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Kaolinitic calcined clays: Factors affecting its performance as pozzolans

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ABSTRACT

Five natural kaolinitic clays from different regions of Argentine, with different kaolinite content, different impurities and different degree of crystallinity were calcined in a fixed-bed electrical furnace at 700 °C. Clays were characterized by X-ray diffraction (XRD) and Fourier transformed infra-red spectrometry (FTIR) that provides an index about the order/disorder of the structure. After heat treatment, the structural changes were characterized by XRD and FTIR, and pore size distribution and specific surface were determined. Their pozzolanic activity was evaluated with the Frattini test, electrical conductivity in saturated $Ca(OH)_2$ solution and compressive strength on mortars at 7, 28 and 90 days. Among tested clays, four of them can be classified as pozzolan by the Frattini test. The pozzolanic activity of the natural clays showed good correlation with the content of kaolinite, the inversed of structure order determined by FTIR, and the specific surface of calcined clays. This study confirms that natural clays other than pure kaolinite can be interesting pozzolanic materials when thermally activated.

1. Introduction

Portland cement is the most used construction material in the world due to the abundance of raw materials for cement manufacture, its relatively low cost and concrete versatility. The production of Portland cement consumes a large amount of energy and emits large quantities of carbon dioxide (CO_2) to the atmosphere making its future vulnerable [1,2]. Energy is computable for extracting, transporting and processing materials in cement plants and transporting the end product to consumers.

Environmental concerns can be dealt with by replacing part of the Portland cement clinker with pozzolanic materials in mortars and concretes [1,3]. In this way, the use of industrial by-products such as slag, fly ash or silica fume increases around the word. In developed countries, as there is either a poor availability of these by-products or transport results expensive, the use of kaolinitic calcined clays, which is an abundant material, has gained importance as an alternative pozzolanic material [4,5]. Usually, clay deposits contain a mixture of different clay minerals (kaolinite, illite, montmorillionite, palygorskite, and others) and a large proportion of impurities of non clay materials, such as quartz, calcite, feldspars, mica, anatase and sulfides. These impurities are very difficult to eliminate and require wet beneficiation treatment and the subsequent drying of raw materials, which also consumes energy and produces a large proportion of waste [5].

Calcination of pure kaolinitic clays at temperatures ranging between 550 and 900 °C produces an amorphous silica compound (metakaolinite – MK), which is a very reactive aluminosilicate pozzolan [6]. At ambient temperature, MK reacts with $Ca(OH)_2$ in the presence of water producing a cementing compound like C–S–H and some hydrates of alumina bearing phase [7]. The pozzolanic properties of high quality commercial MK obtained from calcinations of pure kaolinitic clays are widely discussed in cement literature [1–4,6,8–11]. The production of MK reduces the amount of energy used and CO_2 emissions. Energy saving occurs because calcination temperature of clays is lower than that of clinker and they are also easy to grind [12]. On the other hand, a great quantity of CO_2 is generated in the decomposition of calcite during clinker production, whereas deshydroxilation of kaolinitic clays emits water vapor.

The aim of this study is to identify the main parameters in natural kaolinitic clays that control its pozzolanic activity after a prefixed heat treatment. Five natural calcined clays with different kaolinite content, different impurities and different degree of crystallinity were characterized and their pozzolanic activity was evaluate with several methods. The pozzolanic reactivity of clays showed good correlation with the content of kaolinite, the crystallinity determined by FTIR and the specific surface of calcined clays.

2. Materials and methods

2.1. Materials and characterization

Clays used in this study were obtained from different locations of Argentine (Provinces of La Rioja, Río Negro, Chubut, and Santa Cruz). The chemical composition, determined by ICP-AES analysis in external laboratory (ALS, Argentine), and

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loss on ignition of clays are shown in Table 1. According to the chemical analysis, clays were classified as decreased content of alumina as A1, A2, A3, A4 and A5; and they presented an inverse content of silica. It can be observed that A5 clay presents the highest alkali content.

