Kaolinitic calcined clays – Portland cement system: Hydration and properties

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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.

ARTICLE INFO

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.

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 CO_2 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

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 μm), 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 °C and the residence time was 30 min. For the A2-clay, these values were 750 °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 μm 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 μm sieve). Then, the mean particle size (d_{50}) of A1 (19.1 μm) is greater than the d_{50} of A2 (7.4 μm) 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 m²/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
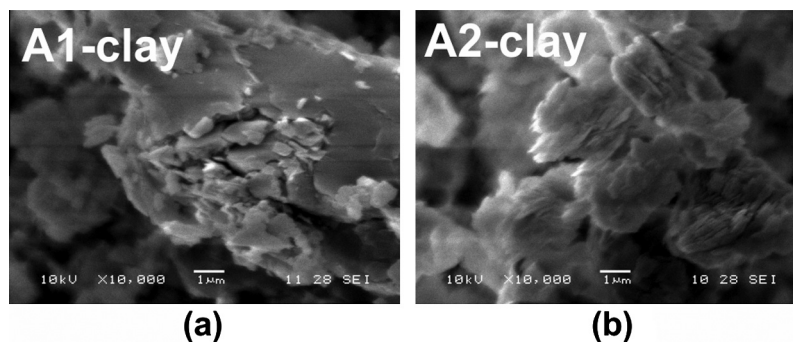
Fig. 1. SEM micrographs of kaolinitic clays: (a) A1-clay and (b) A2-clay.

Table 2
Metakaolinite content, particle size distribution, specific surface (SS) BET and Blaine of calcined clays.

Kaolinitic calcined clay	MK (%)	Particle size distribution (µm)			SS_{BET} (m²/kg)	SS_{Blaine} (m²/kg)
		d_{10}	d_{50}	d_{90}		
A1	93	1.3	19.6	131.4	8,117	997
A2	73	2.1	7.4	47.0	38,997	1365

For blended cements, kaolinitic calcined clay was added as a partial replacement of Portland cement at levels of 15% and 30% by mass. Blended cement designation is based on the replacement level and the type of clay used (15A1, 30A1, 15A2, 30A2).

Pozzolanic activity of blended cements was measured using Frattini test [15]. In this method, 20 g of blended cement was mixed with 100 ml of boiled distilled water. After preparation, samples were left for 2, 7 and 28 days in a sealed plastic container at 40 °C. At test time, samples were vacuum filtered through paper and cooled at ambient temperature in sealed Buchner funnels. The filtrate was analyzed for [OH⁻] by titration against dilute HCl with methyl orange indicator and for [Ca²⁺] by pH adjustment to 13, followed by titration with 0.025 M EDTA solution using Murexide indicator. This test compares the [Ca²⁺] and [OH⁻] contained in an aqueous solution that covers the hydrated sample with the solubility curve for CH in an alkaline solution at the same temperature.

Compressive strength and sorptivity tests were assessed on mortars made with RILEM standard sand (1:3) and water to cementitious material ratio (w/cm) of 0.50. The mortar was mixed in planetary mixer, the specimens were cast and compacted by vibration and cured in the molds in a moist cabinet for 24 h. Then, they were removed from the mold and immersed in lime-saturated water until test age at 20 ± 1 °C. Compressive strength was measured on mortars cubes (25 × 25 × 25 mm) at 2, 7, and 28 days.

The sorptivity coefficient (S) based on the rate of absorption of water was obtained on mortar slices (100 mm diameter and 50 mm height) pre-conditioning according to IRAM 1871 standard [16]. Slices were obtained from cylinders molded and cured in water during 28 days. The first slice was sawed to 30 mm from the base of cylinder and discarded, and then the test slices were sawed perpendicular to the generatrix of the cylinder with a height of 50 mm. The specimens were dried in an oven at 50 ± 2 °C to constant mass. Waterproof paint was applied on the lateral surface to prevent absorption. The specimens were put on the support base into a plastic container with a height of water 2 ± 1 mm up to the surface of absorption at 20 ± 2 °C. Mass increase per unit area (C_t in mm) is plotted as a function of square root of time ($\sqrt{t}$ in min⁰·⁵) and the sorptivity coefficient (S in mm/min⁰·⁵) is calculated as the slope of the line obtained by least squares method.

