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## Blended Cements Elaborated with Kaolinitic Calcined Clays

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### Abstract

In the clinker production process, the main component of Portland cement (PC), large amount of CO<sub>2</sub> are emitted into the atmosphere. The use of calcined kaolinitic clays as supplementary material of cement is an alternative to mitigate the environmental impact. In this paper, the influence of the replacement of PC by two calcined kaolinitic clays (15 and 30%), with high content of metakaolinite and different reactivity was studied. Calcined kaolinitic clays were characterized, the pozzolanic activity using Frattini test, the compressive strength, rate of water absorption (sorptivity), the assemblage of hydration products and the pore size distribution were determined at 28 days. The results show that the replacement of high percentage (30%) of very reactive clays improves the mechanical behavior and durable parameters compared with those obtained for plain PC

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### 1. Introduction

In the clinker production process, the main component of Portland cement (PC), large amounts of CO<sub>2</sub> are emitted into the atmosphere (Chen et al. 2010). An alternative to reduce this emission, the partial replacement of clinker by supplementary cementitious materials (Schneider et al. 2011), such as limestone, fly ash, slag or calcined clay, are proposed. Kaolinite clays develop a good pozzolanic activity when they are calcined at temperatures

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between 500 and 800 °C (Chakchouk et al. 2009). During the thermal decomposition of kaolinitic clays, metakaolinite, a reactive amorphous phase with pozzolanic activity, is obtained and the decomposition releases H<sub>2</sub>O instead the CO<sub>2</sub>-emissions occurring during the decarbonation of limestone in the clinker process. Furthermore, this process requires less energy (Sabir et al. 2001). The effectiveness of calcined kaolinitic clay as pozzolan depends on the type of Portland cement used, the metakaolinite content (MK) in the sample, their specific surface and the replacement level (Samet et al. 2007).

The aim of this study is to evaluate the influence of PC replacement level for calcined kaolinitic clays, with high content of metakaolinite and different pozzolanic activity on the mechanical behavior and the water sorptivity, a durability parameter, of the blended cements.

### Nomenclature

Shorthand notation which has universal use among cement scientists

C	CaO
S	SiO <sub>2</sub>
A	Al <sub>2</sub> O <sub>3</sub>
H	H <sub>2</sub> O
Є	CO <sub>2</sub>

Other nomenclature used

MK	metakaolinite
PC	Portland cement
SS	specific surface
CS	compressive strength
S	sorptivity coefficient

## 2. Materials and methods

### 2.1. Materials

Two Argentine kaolinitic clays (A1 and A2) with high kaolinite content and different degree of crystallinity have been employed:

- A1 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). The kaolinite content was 94 % with an ordered structure (Tironi et al. 2012 b).
- A2 was collected at Ingeniero Jacobacci, Río Negro province, this being a quaternary sedimentary deposit with coalescing dejection cones of the Choiquepal Fm (Volkheimer, 1973). The kaolinite content was 76 % with a disordered structure (Tironi et al. 2012 b).

The samples were calcined in a fixed-bed electrical furnace at optimal temperature determined in previous research (Tironi et al. 2012 b): A1 at 700 °C during 30 min, and A2 at 750 °C during 20 min. The calcined clays were ground in a mortar type mill (Fritsch Pulverisette 2) until 80% of mass passed through the 45 μm sieve (# 325).

The plain cement used is a normal Portland cement (PC) of strength class 40 (standard compressive strength > 40 MPa at 28 days) according to national standard IRAM 50000. This cement has a Blaine fineness of 383 m<sup>2</sup>/kg, a composition mineralogical, calculated by Bogue's formula of 47% C<sub>3</sub>S, 22% C<sub>2</sub>S, 8% C<sub>3</sub>A and 9% C<sub>4</sub>AF by mass and alkalis (as Na<sub>2</sub>O equivalent) of 1.38 %. For this cement, limestone is added as minor component (< 5%).