The mineralogical composition of clays was analyzed by X-ray diffraction (XRD) and Fourier transformed infra-red spectrometry (FTIR). XRD was performed using a Philips PW 3710 diffractometer operating with Cu Kα radiation at 40 kV and 20 mA. FTIR spectrums were obtained using a Nicolet Magna 500 spectrophotometer ranged from 4000 to 400 cm^{-1}.

After the identification of clay minerals present in the samples by XRD, the kaolinite content (K) was estimated by stechiometry using the results of chemical analysis [13]. For the sample without illite, the Al_2O_3-total is assigned to kaolinite calculating its proportion and thereafter the percentage of SiO_2 present in the kaolinite is determined. The latter is deducted from the SiO_2-total and the remainder is assigned to quartz. When the sample contains illlite, the K_2O is used to calculate the percentage of illite in the sample, and then the amount of Al_2O_3 and SiO_2 combined in illite is determined. The subtraction of Al_2O_3-total minus Al_2O_3 combined in illite allows to calculate the percentage of kaolinite in the sample. The sum of SiO_2 in illite and in kaolinite is deducted from the SiO_2-total obtained in chemical analysis and it is assigned to quartz. If the sample contains feldspar, potassium is divided between feldspar and illite.

A normal Portland cement (PC) was used for pozzolanic activity tests. Its chemical composition, determined by the X-ray fluorescence, is reported in Table 1. The mineralogical composition calculated using the Bogués formula was $C_3S = 47\%$, $C_2S = 22\%$, $C_3A = 8\%$ and $C_4AF = 9\%$. This PC has a strength class of 40 (standard compressive strength >40 MPa at 28 days) and its Blaine specific surface was 383 m^2/kg.

2.2. Thermal treatment and characterization of calcined clays

Raw clay samples were reduced to particle size smaller than 4 mm. The thermal treatment of clays was carried out in a programmable laboratory furnace using a fixed bed technique. The samples were heated from the ambient temperature up to 700 °C, a recommended temperature that transforms kaolinite into an amorphous phase for this type of clays [1,4,14]. In this process, the heating rate was set at 13 °C per minute and the time of residence at high temperature was 5 min, totalizing the duration of heat-cycle in one hour. After cooling, the calcined clays were ground in a mortar type mill (Fritsch Pulverisette 2) until 100% of mass passed through the 45 μm sieve (# 325). Then, they were analyzed by XRD and FTIR to determine the mineralogical transformations caused by heat treatment.

Physical characterization of calcined clays includes the pore size distribution by mercury intrusion porosimeter (MIP) and the Blaine fineness. Before grinding, the pore size distribution was determined using a Carlo Erba 2000 MIP Instrumental. This technique is able to characterize the whole range of pore radius from 3.7 to 7500 nm including meso and macropores. After grinding, the specific surface was measured using the Blaine method according to ASTM C 204-04 standard [15].

2.3. Pozzolanic activity test methods

Pozzolanic activity of calcined clays was proved as described below.

Electrical conductivity was carried out using a similar procedure proposed by Luxan et al. [16] and modified by Qijun et al. [17]. It consists in monitoring, at regular intervals of time, the electrical conductivity of 20 ml of saturated solution of calcium hydroxide at 40 °C after adding 2 g of calcined clays, using a conductivity meter (Jeway 4010). The measured values gradually decrease with the time when the added material is highly reactive due to the consumption of ions by pozzolanic reaction.

Frattini test was carried out according to the procedure described by EN 196:5 standard [18]. The tested sample was a blend of 70% of Portland cement (PC) and 30% by mass of ground calcined clay. This test implies the determination of the amount of Ca^{2+} and OH^- in the water of contact with the tested samples stored at 40 °C during 7 and 28 days. Then, comparing the amount of these ions with the solubility isotherm of $Ca(OH)_2$ in an alkaline solution at the same temperature, the calcined clay is considered as active pozzolan when the $[Ca^{2+}]$ and $[OH^-]$ determined in solution are located below the solubility isotherm [19].

