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Research paper

# Potential use of Argentine kaolinitic clays as pozzolanic material

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## ABSTRACT

Different Argentine kaolinitic clays were selected to study their potential pozzolanic activity. The incidence of several factors such as the origin of deposits (primary or sedimentary clays), mineralogical composition, and the order/disorder degree of kaolinite structure on the pozzolanic activity was analyzed. Five clays were characterized by chemical analysis, X-ray diffraction (XRD), Fourier transformed infra-red spectroscopy (FTIR), differential thermal analysis combined with thermo-gravimetric analysis (DTA/TG), and Scanning Electron Microscopy (SEM). The crystallinity of kaolinite in raw clays was estimated by five indexes: FWHM-001, FWHM-002, Hinckley Index (HI), and R2 on the XRD patterns, whereas the  $P_0$  index was determined on the FTIR spectra.

Clays were calcined at 700 °C and ground until all mass passed through a 45 µm sieve. Pozzolanic activity was evaluated by the Frattini test and the strength activity index (SAI) at 7, 28 and 90 days using a blended cement containing 30% by weight of calcined clay. Complementary, the presence of remaining  $\text{Ca}(\text{OH})_2$  in mortar was checked by XRD at 28 and 90 days.

Results indicate that four blended cements presented a very good pozzolanic activity evaluated by the Frattini test at 7 and 28 days and they have a different compressive strength with a SAI > 1 at 90 days. In these blended cements, the  $\text{Ca}(\text{OH})_2$  released by cement hydration was consumed. Analyzing the incidence of factors on pozzolanic activity, it can be concluded that clays containing more than 50% kaolinite provide enough amount of reactive material, and that the rate of the pozzolanic reaction is improved when the kaolinite mineral present in the clay has a disordered structure.

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## 1. Introduction

Pozzolans are defined as silico-aluminous materials which react chemically with calcium hydroxide at ordinary temperature to form compounds with cementitious properties. The replacement of part of Portland cement clinker by pozzolan is the key to reduce the overall environmental impact and energy consumption in the manufacture of cementitious materials. The technical reasons to use pozzolan in concrete consist of the enhancing of mechanical properties of paste/mortar/concrete (Siddique and Klaus, 2009; Janotka et al., 2010), the reduction of hydration heat, the decrease of permeability and the increase of chemical resistance for more durable concrete (Sabir et al., 2001; Habert et al., 2008). Highly reactive pozzolans, including calcined clays, can lead to help the sustainable concrete production.

Metakaolin (MK) is a pozzolanic material obtained by the calcination of kaolinitic clay at temperatures ranging between 500 °C and 800 °C (Shvarzman et al., 2003; Samet et al., 2007; Habert et al., 2009; Siddique and Klaus, 2009). Rock and soil containing kaolinite minerals occur over wide areas on most continents, but large high-purity kaolin

deposits are rare (Kogel et al., 2006). Generally, natural deposits contain a mixture of different clay minerals (kaolinite, illite, montmorillonite and others) and a large proportion of impurities of non-clay materials, such as quartz, feldspars, mica, anatase, calcite and sulfides. These impurities are very difficult to eliminate, since this could require large processing facilities, consume a lot of water and energy, and produce a large proportion of waste.

In Argentina, there are primary and sedimentary kaolinitic clays. The lithological differences among parent rocks of primary kaolinitic clays as well as the distinct influences of erosion areas and the sedimentary clay stratigraphic position imply differences in mineralogy and grain size distribution that should have direct consequences on the ceramic properties of the different clays (Domínguez et al., 2008; Dondi et al., 2008). Kaolinitic clays used as pigment or as functional filler must be soft and non-abrasive to prevent excessive wear on equipment used during processing or application. The occurrence of hard particles such as quartz and feldspar in the clay will increase its abrasiveness (Kogel et al., 2006). Processing of kaolinitic clays is technically complicated and a costly barrier for entry into many markets where purity, consistency, handling characteristic, and appearance are valued properties. Considering these difficulties, the use of kaolinitic clays as a pozzolan is a good alternative in regions where there is a lack of natural pozzolans

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or sub-products and the economical or environmental impact of transport begins to be a disadvantage. On the other hand, the possibility to obtain constant properties using clays of large deposits is an advantage over other natural pozzolans.

The objective of this research is to study the potential pozzolanic activity of selected Argentine kaolinitic clays with different geological origins. The kaolinitic clays were selected in order to find the incidence of several factors, such as the origin of deposits (primary or sedimentary clays), mineralogical composition, and order/disorder degree in kaolinite structure, on the pozzolanic activity with Portland cement.

## 2. Experimental

### 2.1. Materials

Five different kaolinitic clays from different sites in Argentina have been employed as raw-stuff to obtain MK by calcination at 700 °C. The samples were obtained from different operating quarries and their locations are shown in Fig. 1.

- K1 was collected at La Rioja province, in the Patquia Formation (Fm) from the Neopaleozoic units of the Paganzo Group. This primary structure has a diagenetic origin, resulting in a kaolinite with good crystallinity (Andreis, 2006).
- K2 was collected at Ingeniero Jacobacci, Río Negro province, this being a quaternary sedimentary deposit with coalescing dejection cones of the Choiquepal Fm (Volkheimer, 1973).