To study the progress of hydration and the pore size distribution, blended cement pastes were prepared using a w/cm of 0.5 and curing in water at 20 °C during 2, 7 and 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 crystalline hydration phases were identified by XRD analyses on powdered paste samples (<45 µm). Determination was performed on Philips PW 3710 diffractometer operating with Cu Kα radiation at 40 kV and 20 mA using carbon monochromator.

The amount of hydration compounds, crystalline and amorphous, were determined by thermogravimetric analysis (TG) using a NETZCH STA 409 thermobalance. The temperature range for phase calculations was: 40–440 °C for dehydration of C—S—H, C—A—H and C—A—S—H phases, and 440–560 °C for CH dehydration [3,17].

The pore size distribution was determined using a Termo Fisher Scientific S.p.A. PA 440 mercury intrusion porosimeter (MIP) in the pore size radius from 3.7 to 6500 nm [18].

3. Results

3.1. Pozzolanity of blended cements

The results of Frattini test (Fig. 2) reveals that 15A2 and 30A2 blended cements have pozzolanic activity at 2 days. At the same age, 15A1 has no pozzolanic activity and 30A1 is located on the calcium isotherm curve. At 7 days, four blended cements are classified as pozzolanic and the 30A2 has the highest pozzolanic activity. At 28 days, the best index of pozzolanic activity was for 30A2, followed by 30A1, and finally 15A2 and 15A1 with comparable values. This test determines that both samples have good pozzolanic activity appearing A2 as more reactive (Fig. 2), which is attributable to the larger specific surface (Table 2).

3.2. Compressive strength

Fig. 3 shows the compressive strength at 2, 7 and 28 days. For both replacement levels, the increase in compressive strength of mortars with A2 blended cements was more prominent than those of A1 blended cements at all ages. At 2 days, the 15A1 and 15A2 blended cements achieve 81% and 95% of compressive strength of PC, respectively. Compressive strength of both A2 blended cements was higher than that of PC at 7 days, and the 30A2 has the highest compressive strength at 28 days. For 30A1 blended cement, the compressive strength was always lower than that of PC mortar, while 15A1 attains similar compressive strength to PC at 28 days. At 28 days, 30A1 and 30A2 achieve 88% and 127% of compressive strength of PC, respectively.
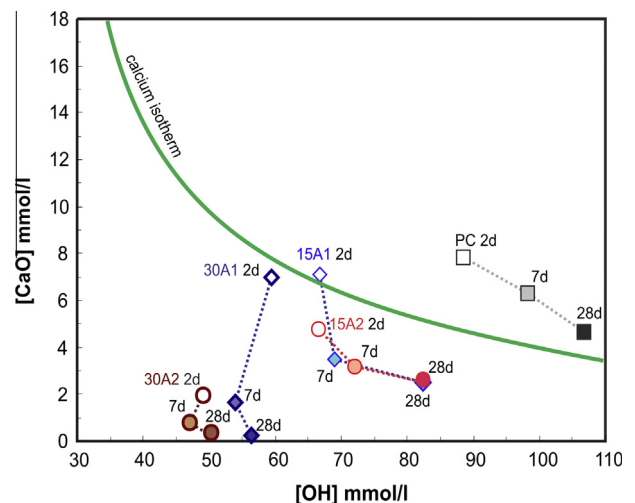