Compressive strength was assessed on mortars cubes (25 × 25 × 25 mm) made with standard sand (1:3) and a water/cementing material ratio of 0.50. The cementing material consisted in a blend of 30% by mass of ground calcined clay and 70% of PC. Mortars were prepared by mechanical mixing and compaction in a mold using a standard compaction. The specimens were cured in the molds in a moist cabinet for 24 h and then immersed in water saturated with lime until test age at 20 ± 1 °C. At 7, 28 and 90 days, compressive strength was determined as the average of three specimens using universal testing machine Instron 4485. Finally, the strength activity index (SAI) was calculated as the ratio of the compressive strength of blended cement to the strength of the Portland cement at the same age.

3. Results and discussion

3.1. Raw clays

For the studied clays, the kaolinite content determined by stoichiometric calculation is reported in Table 2. According to these values, clays can be classified as high (A1 and A2), medium (A3 and A4) and poor (A5) kaolintic-clays.

XRD patterns of raw clays (Fig. 1a) show that A1-clay presents very strong peaks of kaolinite (K), and a very low intensity of the main peak of quartz (Q). For A2, A3 and A4 clays, XRD patterns show well-defined peaks of kaolinite and quartz, accompanied with a weak main peak of illite (I). A5-clay presents kaolinite, quartz, illite and alkali feldspars as anorthite (An) and orthoclase (O). For all samples, XRD reveals a poor intensity peak of anatase (A). The intensity of the peaks assigned to kaolinite decreases from A1 to A5-clay according to the kaolinite content (Table 2), while the intensity of peaks of quartz increases according to the increase of SiO_2 content. Fig 1a also shows that the main peak of kaolinite ($2\theta = 12.34°$) for A1-clay has a sharp shape and its base is less wide than that corresponding to A2 and A3-clays, indicating a well-ordered crystalline structure.

The FTIR spectrums of raw samples appear in Fig. 2a and they provide qualitative and quantitative information about the order or the disorder of the structure, depending on the relative intensity of the OH band in the 3700–3600 cm^{-1} region [9,20]. In the FTIR spectrums of kaolinite, the band near 3620 cm^{-1} arises from internal OH groups, and that near 3700 cm^{-1} arises from internal surface OH groups. Structure disorder in kaolinite is detectable mainly in the OH^- stretching region, although some general broadening of all bands in the spectrum may also occur. While the 3620 cm^{-1} and 3700 cm^{-1} bands are essentially unchanged, the 3669–3652 cm^{-1} doublet is replaced by a single broad band at 3653 cm^{-1} [21].

FTIR spectrum of A1-clay, which has the highest content of kaolinite, shows the four well-defined OH group bands. In the spectrum of A2-clay, the OH group bands for 3670 and 3650 cm^{-1} are not appreciated. These bands are mild for A3 and A4 clays although their kaolinite content is lower than that corresponding to A2-clays. For A5-clay, the OH group bands present low intensity due to the poor kaolinite content, but these bands are well-defined. To determine quantitatively the order/disorder of kaolinite structure, the P_0 index was calculated as the ratio between the intensities of the bands at 3620 cm^{-1} and 3700 cm^{-1}, reported in Table 2. According

Table 1
Chemical analysis and loss on ignition of PC and clays used.

Sample	Chemical composition (%)									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	LOI
PC	20.1	4.8	2.98	60.3	3.47	3.21	0.72	1.00		3.44
A1	45.9	37.0	0.77	0.08	0.12		0.06	0.40	0.99	13.30
A2	51.4	31.3	0.92	0.40	0.19		0.36	0.38	1.42	12.15
A3	59.4	27.1	0.76	0.15	0.12		0.14	0.41	0.26	9.65
A4	65.7	21.1	0.85	0.26	0.22		0.07	0.68	0.43	7.77
A5	74.8	14.8	1.10	0.30	0.26		0.92	3.71	0.18	3.44

Table 2
Characterization of kaolinitic clays before and after calcination.

