



Research paper

Pozzolanic activity of calcined halloysite-rich kaolinitic clays

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ABSTRACT

The aim of this study is to determine the pozzolanic activity of clays with high content of halloysite/kaolinite, and to evaluate the influence of halloysite/kaolinite ratio and halloysite morphology in the development of pozzolanic activity of the calcined clays. For this purpose, three different natural clays from Río Negro Province, Argentina, were selected and completely characterized. After calcined at 700 °C and ground to 80% of particle size < 45 μm, pozzolanic activity was determined using the electrical conductivity test, the Frattini test and the compressive strength index. Results show that all calcined clays are classified as high reactive pozzolana. The presence of kaolinite and spheroidal halloysite exerts great influence at early ages; while tubular halloysite has greater influence in the pozzolanic activity and the compressive strength of mortars at later ages.

1. Introduction

The use of calcined kaolinitic clays as supplementary cementitious materials (SCMs) has exhibited considerable influence in enhancing the mechanical properties and the durability of mortar and concrete (Siddique and Klaus, 2009). The calcination of a kaolinitic clay at temperature ranging between 500 °C and 800 °C produces the complete dehydroxylation and the formation of an amorphous phase (meta-kaolin, MK) with high pozzolanic activity (Murat, 1983; Kakali et al., 2001; Siddique and Klaus, 2009; Bich et al., 2009; Tironi et al., 2014a). When kaolinitic clay (1:1) is calcined, the pozzolanic activity is higher than that of calcined 2:1 clays such as montmorillonite and illite (Fernandez et al., 2011; Tironi et al., 2012b; Taylor-Lange et al., 2015; Alujas et al., 2015). Moreover, the compressive strength of blended cements with 30% of calcined kaolinitic clay with medium and high kaolinite content reaches or surpasses the compressive strength of plain Portland cement mortar at 28 days (Tironi et al., 2012a). Additionally, the pozzolanic activity increase when the structural disorder and/or the content of kaolinite increase (Tironi et al., 2014a). Morsy et al. (2010) calcined kaolin nanoclay with a specific surface Blaine (SSB) ≈ 48 m²/g during 2 h at 750 °C to obtain an active amorphous phase (nano-MK), that was substituted in Portland cement from 0 to 8% by weight. Compressive strength of mortars containing nano-MK increased with the increase of nano-MK content.

Less attention has been paid to the thermal transformation of halloysite than that of kaolinite (Yuan et al., 2015), and the possibility of using it as SCMs. Halloysite and kaolinite have an identical chemical composition, except that halloysite may have as many as two molecules

of H₂O, as interlayer water (Churchman et al., 2010). Smith et al. (1993) demonstrated that the thermal transformation of halloysite is largely similar to that of kaolinite. The reaction scheme for the calcination of kaolinite or halloysite initially involves the dehydroxylation between 600 °C and 850 °C, where most of the hydroxyl groups are removed, leading to reduce the coordination of the originally octahedral aluminum (Yuan et al., 2015).

The additional water in the interlayers of halloysite has a decisive influence upon its crystal morphology, which is generally curled rather than platy form as occurred in kaolinite. Common forms are elongated tubes and spheroids (Cravero et al., 2016). For both morphologies different applications have been studied (Yuan et al., 2015; Fernández et al., 2015; Cravero et al., 2016). The nanosized tubular halloysite has an excellent mechanical properties and a very good biocompatibility. These advantages allowed a variety of potential applications in many fields, such as filler in polymers, carrier for the loading and controlled release of guest molecules, adsorbent for pollution remediation, and a nanoreactor/nanotemplate for the synthesis of functional materials (Yuan et al., 2015). The tubular structure of halloysite with one-dimensional mesoporosity or macroporosity allows the encapsulation of various active guests in the lumen of halloysite that acts as nanoscale container, as well as the subsequent controlled release of the guests (Yuan et al., 2015). The use as nanofiller in CPN was effective because halloysite is naturally dispersed, unlike the traditional micron-sized counterparts such as glass fibers and other clay mineral nanofillers such as montmorillonite that have to undergo exfoliation pretreatments to produce nano-layers (Du et al., 2006; Pasbakhsh et al., 2013). The spheroidal halloysite, chemically modified, has given good results for

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petroleum and Ag removal in contaminated waters (Fernández et al., 2015; Cravero et al., 2016).

The incorporation of halloysite in cements was studied by Farzadnia et al. (2013). Tubular halloysite, with a surface area $\approx 64 \text{ m}^2/\text{g}$ was substituted in Portland cement with 3% by weight. At 28 days, the compressive strength of mortar increases 24% comparing with the control sample. Considering these results and those obtained when calcined kaolinite was used as SCM, it is expected to get good pozzolanic activity when halloysite is calcined.