- K3 is a blend of kaolins from residual and primary deposits located at the Jurassic Marifil Fm (Chubut province), consisting of rhyolitic volcanites. This sample underwent an industrial processing cycle consisting of washing, coarser fraction settling, clay-rich suspension separation, filter-pressing and drying (Domínguez et al., 2008).
- K4 was collected at a quarry operating on the surface of the Baqueró Fm, Santa Cruz province. This formation is a thick continental sequence that during Cretaceous was sedimented in a fluvial and lacustrine environment over the Chon Aike Group and the Bajo Grande Fm. Its composition is dominated by poorly ordered kaolinite, quartz and some illite (Domínguez et al., 2008).
- K5 was collected at a quarry located in primary deposits developed in Marifil Fm, Chubut province. This deposit is in the uppermost part of the volcanic sequence and it appears to be linked to the unconformity with the overlying sedimentary units. In the composition of this formation, quartz is predominant over kaolinite and it presents an open texture.

The mineralogical composition of natural kaolinitic clays coming from primary (K1 and K5) or sedimentary (K2 and K4) deposits is inconclusive about a weathering versus hydrothermal genesis of these clays (Domínguez et al., 2008).

### 2.2. Instrumental techniques

The chemical composition of the whole rock sample was determined by ICP-AES analysis.

The mineralogical composition of clays was analyzed by X-ray diffraction (XRD), Fourier transformed infra-red spectroscopy (FTIR), and differential thermal analysis combined with thermal gravimetric analysis (DTA–TG). XRD was performed using a Philips PW 3710 diffractometer operating with CuK $\alpha$  radiation at 40 kV and 20 mA. FTIR spectra were obtained using a Nicolet Magna 500 spectrophotometer that ranged from 4000 to 400 cm<sup>−1</sup>. DTA–TG was carried out using a NETZSCH STA 409 thermobalance.

After the identification of clay minerals by XRD, using the results of chemical analysis the kaolinite (K) content was estimated by stoichiometry calculation – a normative mineralogical composition – (Bich, 2005), and then corroborated by TG analysis (Shvarzman et al., 2003). Data obtained by DTA were used to determine the optimum range of calcination temperatures of each sample to produce the complete dehydroxylation of kaolinite.

The crystallinity of kaolinite in clays was evaluated by different indexes obtained by XRD and FTIR (Murat, 1983; Kakali et al., 2001; Bich et al., 2009; Chakchouk et al., 2009). The XRD based indexes used were full width at half maximum (FWHM-001 and FWHM-002), Hinckley Index (HI), and random defects (R2) (Kingerly et al., 1976; Wilson, 1987; Aparicio and Galan, 1999; He et al., 2005).  $P_0$  is the FTIR based index that provides information about the order or the disorder of the structure (Murat, 1983; Wilson, 1987; Bich et al., 2009).

The morphological aspect of clays was observed by Scanning Electron Microscopy (SEM, Jeol JSM-6460LV) on small fragments mounted on the holder and coated with gold using a Denton Vacuum Desk II coater system.

The development of pozzolanic properties occurs when the kaolinitic clays are calcined over 590 °C; what produces the removal of the crystal lattice water and the formation of MK (Chakchouk et al., 2006; Konan et al., 2009). The samples were reduced to particle size less than 4 mm and calcined in a programmable laboratory furnace using a fixed-bed technique. The samples were heated at ambient temperature up to 700 °C (Tironi et al., 2012). At the end of this period, the sample was cooled in the furnace until 450 °C and finally cooled down in a desiccator at ambient temperature.

After calcination, the clays were analyzed by XRD, FTIR and SEM to verify that all kaolinite was effectively transformed to MK. The total pore volume was determined using a Carlo Erba 2000 mercury intrusion

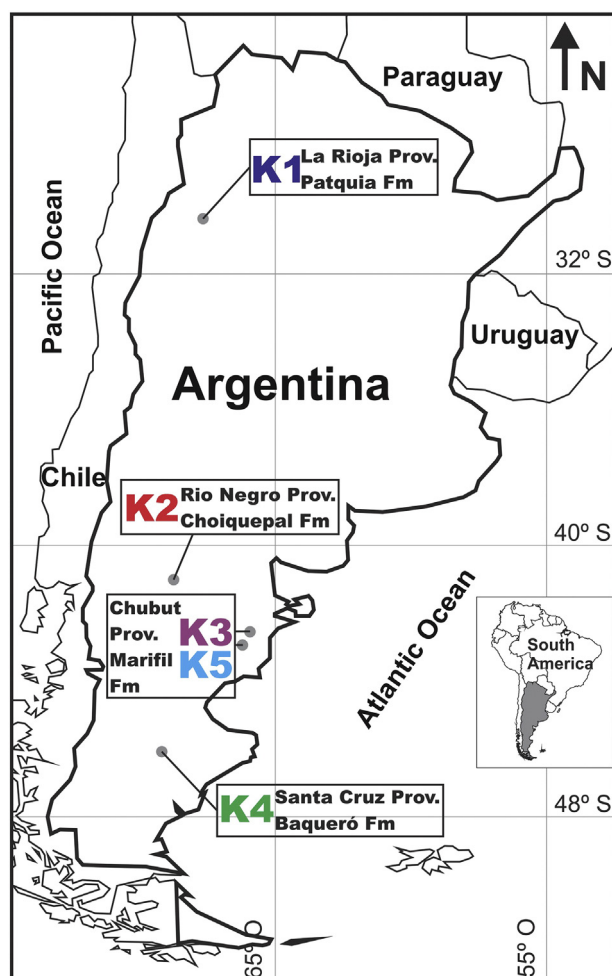


Fig. 1. Locations of the sites from five kaolinitic clays studied (K1 to K5).

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