Clays	Before calcination				After calcination							
	Kaolinite content		Structural parameters		Volume of pore (mm^3/g)							Specific surface Blaine
					>100 nm		20–100 nm		<20 nm		Total	
	%	Class	$P_0 = I_{3620}/I_{3700}$	Order/disorder	mm^3/g	%	mm^3/g	%	mm^3/g	%	mm^3/g	m^2/kg
A1	94	High-K	1.121	Order	6	7	8	9	76	84	91	1461
A2	76	High-K	0.477	Disorder	69	17	191	48	143	35	403	2287
A3	65	Medium-K	0.805	Disorder	45	13	208	60	95	27	348	1865
A4	48	Medium-K	0.898	Disorder	52	18	100	35	133	47	285	981
A5	16	Poor-K	1.687	Order	94	37	78	31	82	32	254	1399

to Bich et al. [9], kaolinite is a well-ordered structure when $P_0 > 1$. For the studied clays, A1 and A5-clays present a $P_0 > 1$ with an ordered kaolinite structure; while A2, A3 and A4-clays present a $P_0 < 1$, indicating a disordered structure.

3.2. Calcined clays

XRD patterns of calcined clays (Fig. 1b) show that peaks corresponding to kaolinite disappeared completely for A2, A3, A4 and A5, showing that thermal treatment (5 min at 700 °C) is adequate to complete the kaolin–metakaolin transformation in these clays. Very weak peaks are identified for A1-clay, so that the temperature or residence time of heat treatment could be insufficient. When this clay was heat treated during 5 min at 800 °C, complete conversion occurred. The presence of amorphous material was denoted by a dome around $2\theta = 21.8$. Quartz, illite, anatase and feldspars are easily identified because they are not altered by the heat treatment.

In agreement with Chakchouk et al. [14], the FTIR spectrums of calcined clays (Fig. 2b) present the following changes: the absence of detectable –OH and Al–OH bands; the transformation Si–O characteristic bands of kaolinite present in the raw clay to a single absorption band which is characteristic of the amorphous silica; the disappearance of the band at 534 cm^{-1} relative to Al–O–Si; and the displacement of the Si–O band at 470 cm^{-1} to high wave numbers. From XRD and FTIR analyses, both techniques confirm the transformation of kaolinite into reactive amorphous phase by heat treatment.

3.3. Physical characteristics of calcined clays

Fig. 3 shows the pore size distribution of clays after heat treatment. Complementary, the volume of very large pores (>100 nm), medium-size pores attributable to original kaolinite inter-particles voids (20–100 nm), very fine pores within particles (<20 nm) and total pores volume are reported in Table 2.

The total volume of pore intrudable by mercury is an index of system porosity [22], A2-clay presents the highest total porosity and A1-clay has the lowest. Both clays, however, present a high-K (see Table 2). A2, A3 and A4 clays present an intermediate total volume of pores.

Regarding MIP results, curves are essentially convex to the pore-size axis for A2 and A3 clays and become increasingly concave for the A1, A4 and A5 clays. A1, A2, A3 and A4 clays have high pore volume below 100 nm (>80%), while A5 clay presents a large proportion of coarse pores (37%). The curve corresponding to A1 clay shows a strong upward trend below 20 nm of pore radius (84% of total volume). For A2-clay, the shift of curvature for cumulative volume of pores occurs in a radius range from 20 nm to 100 nm, while for A3-clay, it occurs in the range of 40–100 nm. A4 and A5-clays show no indication of the bulge in the pore-size distribution. Pores from 20 to 100 nm occupy 35–60% of total porosity for calcined clays derived from disorder structures or the greater surface roughness in the particles, while A1-clay has a low pore volume in this region.

