



Kaolinitic calcined clays – Portland cement system: Hydration and properties



Alejandra Tironi ^{a,*}, Claudia C. Castellano ^a, Viviana L. Bonavetti ^a, Mónica A. Trezza ^a, Alberto N. Scian ^b, Edgardo F. Irassar ^a

^a Facultad de Ingeniería, CIFICEN (CONICET – UNCPBA), Av. del Valle 5737, B7400JWI Olavarría, Argentina

^b Centro de Tecnología de Recursos Minerales y Cerámica – CONICET – UNLP, Cno. Centenario y 506, Gonnet, Argentina

HIGHLIGHTS

- Kaolinitic calcined clays are an effective pozzolan when they are appropriately calcined and ground.
- The reactivity of kaolinitic calcined clays depends on the structure of kaolinite in raw clay.
- The rate of pozzolanic reaction of kaolinitic calcined clays modifies the mechanical properties of the blended cement.
- After calcination and grinding, raw clay containing disordered structure has very high pozzolanic activity.
- Kaolinitic calcined clays produce a high reduction of the water sorptivity coefficient.

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ABSTRACT

This paper examines the influence of type of kaolinite in the raw clay on the performance of calcined clays as supplementary cementing materials. Two kaolinitic clays were characterized, calcined then ground and used as partial replacement of Portland cement at 15% and 30% by mass. The results show that both kaolinitic calcined clays are an effective pozzolan with different reaction rate. The reactivity is related to the specific surface area obtained after calcination and it depends on the structure of kaolinite. Raw clay containing disordered structure presents a very high pozzolanic activity allowing high replacement levels (30%) in blended cements.

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1. Introduction

Calcined kaolinitic clays may be used as partial replacement of Portland cement (PC) in the formulation of blended cements, causing a modification of mechanical properties and durable performance. Today, this practice appears as a reliable contribution to the reduction of green-house gas emission and the energy saving requirement for the same cement efficiency. Kaolinite clays develop a good pozzolanic activity when they are calcined at temperatures between 500 and 800 °C due to the formation of reactive amorphous phase named metakaolinite (MK). During the thermal decomposition of kaolinitic clays, water is released to the environment instead of the CO₂ that occurred during the decarbonation of limestone in the clinker process. Furthermore, this process requires

less energy [1]. Metakaolinite reacts with CH released during PC hydration in the presence of water producing a cementing compound like C–S–H, C–A–H and C–A–S–H.

The influence of calcined kaolinitic clays as replacement for PC has been reviewed by Sabir et al. [1] and Siddique and Klaus [2]. These papers are focused on the hydration products, the replacement level and the mechanical and durable properties of PC + MK mixtures. In the last decade, there have been several investigations on this topic and the conclusions about the mechanical efficiency differ when using different calcined kaolinitic clays. Recently, Kuliffayová et al. [3] reported an increase of the compressive strength and a decrease in total porosity for blended cement containing 5–15% of kaolinitic calcined clays. These results agree with those presented by Singh and Garg [4] using four calcined clays at 10% replacement. On the other hand, Frías et al. [5] reported that the porosity increases for replacement of 10–25%, in accordance with the results presented by Vejmelková et al. [6] for 10% of

* Corresponding author. Tel./fax: +54 2284 451055.

E-mail address: atironi@fio.unicen.edu.ar (A. Tironi).

replacement, causing low relative compressive strength at 28 days. Badogianis et al. [7] and Chakchouk et al. [8] conclude that the compressive strength decreases when the replacement percentage is increased.

Regarding the characteristic of raw clays as source of metakaolinite, Murat [9] concluded that calcined clay resulting from raw clay containing kaolinite with disordered structure produces the highest compressive strength of blended cement. Analyzing four kaolinitic clays with different kaolinite crystallinity, Kakali et al. [10], determined that clays containing kaolin with ordered structure has a low reactivity after heat treatment. These results agree with those obtained by Tironi et al. [11] analyzing five different kaolinitic clays with different content and order/disorder of kaolinite.

The different results obtained when using calcined kaolinitic clays suggest the opportunity to examine integrally the factors that influence the performance of calcined kaolinitic clays as supplementary cementing materials. For this purpose, two kaolinitic clays are chemically, mineralogically and structurally characterized. They are thermally treated, physically characterized, and evaluated in their pozzolanic behavior when used in blended cement as 15% and 30% by mass replacement. The hydration process and the porosity are determined to justify the mechanical performance and the water transport by sorptivity. The large specific surface area occurred when disordered kaolinite is calcined producing a different rate of pozzolanic reaction that causes a different blended cement performance according to the replacement level used.

2. Materials and methods

2.1. Raw clays

In this study, two Argentine kaolinitic clays were used: A1 obtained from a primary deposit at La Rioja Province, and A2 obtained from a sedimentary deposit at Río Negro Province. For both clays, Table 1 reports the chemical composition, the loss on ignition (LOI) and the mineralogical composition obtained by X-ray diffraction (XRD). The kaolinite content was very high (94%) for A1-clay and its structure was ordered; while for A2-clay, it was 76%, and its structure disordered. Complete details for these clays can be obtained elsewhere [11]: A2-clay presents high total porosity and A1-clay has low.