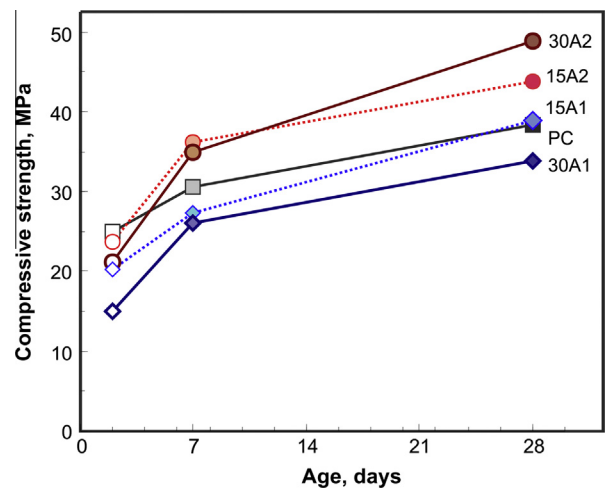**Fig. 2.** Frattini test at 2, 7 and 28 days.

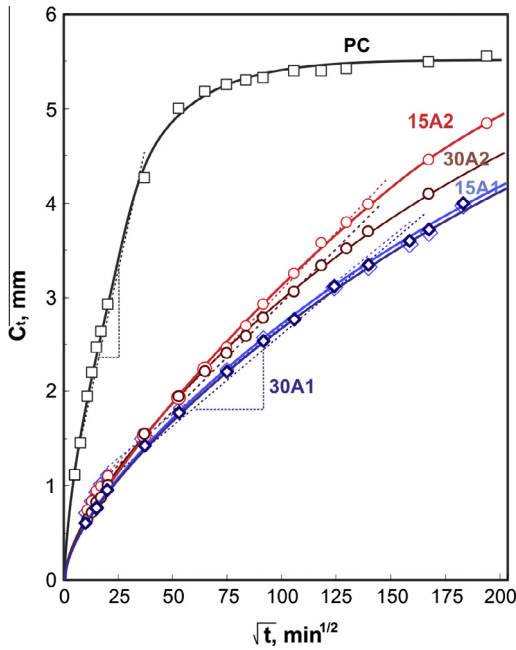**Fig. 3.** Compressive strength at 2, 7 and 28 days.

Fig. 4. Determination of the sorptivity coefficient based on the rate of water sorption at 28 days.

3.3. Sorptivity

Fig. 4 shows the calculation of sorptivity coefficient (S) based on the rate of absorption of water. The sorptivity coefficient was 0.094, 0.018, 0.019, 0.023, and 0.022 mm/min$^{0.5}$ for PC, 15A1, 30A1, 15A2, and 30A2, respectively. S-coefficient for blended cements with A1 is five times lower than PC, and this parameter is four times lower than PC for A2. Independently of the pozzolanic activity and the replacement level of calcined clay, this parameter is lower in mortars made with blended cements in agreement with results obtained by Badogiannis and Tsivilis [19] for calcined clays derived from poor Greek kaolin.

3.4. Hydration

Fig. 5 illustrates the XRD patterns for plain and blended cement pastes at different ages. At 2 days (Fig. 5a), the pattern of PC shows the presence of ettringite (Ett) and CH, accompanied by low intensity of hemicarboaluminate (HC) and C_4AH_{13} peaks. After 7 days (Fig. 5b), the incipient formation of monocarboaluminate (MC = $C_4A\bar{C}cH_{11}$) is revealed together with a low intensity of HC and C_4AH_{13} peaks. The MC is a well-defined hydrated product at 28 days (Fig. 5c) accompanied by Ett and CH. The transformations to C_4AH_{13} first to HC and then to MC, uptake of carbonate is required, then transition between reactive and inert $CaCO_3$ added as a "filler", depends on cement C_3A content [20]. The content of C_3A in PC used (8%) promotes the formation of C_4AH_{13}, and its later transformation is attributed to the presence of limestone filler as minor component in the PC.

The pozzolanic reaction between metakaolinite and CH produces a cementing compound like C—S—H and some alumina hydrates phases that depend on CH available. According to Murat [9], the reaction produces C_4AH_{13} when the CH content is higher, and strätlingite (Str) when the CH content is lower at 28 days.