After calcination and grinding, the specific surface of clays measured by the Blaine method is reported in Table 2. These values are

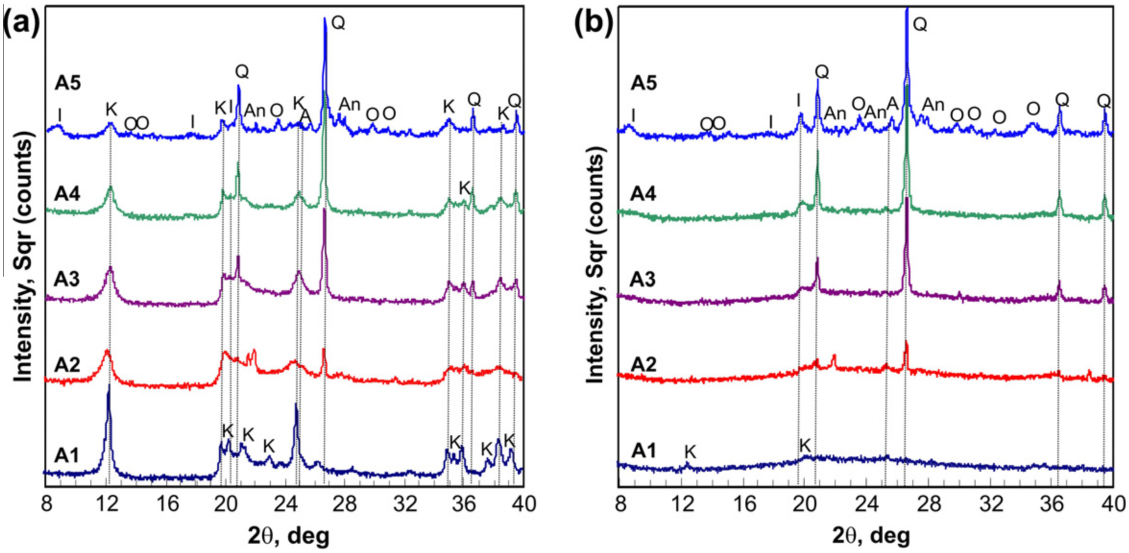

Fig. 1. XRD patterns: (a) natural clays, and (b) calcined clays. K-kaolinite, Q-quartz, I-illite, A-anatase, O-orthoclase, An-anorthite.

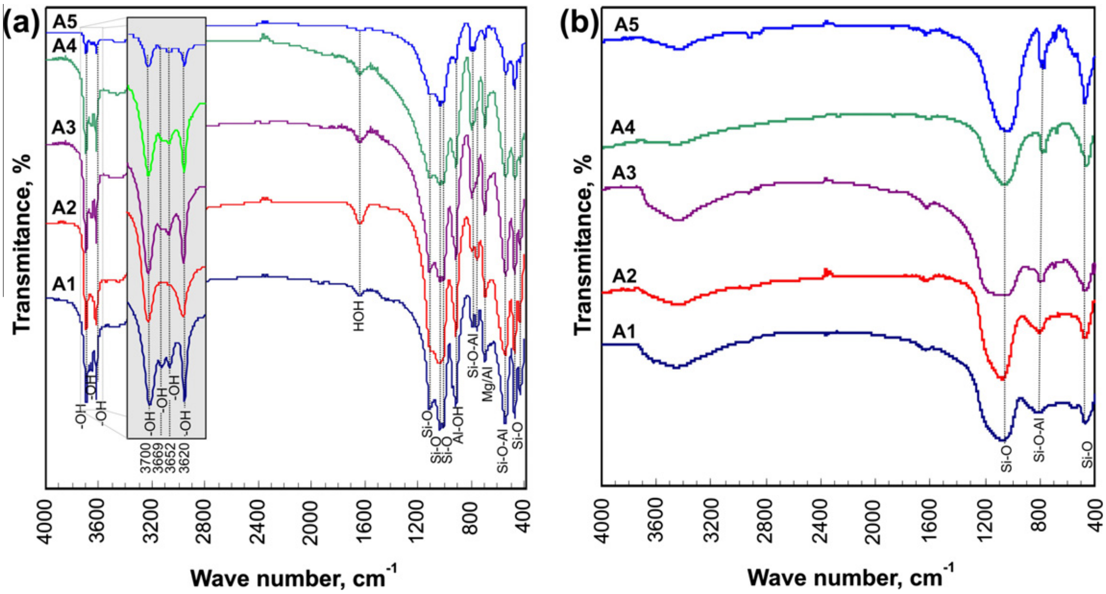

Fig. 2. FTIR spectra of natural clays (a) and calcined clays (b).