### 2.2. Characterization of calcined clays

The metakaolinite content (MK) was estimated by stoichiometry using the kaolinite content value, previous calcination. The particle size distribution was determined by Malvern Mastersizer 2000 laser particle size analyzer and the d<sub>90</sub>, d<sub>50</sub>, and d<sub>10</sub> diameters were calculated. The specific surface obtained was measured using the Blaine method (ASTM C 204-04), and the BET method (Micromeritics ASAP 2020). The pozzolanic activity of kaolinitic calcined clays was proved using Frattini test (EN 196:5; Tironi et al. 2013).

### 2.3. Blended cements

Four blended cements were formulated replacing Portland cement (PC) by 15% and 30% by mass of kaolinitic calcined clays (A1, A2) and they were identified as 15A1, 30A1, 15A2, 30A2, respectively.

The compressive strength and the sorptivity tests were assessed on mortars made with RILEM standard sand (1:3) and water/cementitious material of 0.50 at 28 days. Compressive strength was measured on mortars cubes (25 x 25 x 25 mm). The sorptivity coefficient (in  $\text{g}/\text{m}^2 \text{s}^{1/2}$ ), based on the rate of absorption of water, was obtained on mortar slice of 100 mm diameter and 50 mm high, pre-conditioning according to IRAM 1871 (dried in oven until constants weight at 50 °C).

Blended cement pastes were prepared using a w/cm of 0.5 to study the amount of hydration compounds and the pore size distribution, at 28 days. At this time, fragment of paste sample was immersed in acetone during 24 h to stop the hydration, dry overnight in oven at 40 °C and then cooled in a desiccator.

The amount of hydration compounds, crystalline and amorphous, were determined by thermal analysis (DTA/TG) using a NETZCH STA 409 thermobalance. The temperature range for TG calculations was adopted as: at about 40-440 °C for dehydration of C-S-H, C-A-H and C-A-S-H phases, and at about 440-560 °C for CH dehydroxylation (Kuliffayová et al. 2012, Antoni M. et al. 2012). These values are related with the amount of these phases in the blended cement pastes. Complementarily, the crystalline hydrated phases at 28 ages were identifies by XRD analysis on powdered paste samples. XRD measurements were performed on Philips PW 3710 diffractometer equipped with carbon monochromator using  $\text{CuK}\alpha$  radiations and operating at 40 kV and 20 mA.

The pore size distribution was determined using a Termo Fisher Scientific S.p.A. Mod. PA 440 mercury intrusion porosimeter (MIP) in the pore size radius from 3.7 to 6500 nm (ASTM D-4404).

## 3. Results and discussion

### 3.1. Characterization of calcined clays

Table 1 presents results of MK content, particle size distribution, specific surface (SS) Blaine and BET, and pozzolanic activity of kaolinitic calcined clays.

Table 1. Metakaolinite content (%MK), particle size distribution, specific surface (SS) Blaine and BET, and pozzolanic activity of kaolinitic calcined clays.

Kaolinitic calcined clay	%MK	Particle size distribution ( $\mu\text{m}$ )			$\text{SS}_{\text{Blaine}}$ ( $\text{m}^2/\text{kg}$ )	$\text{SS}_{\text{BET}}$ ( $\text{m}^2/\text{kg}$ )	Pozzolanic activity
		$d_{10}$	$d_{50}$	$d_{90}$			
A1	93	1,3	19,6	131,4	997	8117	good
A2	73	2,1	7,4	47,0	1365	38997	very good

Both samples presents high content of MK. A1 has a good pozzolanic activity according to Frattini test, while the pozzolanic activity was very good for A2. The specific surface of A2-calcined clay was higher indicating elevated amount of access points, and also it have the lowest average particle size ( $d_{50}$ ).