For A1 blended cement, Ett, HC, MC and CH are the hydrated crystalline compounds detected. HC appears at 2 days for 30A1 cement and then increases significantly at 7 and 28 days, while MC appears as incipient compound. The intensity of MC peaks is higher for 15A1 cement. At 28 days, some traces of Str are also found in 30A1 blended cement. The intensity of CH peaks decreases with age, as the pozzolanic reaction progresses. However, well defined peaks of CH are detected for 30A1 and 15A1 blended cements.

At 2 days, A2 blended cements have the same assemblage of hydration products containing Ett, HC and CH. Thereafter, the HC peak is very intense at 7 and 28 days. Traces of MC are identified in 15A2 cement, but it cannot be identified for 30A2 cement. The CH decreases significantly for 15A2 cement and it is not detected for 30A2 blended cement at 28 days.

Fig. 6 shows the amount of mass loss attributed to the hydrated phases (CSH, CAH and CASH) and to the CH-dehydration. Some of
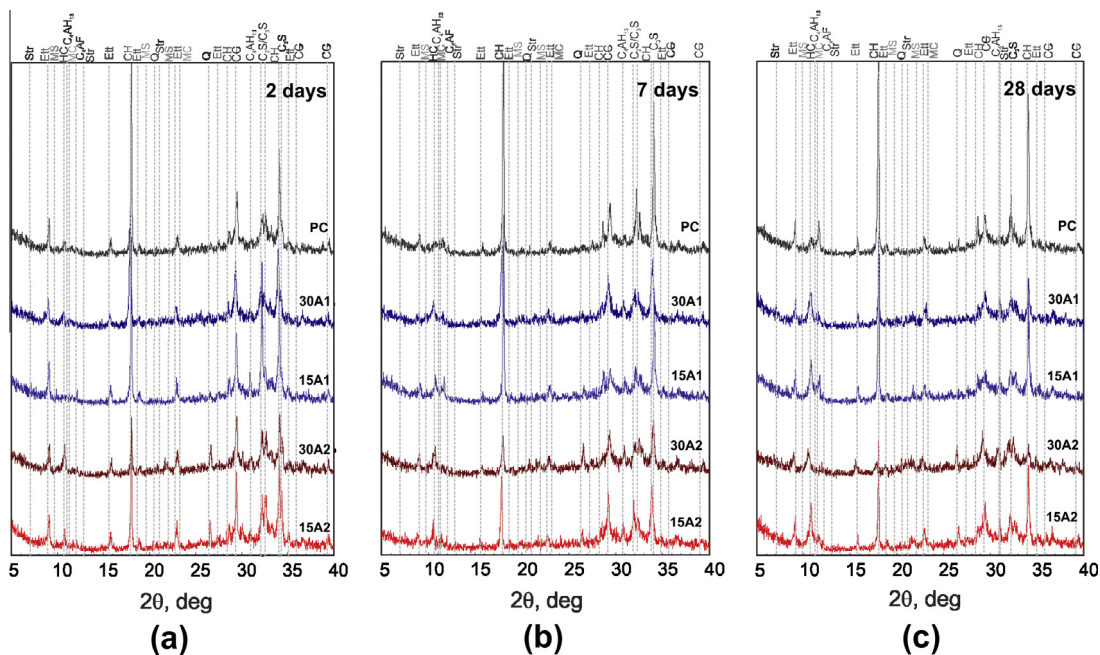

Fig. 5. XRD patterns for hydrated pastes at: (a) 2 days; (b) 7 days and (c) 28 days.

the hydrated phases have a low degree of crystallinity and they are difficult to detect by XRD. The amount of mass loss of hydration compounds, crystalline and amorphous was determined from 40 to 440 °C. Fig. 6a shows that 30A2 has a large mass loss compared with PC at all ages. For 15A2 it occurs after 7 days and it does not exceed the mass loss of 30A2. Blended cements made with A1 have a lower amount of hydrated phases than PC at all studied ages. For A1 blended cements, the amount of water loss during dehydration decreases from 7 to 28 days, indicating the formation of hydrated phases with less water in their structure.