similar to those obtained by previous research [8]. The A2-clay presents the largest specific surface in accordance with its large volume of pores and the same trend is revealed for A3 and A4-clays. The analysis is different for A1 and A5, both clays have a similar specific surface value (≈1400 m^2/kg), but they have a quite different pore size distribution, total porosity and K-content. This observation indicates that specific surface is due to the external surface area of particles and the surface area of pores within particles. For A1-clay, specific surface will be attributable to the external surface area of particles; while the specific surface of A5-clay could be attributable to the internal porosity of particles, including feldspar particles.

3.4. Pozzolanic activity

Fig. 4 shows the *electrical conductivity* of calcined clay–lime solution as a function of time. During the first 30 min, the A2-clay addition produces a drastic drop of electrical conductivity of lime-solution due to a high consumption rate of Ca^{2+} and OH^- ions [16] and it is attributed to the fixation of dissolved $Ca(OH)_2$ by calcined clay particles [7,17]. This behavior indicates the high reactivity of this clay with $Ca(OH)_2$ and it can be a measure of its pozzolanic activity. A3-clay is in the second place of reactivity with $Ca(OH)_2$. On the other hand, A1-clay, with high-K, appears as less reactive pozzolan and the solution has similar electrical conductivity to that of A5-clay with poor-K. Analyzing the first hour of reaction, the reactivity of clays, measured as drop of electrical conductivity, was A2, A3, A1, A5 and A4. These values are closely related with the specific surface of calcined clays. Then, A4-clay result the less reactivity.

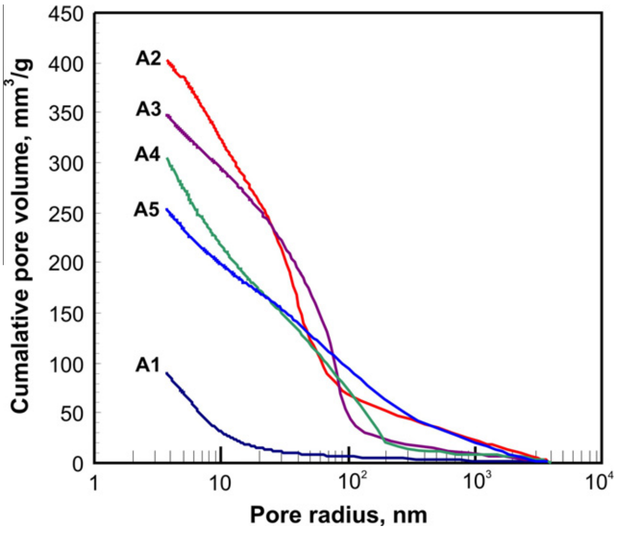

Fig. 3. Pore size distribution calcined clays before ground.

After 24 h, judged by the residual electrical conductivity of $Ca(OH)_2$ solution, the more reactive calcined clay is A2, followed by A3, A4, A5 and, finally A1. The highest decrease of electrical conductivity was recorded in the calcined clays with disordered kaolinite. The most reactive was A2 with high-K, followed by A3 and A4-clays with a medium-K. A5 and A1 were less reactive; both come from ordered kaolinite before calcination. A1 clay calcined at a higher temperature (800 °C) showed an even lower reactivity (Fig. 4). According to this test, related to the Blaine surface area of calcined clays, when the specific surface is higher, the reduction of electrical conductivity in the first two hours of reaction is high.