### 3.2. Blended cements: mortars

Table 2 reports the results of compressive strength (CS) and the sorptivity coefficient (S) for mortars elaborated with blended cements at 28 days. For A2 calcined clay, the increase of replacement levels in blended cement increases the CS from 14 to 27%, compared with the mortar PC. For A1 calcined clay, the CS decreases when increasing the content of addition, resulting for 30A1 12% lower than PC-mortar. Sorptivity coefficient in mortars with A1 is five times less than the PC-mortar, and four times lower in mortars with A2. Independently of the pozzolanic activity of the kaolinitic calcined clay, and the replacement levels, S-coefficient is lower in mortars made with blended cements, according to determined by Badogiannis and Tsvivilis (2009) for the metakaolin derived from a poor Greek kaolin.

Table 2. Analysis of mortars and pastes at 28 days of age.

Sample	CS (MPa)	S (g/m <sup>2</sup> s <sup>1/2</sup> )	Hydrated phases, %				Accumulated volume of pores (mm <sup>3</sup> /g)
			C-S-H/C-A-H/C-A-S-H		CH		
			110 - 440 °C		440 - 560 °C		
PC	38,4	12,22	12,2	% about PC	3,9	% about PC	198
15A1	38,8	2,34	10,5	86	1,8	47	191
30A1	33,9	2,42	10,1	82	0,7	17	206
15A2	43,7	2,97	13,4	110	1,4	37	177
30A2	48,8	2,90	14,2	116	0,5	12	156

### 3.3. Blended cements: pastes

Fig. 1 shows the thermograms obtained using DTA from hydrated pastes at 28 days. Endothermic peaks up to 440 °C, corresponds to the dehydration of hydrated phases, such as CSH, CAH, and CASH (Kuliffayová et al. 2012; Meller et al. 2009). The first three phases are obtained during PC-hydration (Taylor 1967) and also as hydration products of the pozzolanic reaction (Murat 1983). On the other hand, the CASH phases are only obtained as product of the pozzolanic reaction when the availability of CH is low (Murat 1983). The endothermic peak assigned to the dehydroxylation of the CH is between 440 and 560 °C (Kuliffayová et al. 2012).

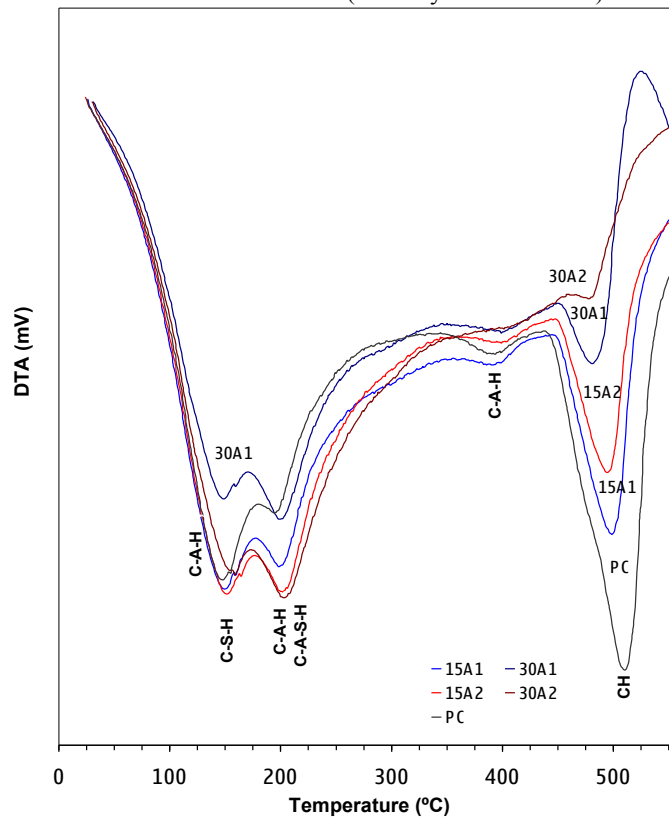


Fig. 1. DTA hidrated pastes at 28 days.