Rabehi et al. (2012) studied natural clay composed of halloysite and kaolinite as dominant minerals, and calcite, quartz and illite as impurities. The clay was calcined between 650 and 800 °C and ground to obtain a SSB of $0.56 \text{ m}^2/\text{g}$. Calcined clay was used as 0–20% replacement of Portland cement by weight. For 5% replacement, the compressive strength of mortar was 9.88% higher than that of the reference mortar. Tironi et al. (2012a) use calcined kaolinitic clays with SSB from 0.98 to $2.29 \text{ m}^2/\text{g}$ to elaborate mortars with 30% of replacement. Authors concluded that the SSB of calcined clay has a great importance up to 7 days and then its significance decreased. So a high compressive strength would be expected when the fineness of calcined halloysite clays is increased. It is expected that the increase of the fineness could contribute to improve the pozzolanic activity at the same time as contributing as filler. These studies were carried out using tubular halloysite, but none has been tested on halloysites of spheroidal morphology. In Argentina, halloysite deposits are characterized by the presence of both tubular and spheroidal halloysite, where the latter sometimes predominate. The aim of this study is to determine the pozzolanic activity of Argentinian clays with a high content of halloysite/kaolinite, and to evaluate the influence of the halloysite/kaolinite ratio and the halloysite morphology in the development of the pozzolanic activity of calcined clays.

2. Materials and methods

2.1. Clays

Three different natural clays from Río Negro Province, Argentina, were studied and they are labeled as NC1, NC2, and NC3. NC1-sample comes from Meliqueo deposit and NC2 and NC3-samples are from Pama and Belgrano deposits in the Mamil Choique area (Fig. 1). Halloysite is found in Huitrera Formation (Eocene in age) as an alteration product of volcanic-pyroclastic rocks (Cravero et al., 2016). These clays have high percentage of halloysite and less kaolinite. Spheroidal morphology predominates in almost all the deposits. The chemical composition of natural clays was determined by XRF analysis and it is reported in Table 1. For performing the pozzolanic tests, a Portland cement (PC)

was used and its chemical composition is also reported in Table 1. The mineralogical composition of clinker provided by a cement factory was $\text{C}_3\text{S} = 63.6\%$, $\text{C}_2\text{S} = 15.1\%$, $\text{C}_3\text{A} = 2.8\%$ and $\text{C}_4\text{AF} = 15\%$; gypsum (Gyp) is used as set regulator and limestone is the minor component, this phases are identified by XRD (Fig. 2). Its BSS was $0.35 \text{ m}^2/\text{g}$.

2.2. Characterization of natural and calcined clays

The mineralogical composition of natural clays was determined by X-ray diffraction (XRD) using a Bruker D2 PHASER diffractometer. Whole rock composition was determined on powder random oriented samples. Oriented films on glass slides were prepared on the $< 2 \mu\text{m}$ fraction obtained by centrifugation of clay-water suspension and were analyzed before and after formamide intercalation, and the halloysite/kaolinite ratio was determined (Churchman et al., 1984; Cravero et al., 2016). FTIR spectrum were obtained using a Nicolet Magna 500 spectrophotometer.

The thermal stability of phases and the temperature range corresponding to the dehydroxylation were analyzed with differential thermal analysis combined with thermal gravimetric analysis (DTA-TG). DTA-TG was carried out using a NETZSCH STA 409 thermobalance. Data obtained by DTA were used to determine the minimum temperature of calcination of these clays to produce the complete dehydroxylation of halloysite and kaolinite (Tironi et al., 2014b). Natural clays morphology was evaluated by Scanning and Transmission Electron Microscopy (SEM, FEI Quanta 200, and TEM, JEOL JSM-100 CX II).

Natural clays (NC) were reduced to particle size $< 4 \text{ mm}$ and calcined in a programmable laboratory furnace Indef 272 using a fixed bed technique, the heating rate was set at $13 \text{ }^\circ\text{C}$ per minute. The calcination temperature was selected from the DTA analysis as discussed later. Then, they were ground in a mortar type mill (Fritsch Pulverisette 2) until 80% of mass passed through the $45 \mu\text{m}$ sieve (#325).

The calcined clays (CC) were analyzed by DTA-TG and XRD to verify that the dehydroxylation was completed, and all halloysite and kaolinite were effectively transformed to amorphous phase MK. XRD was performed using a Philips PW3710 diffractometer. A Rigaku EVO2 Plus device was used to perform DTA-TG analysis, samples were heated at $10 \text{ }^\circ\text{C}/\text{min}$ rate up to $1200 \text{ }^\circ\text{C}$ under O_2 atmosphere. The CC morphology was evaluated by SEM (FEI Quanta 200). The particle size distribution was determined by Malvern Mastersizer 2000 laser particle size analyzer and the d_{10} , d_{50} , and d_{90} diameters were calculated, and the SSB (Specific Surface Blaine) was determined according to ASTM C 204-04 standard.



Fig. 1. Localization of the halloysite deposits where the studied samples come from NC1: Meliqueo deposit, NC2 and NC3: Mamil Choique area.

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