For PC paste, the mass loss attributed to CH-dehydration increases with the time (Fig. 6b). For A1 blended cements, the CH decreases from 7 to 28 days, whereas for A2 blended cement it decreases from the first measure (2 days). It is clear evidence of the high rate of pozzolanic reaction of A2 calcined clays as determined by Frattini test (Fig. 2). For the same percentage of replacement, the CH-consumption was always higher for A2, however at later ages this difference becomes less noticeable. At 28 days, the low amount of CH due to the progress of pozzolanic reaction causes the change in assembling in alumina bearing phases.

3.5. Porosity

Fig. 7 shows the pore size distribution of pastes. The pore system was refined from 2 to 28 days as the progress of PC hydration and pozzolanic reaction. At 2 days (Fig. 7a), all blended cements have a coarser distribution of pores size than those of PC. 30A1 has the highest proportions of pores >300 nm and 15A1 has the largest volume of pores >100–300 nm. For 30A2 and 15A2 cements, the coarse porosity (>100 nm) is greater than that obtained for PC-paste, but they have a large volume of smaller pores (<50 nm, especially of 5 nm). The coarse pore size of blended cements is in accordance with compressive strength results at 2 days: 30A1 has the lowest compressive strength, and the coarse pore size is reduced in increasing order of compressive strength (15A1, 30A2, 15A2 and PC). At 7 days (Fig. 7b), 30A1 and 15A1 have a larger volume of pores radius >100 nm than the PC paste and, consequently, the compressive strength is lower. 30A2 and 15A2 have a very low volume of pore radius <100 nm and a great volume of pores with radius <25 nm and the relative strength is high (Fig. 3). At 28 days (Fig. 7c), the volume of pores radius >25 nm decreases and the volume of pores radius <25 nm increases for all the blended cement since the progress of the pozzolanic reaction and the compressive strength is similar to or higher than that of PC paste.

According to Mindess and Young [21], pores with radius in the range of 5–5000 nm affect the compressive strength and the permeability of cement based materials. At 28 days, the pore volume with radius larger than 5 nm is ~100 mm³/g for blended cement pastes and it is ~150 mm³/g for the PC-paste. This important
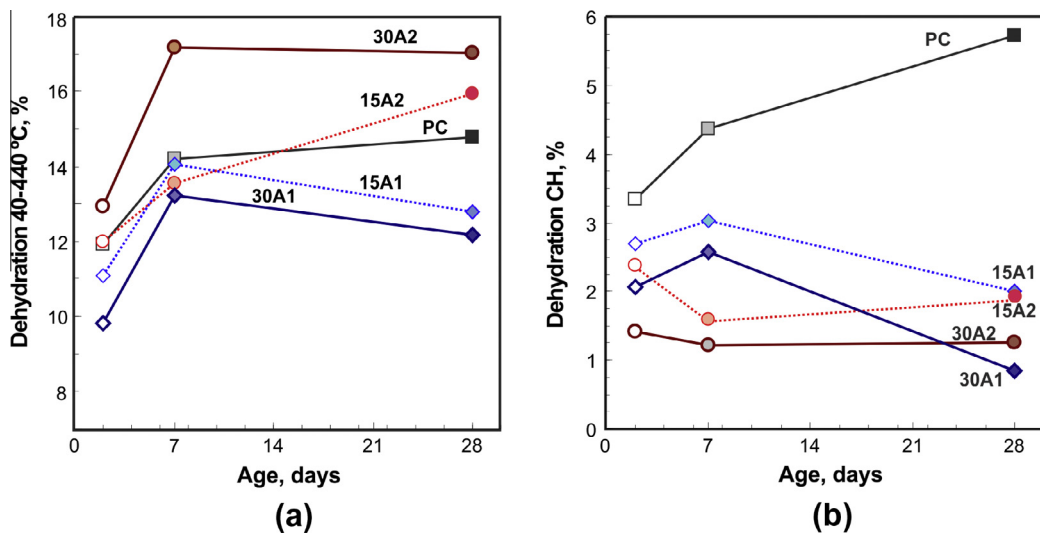