Fig. 5 shows the results of the *Frattini test* at 7 and 28 days plotted on the $[OH^-]$ vs. [CaO] diagram. For A1–A4 clays, the points are located in the undersaturation area, indicating that a large proportion of calcium hydroxide supplied during Portland cement hydration has been consumed by the pozzolanic reaction. From 7 to 28 days, the pozzolanic reaction was detected by a reduction of $[OH^-]$ and [CaO] in these samples. From ion consumption, the pozzolanic reactivity of calcined clays in increasing order was A2, A3, A1 and A4. For A5-clay, results at 28 days indicate that the increase in the concentration of OH^- in the Frattini test could be due to the contribution of alkalis released from clay (see chemical composition in Table 1 that increases the $[OH^-]$ while [CaO] remains constant.

Results from the Frattini test and electrical conductivity showed that A2 and A3-clays were the most reactive, although these clays had high and medium-K. However, they have a disordered structure before calcination and a large specific surface after calcination and grinding. A1-clay has high-K (94%) but it has an ordered

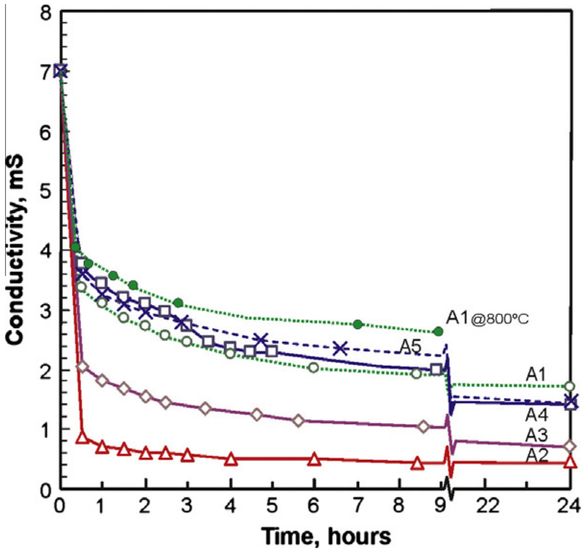

Fig. 4. Electrical Conductivity clays A1–A5 calcined at 700 °C and A1 calcined at 800 °C.

structure; before calcinations, it did not show the highest reactivity in both tests. A5-clay has the lowest content of kaolinite (16%), ordered structure and high percentage of alkali impurities, consistent with its regular pozzolanic behavior.

Results of compressive strength at 7, 28 and 90 days are summarized in Table 3. For 30% replacement of PC with calcined clay, the blended cements with A2-clay have the highest compressive strength at all test ages. Compressive strength (SAI = 1.05) similar to that obtained by PC at 7 days occurs, being then higher than PC at 28 and 90 days. Regarding other clays, blended cements show lower strength than the corresponding to PC at 7 days of curing. Then, blended cement with A3-clay shows a higher strength than PC (SAI = 1.07 and 1.18 at 28 and 90 days, respectively). For A1 and A4-clays, blended cements present a similar development of strength with a SAI close to 1.00, while blended cement with A5-clay never attains the compressive strength of PC.

The strength development in blended cement with calcined clays depends on PC hydration and the pozzolanic activity of metakaolin obtained from calcination processes. According to Badogiannis et al. [23], the metakaolinite content is the main factor that influences the strength development of poor Greek metakaolins. Also, Habert et al. [5] conclude that the compressive strength is, at first approximation, correlated with the percentage of activated clay and less with the nature of the clay assemblage. However, A1-clay has high-K and, consequently, a high content of MK after calcination, but it is not the most reactive. This phenomenon is attributable to the order structure of kaolinite ($P_0 > 1$) [9,13]. In contrast, blended cement containing A2-clay exhibits higher values of compressive strength attributable to the high-k, disordered structure ($P_0 < 1$), and calcined clay with large total porosity and specific surface, causing an early reactive pozzolanic reaction. Then, compressive strength also depends on the structural and physical factors that determine the rate of pozzolanic reaction of MK.