The intensity of the peak assigned to dehydroxylation of CH is higher in PC-paste, and lower in the pastes content kaolinitic calcined clays, due to CH was consumed during the pozzolanic reaction. For 30A2 blended cement, the intensity of CH-peak is lower, and the endothermic peaks assigned to dehydration aluminous phases are different. For paste 30A1, CH intensity is lower, and the area of peak assigned to the hydrated phases is lower too. The amount of CH present in the blended cement paste depends on the replacement levels, and consumption in pozzolanic reaction, can be quantified by TG analysis (Kuliffayová et al. 2012). Furthermore, the amount of the hydration products (CSH/CAH/CASH) may be approximately determined by the mass loss due to dehydration at about 110 and 440 °C. Table 2 reports the results obtained in TG analysis. For replacement levels of 15%, the amount of CH expected would be about 85% on blended cements when the complete dilution is computed for no-pozzolanic addition, and it values is 70% while for the 30% of replacement. For all blended cements, the amount of CH at 28 days is less than the computed for dilution effect indicating the progress of the pozzolanic reaction. At the same replacement level, the amount of CH is always less in pastes made with A2, indicating a great progress of pozzolanic reaction. For blended cement with A2, mass loss by dehydration of silico-aluminous hydrated phase was greater than those determining in PC paste indicating a greater amount of hydration products. However, it can be point out that this determination depends on the amount of water (H) present in each aluminic phase and, may influence the results.

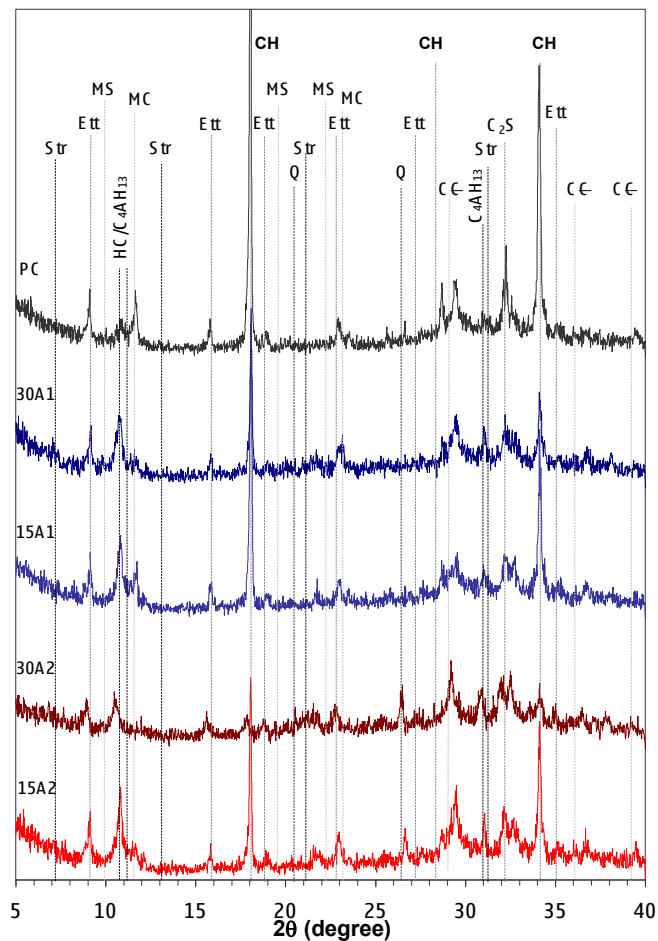


Fig. 2. XRD patterns hydrated pastes at 28 days.