Fig. 6. Mass loss obtained by TG during: (a) the dehydratation of CSH, CAH and CASH phases and (b) dehydratation of CH.
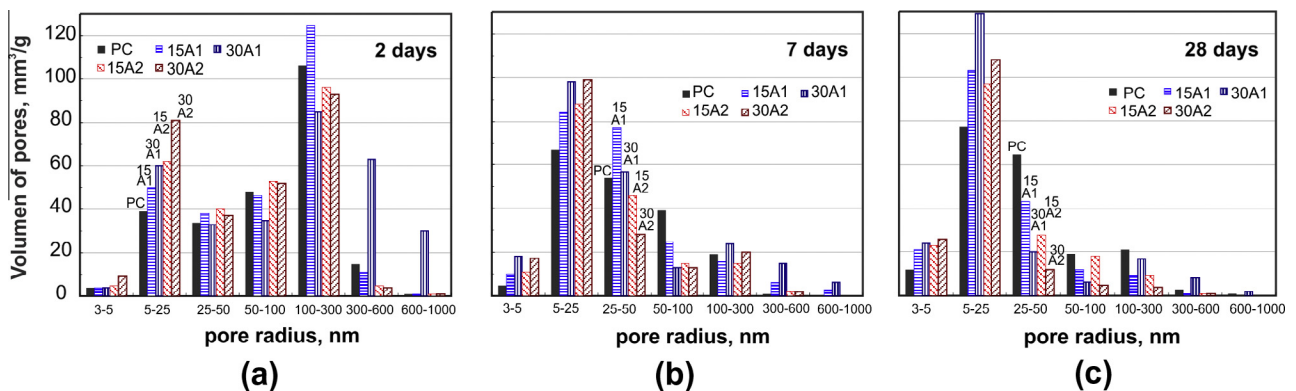

Fig. 7. Pore size distribution of paste at: (a) 2 days; (b) 7 days and (c) 28 days.

reduction of total capillary porosity justifies the lowest sorptivity coefficient of mortars with calcined clays (Fig. 4). According to results of Badogiannis and Tsivilis [19], the addition of kaolinitic calcined clays refines the pore system causing an improved transport coefficient that could improve the durability of material.

4. Discussion

The amount and type of hydration compounds obtained during the progress of hydration depend on the formulation of blended cements, the amount and characteristics of kaolinitic calcined clays used. The incorporation of calcined clays produces the acceleration of cement hydration, the dilution of cement (increase of w/cm) and the pozzolanic reaction that produces cementing compounds at different rate from Portland cement [11,22]. When the dilution effect is greater than the compensating effect of the pozzolanic reaction, the amount of hydrated phases and CH is small in the system causing a large volume of pores. On the other hand, when the volume of hydration products of the pozzolanic reaction compensates or overpasses the effect of dilution, there are more hydrated phases and a low amount of CH due to pozzolanic consumption causing a small volume of pores.

For all ages, Fig. 8 shows the relationship between the volume of pores (PV) from 10 to 6500 nm and the compressive strength (CS). It is a classical inversely exponential relationship between compressive strength and porosity. Some deviations in this relationship could be attributed to the nature of hydration products formed and the volume that they occupy reducing the pore volume but without contribution to compressive strength. For example, the PC has higher pore volume than the corresponding to 15A1, but both pastes have the same compressive strength at 28 days (Fig. 8). On the contrary, 30A1 presents a lower volume of pores than PC, but it develops low compressive strength at 28 days. This behavior could be justified considering that the hydrated phases (silicates or aluminates) that contribute to the reduction of the pore volume differ depending on the blended cement used.

The formulation of blended cement with calcined kaolinitic clays depends on the characteristics of the calcined clay used.