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 films using a Denton Vacuum Desk II coater system (Fig. 1). It can be observed that A1-clay (Fig. 1a) shows the typical microstructure of kaolinite,

consisting of pseudo-hexagonal plates and clusters of plates. Large kaolinite booklets are present and they are compact with low porosity as indicated in previous analysis [11]. This sample presents a high degree of perfection in translational periodicity of clay, and an ordered structure according to indexes [11]. A2-clay classified as disordered structure (Fig. 1b), the microstructure presents a fine particle size ($<3\ \mu\text{m}$), irregular kaolinite forms and very small flakes. The sheet of booklets appears to be open generating a large space in accordance with high porosity [11].

2.2. Calcined clays

The clays were calcined in a programmable laboratory furnace using a fixed bed technique. Calcination temperature and residence time were selected for the best pozzolanic activity for 30% of replacement determined in previous studies [12,13]. For A1-clay, the calcination temperature was $700\ ^\circ\text{C}$ and the residence time was 30 min. For the A2-clay, these values were $750\ ^\circ\text{C}$ and 20 min, respectively. After thermal treatment, the complete kaolinite transformation was checked by XRD. The calcined clays were ground in a mortar type mill (Fritsch Pulverisette 2) up to 80% of mass passed through the $45\ \mu\text{m}$ sieve (# 325): a typical objective during the grinding in blended cements process.

The metakaolinite content in calcined clays was estimated by stoichiometric calculations based on the kaolinite content of raw clays. The particle size distribution was determined by Malvern Mastersizer 2000 laser particle size analyzer and the d_{90} , d_{50} , and d_{10} diameters were calculated. Complementary, the specific surface area (SS) was determined using the BET technique (Micromeritics ASAP 2020) and the Blaine method [14].

Table 2 summarizes the characteristics of calcined clays. Calcined clay obtained from A1-clay with high content of ordered kaolinite has a high content of metakaolinite, but it has a low specific surface area (BET and Blaine) and it is too hard to grind causing a large maximum particle size for the same grinding objective (20% on $45\ \mu\text{m}$ sieve). Then, the mean particle size (d_{50}) of A1 ($19.1\ \mu\text{m}$) is greater than the d_{50} of A2 ($7.4\ \mu\text{m}$) and their coarser particles (d_{90}) are too larger. This coarse particle size distribution can affect negatively the pozzolanic activity of A1 calcined clays. On the other hand, calcined clay obtained from A2-clay with low content of disordered kaolinite has larger specific surface area than those of A1 (4.8 times larger for specific surface BET and 1.4 times larger for specific surface Blaine) and finer particle sizes distribution for the same grinding procedure (Table 2). A2-clay containing disordered kaolinite were collected in sedimentary deposit; while A1-clay with an ordered structure had their origin in primary deposit. A2-clay presents greater grindability because it has a large volume of pores that cause a largest specific surface [11]. The quartz is presents with a very low grain size into the clay and it does not affect the grinding.

2.3. Blended cements

The plain cement used is a normal Portland cement (PC) with a Blaine fineness of $383\ \text{m}^2/\text{kg}$, an estimated Bogue potential phase composition of 47% C_3S , 22% C_2S , 8% C_3A and 9% C_4AF by mass and alkalis (as Na_2O equivalent) of 1.38%. For this cement, limestone is added as minor component ($<5\%$).

Table 1
Chemical analysis, loss on ignition (LOI), and mineralogical composition of clays used.

	Chemical composition (%)									Mineralogical composition (%)		
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	LOI	Kaolinite	Quartz	Illite
A1	45.9	37.0	0.77	0.08	0.12	0.06	0.40	0.99	13.3	94	2	–
A2	51.4	31.3	0.92	0.40	0.19	0.36	0.38	1.42	12.1	76	15	3

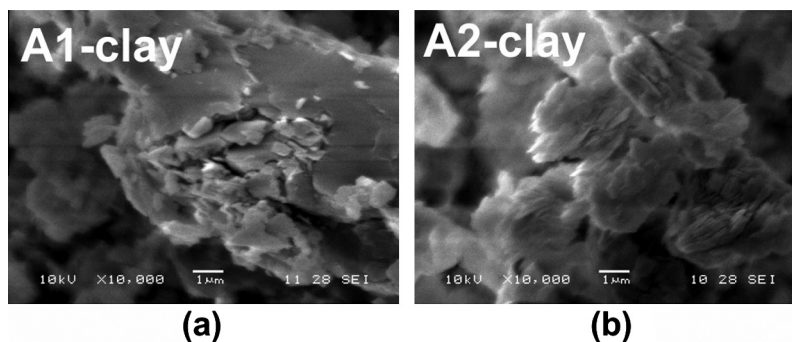


Fig. 1. SEM micrographs of kaolinitic clays: (a) A1-clay and (b) A2-clay.

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