Fig. 2 shows the XRD patterns of hydrated cement pastes at 28 days. It can be observed the significant reduction of the CH peaks ( $2\theta = 18.01$  deg) for pastes containing kaolinitic calcined clays compared to the portland cement paste. The consumption of CH due to the progress of the pozzolanic reaction is the higher for 30A2. These results were agree with those obtained by DTA analyses previously detailed (Fig. 1). Regarding the C-A-H crystalline phases, it can be identify: Ettringite (Ett),  $C_4AH_{13}$ , hemicarboaluminate (HC), monocarboaluminate (MC) and monosulfoaluminate (MS); and the C-A-S-H crystalline phase is strätlingite (Str). These phases were formed as results either the cement hydration or the pozzolanic reaction. Its presence depends on the amount of CH and the availability other of ions ( $CO_3^{2-}$ ,  $SO_4^{2-}$ ) in the system. The  $C_4AH_{13}$  is formed by the metakaolinite reaction when the CH is largely available (Murat 1983). When cement contains a small proportion of limestone filler,  $C_4AH_{13}$  is stabilized as HC (Antoni M. et al. 2012). For highly reactive calcined kaolinitic clays, the amount of CH is too low in the system and the Str phase is formed due to the substitution of calcium by silicon at later ages (Murat 1983). The minor impurities phases identified in the system were calcite (CC) from the limestone filler in cement and quartz (Q) from the calcined kaolinitic clays.

Table 2 reports the accumulated volume of pores for pastes studied. When increased of the replacement level of A2 in paste from 15 to 30%, the accumulated volume of pores decreases 11 and 21% compared with the PC-paste. Results resent an inverse behavior for blended cements containing A1.

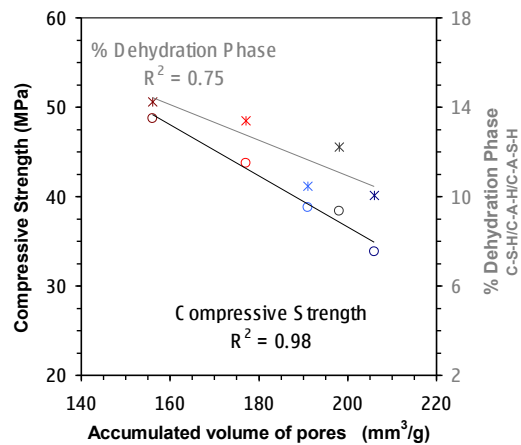


Fig. 3. Relationship of compressive strength and the % dehydration phase, respect to accumulated volume of pore in the pastes.

Fig. 3 shows the relationship between the CS of mortars and two parameters of hydrated paste: the percentage of dehydration of CSH/CAH/CASH phases and the accumulated volume of pores. A lower water loss is corresponding with greater accumulated volume of pores, and it can be inferred that the decrease in accumulated volume of pores in the paste is proportional to the amount of hydrated phases. When analyzing the relationship between the accumulated volume of pores of the paste and the CS developed in mortar, it is observed that there is a linear relationship between both parameters with good fit ( $R^2 = 0.98$ ). For low accumulated volume of pores in the paste, the CS of mortar is highest.

For 30A2 blended cement, the CH consumption is the highest in correspondence with the highest percentage of hydrated phases. This progress on pozzolanic reaction results in a reduction of accumulated volume of pores, causing the high CS and the low sorptivity coefficient.

For A1 blended cements, the reduction in the amount of CH is due to pozzolanic reaction and dilution of PC. Consequently, the pore volume increases when the replacement level increased and CS decreased. Considering these factors, it is possible to infer that when using a clay similar to A1, the level replacement will be lower (15%).

#### 4. Conclusions

When kaolinitic calcined clays were used in the manufacture of blended cements, the pozzolanic activity of these is the principal variable to determining the percentage of replacement.

Kaolinitic clays with high content of kaolinite and disordered structure, calcined and ground has a very good pozzolanic activity and allow to use high percentages in blended cements with better durable and mechanical properties than those achieved by PC.

Kaolinitic clays with a high content of kaolinite and ordered structure, calcined and ground, this replacement is limited to 15%.

The use of kaolinitic calcined clays, produce benefits in terms of technology and helps to reduce CO<sub>2</sub> emissions to the atmosphere generated during the manufacture of the PC.

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