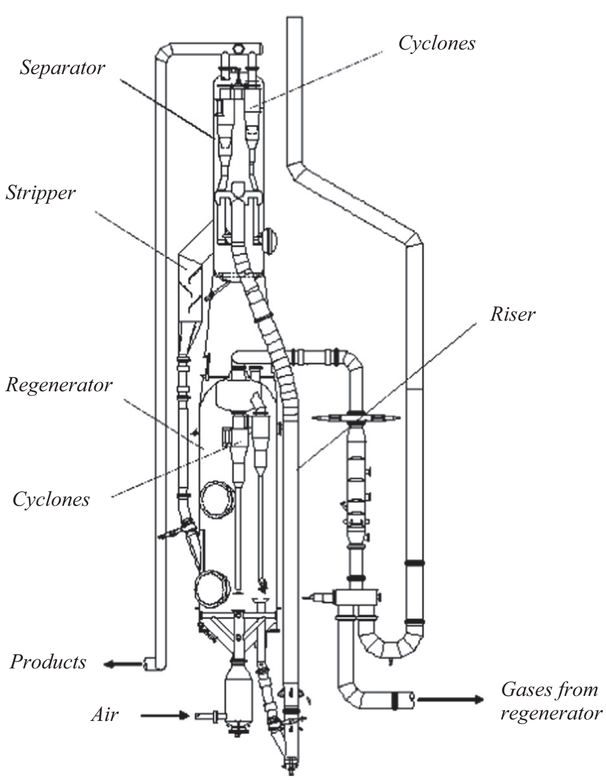

Fig. 1. Typical features of a petrochemical fluid catalytic converter unit — FCCU [9].

2. Experimental

Four self-flowing mullite based castables were designed according to Alfred's packing model (q=0.21) [15]. The compositions comprised coarse synthetic mullite (Mulcoa 70, Al_2O_3=69 wt% and SiO_2=27 wt%, Treibacher, USA) as aggregates, calcium aluminate cement (CAC, Secar 71, Kerneos, France) or hydratable alumina (HA, Alphabond 300, Almatis, USA) as binders, reactive aluminas (CL370C and CT3000SG, Almatis, USA) and a boron-based additive ($d < 45$ μm, S, under patent application) in order to speed up the densification of the refractories in the usual temperatures for petrochemical applications (~800 °C for FCC risers) [3,4]. A sintering additive-free composition (M–4CAC) was also prepared and tested as a reference. Table 1 presents further details of the formulated castables.

The castable dispersion was carried out by adding 0.2 wt% of a polycarboxylate based dispersant (Basf, Germany), leading to 5.8–6.2 wt% water content for suitable shaping (free-flow values = 62–68%). The compositions were prepared in a rheometer especially developed for refractory castables, by adding the mixing water using a two-step procedure [16].

After the mixing step, prismatic samples (150 mm × 25 mm × 25 mm) were molded, cured at 50 °C for 24 h in a humid environment (relative humidity = 80% for castables containing CAC: M–4CAC, M–4CAC–S and M–2CAC–2HA–S, whereas the M–4HA–S samples were kept in a chamber without humidity control), dried at 110 °C for another 24 h, followed by firing at 600, 800, 1000 and 1200 °C for 5 h in electrical furnace (Lindberg Blue, Lindberg Corporation, USA).

Hot modulus of rupture (HMOR) tests were carried out at 600 °C, 800 °C, 1000 °C and 1200 °C (using samples pre-fired for 5 h at the same testing temperature) in HBTS 422 equipment (3-point bending test, Netzsch, Germany) based on the ASTM C583-8 standard. The apparent porosity of the fired samples was measured by the Archimedes method (ASTM C380-00), using kerosene as the immersion liquid. Cold erosion resistance measurements were also performed (using samples fired at 600, 800 and 1000 °C for 5 h), following the ASTM C704 standard (1 kg of no. 36 grit silicon carbide to erode samples 10 cm × 10 cm × 2.5 cm thick, leading to a weight loss that was converted to a volumetric one).

Table 1
General information of the castable compositions.

Raw materials	Compositions (wt%)			
	M–CAC	M–4CAC–S	M–4HA–S	M–2CAC–2HA–S
Mullite aggregates ($d \leq 3$ mm)	84.5	83.5	85.5	83.5
Reactive aluminas	11.5	11.0	9.0	11.0
Calcium aluminate cement	4.0	4.0	–	2.0
Hydratable alumina	–	–	4.0	2.0
Sintering additive ($d \leq 45$ μm)	–	1.5	1.5	1.5