After calcination and grinding, A2-clay with high content of kaolinite and disordered structure has a high specific surface and a very good pozzolanic activity (Fig. 2). These characteristics contribute to increase the amount of hydrated phases (Fig. 6) decreasing the pore volume (Fig. 7) and contributing to the compressive strength (Fig. 3). For this highly reactive pozzolan, the blended cement can be designed with replacement level up to 30% with better mechanical and durable properties. A1-clay with a high content of kaolinite and ordered structure has low specific surface and good pozzolanic activity after calcination and grinding (Fig. 2). The
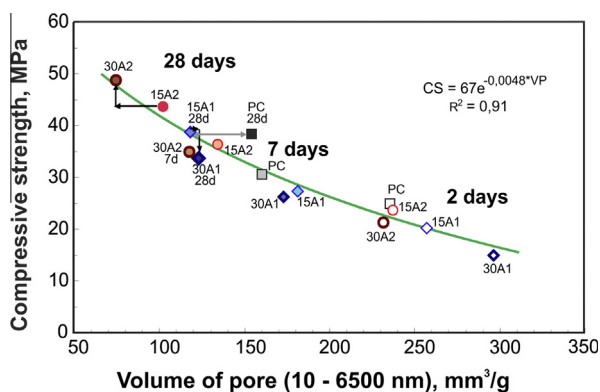
coarse particle size distribution of A1 calcined clays can also affect negatively its pozzolanic activity. The hydrated phases obtained are different, and although the pore volume decreases, the combination of these factors does not contribute significantly to increase the compressive strength (Fig 8). To obtain blended cement with the PC-equivalent mechanical efficiency using A1 calcined clay, a low replacement level is required (15%) instead of its high content of metakaolinite.

For the replacement levels studied, both calcined kaolinitic clays produce a significantly decrease of the sorptivity coefficient compared with the PC mortars at 28 days. It is attributed to the shift in the dominant pore radius in the paste: 5–50 nm for the PC and 5–25 nm for all blended cements.

The different rate of reaction of metakaolin obtained from different raw kaolinitic clay justified the differences in mechanical performance reported in previous research. The rate of reaction is related to the BET specific surface of metakaolinite determined by the structure of kaolinite in raw clay.

5. Conclusions

The experimental results presented here show that kaolinitic calcined clays are an effective pozzolan, but their rate of reaction can change significantly causing modifications in the mechanical properties of the blended cement.

The pozzolanicity of blended cement containing calcined kaolinitic clays determined by Frattini test clearly depends on the level replacement and the reactivity of the calcined clays.

The reactivity of calcined clays is related to the specific surface area developed by the material after calcination. It primarily depends on the structure of kaolinite in raw clays: when kaolinite in raw clay has a disordered structure, after appropriate calcination and grinding, it has a very high pozzolanic activity and allows high replacement level (30%) in blended cements to achieve the same mechanical efficiency of PC. For kaolinitic clays with ordered structure calcined and ground, the replacement level is limited at low percentage (15%) to attain similar level of compressive strength to PC.

Both kaolinitic calcined clays produce a significant reduction of the sorptivity coefficient compared with the PC mortars at 28 days.

For different kaolinitic calcined clays, the optimum level of replacement is associated to the changes in the assembling and proportions of hydration products and its consequence on the porosity. The addition of calcined clays reduces the CH formed during PC hydration, producing large proportions of cementitious compounds together with aluminum crystalline products. The composition of crystalline products depends on the MK/CH ratio determined by the reactivity of clays, replacement level, cement composition and age. Incorporation of kaolinitic calcined clays modifies the volume and structure of pore system in the paste. The pore volume is related to compressive strength and the reduction of the dominant pore size at later ages improves greatly the resistant to transport of water by capillary sorption. Using an appropriate formulation of blended cement, it is possible to obtain good mechanical and durable performance, in addition to the reduction of CO_2 emissions.

Fig. 8. Relationship between the compressive strength and the volume of pores with radius between 10 and 6500 nm.

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