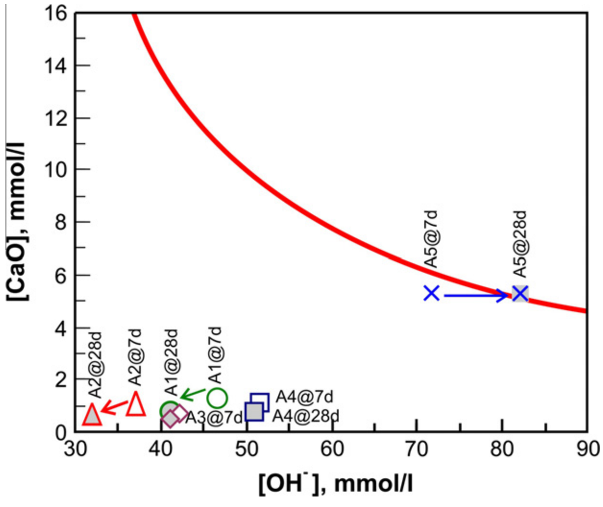

Fig. 5. Result of Frattini test at 7 and 28 days.

Different mathematical models were proposed to relate the compressive strength at different ages with the composition, structure and texture of calcined clays. Among these models, a linear combination of kaolinite content (K) in clay, the specific surface (SS_{Blaine}) of calcined clay and the inverse of the index that provides the degree of order/disorder ($1/P_0$) of the structure before calcined kaolinite, it was found that they best fit with the compressive strength at time t (CS_t) as the following equation

$$CS_t = \alpha_0 + \alpha_1 K + \alpha_2 * SS_{Blaine} + \alpha_3 * (1/P_0) \quad (1)$$

where α_i are the coefficients obtained by the least square method.

Analysis of variance (ANOVA) was used to test the significance of the model. The model is considered statistically significant when the F-test, an evaluation of the term variance with the residual variance, is much larger than the critical value obtained from the table values for an F-distribution based on $\alpha = .05$ and the degree of freedom of treatments and error. A probability less than .05 was considered as significant. Also, a graphical analysis of residuals was carried out to probe that the residuals are normally distributed. Results of α_i-coefficients and the ANOVA are presented in Table 4. The R^2 coefficient is also calculated to probe the correlation between model and experimental values. Fig. 6 shows the compressive strength obtained experimental versus the compressive strength calculated by Eq. (1).

The influence of K, SS_{Blaine} and $1/P_0$ on compressive strength at different ages can be easily analyzed using the α_i-coefficients obtained from the model. The kaolinite content increases its contribution on the compressive strength with the time. It has a similar contribution beyond 28 days, but it increases two times at 90 days. Blaine specific surface has great importance at 7 days and it is later decreased to a half at 28 days. The degree of structural disorder ($1/P_0$) contributes largely to CS when clay has a disordered structure ($P_0 < 1$) at 28 and 90 days, α_3 values increased from 28 to 90 days, but its increment was less abrupt than those occurred between 7 and 28 days. For hypothetical clay with the same SS_{Blaine} and order, the model indicates that a variation of K from 40% to 90% produces a CS-variation of approximately 2.0 MPa and 5.0 MPa at 7 and 90 days, respectively. However, the variation of SS_{Blaine} from 1000 to 2000 m^2/kg produces a CS-variation of approximately 6.0 and 2.0 MPa at 7 and 28 days,

Table 3
Compressive strength (CS in MPa) of the Portland cement and blended cement and strength activity index (SAI).

Age (days)		PC	A1	A2	A3	A4	A5
7	CS	30.6	24.7	32.2	27.1	20.5	20.6
	SAI		0.81	1.05	0.89	0.67	0.67
28	CS	38.4	37.8	49.0	41.2	36.8	30.9
	SAI		0.98	1.28	1.07	0.96	0.80
90	CS	40.8	45.1	57.4	48.0	41.5	34.2
	SAI		1.11	1.41	1.18	1.02	0.84

Table 4
Coefficients (α_i), correlation coefficient and *F*-test probability for the compressive strength model at different ages.

Age (days)	α_0	α_1	α_2	α_3	R^2	Prob > F
7	9.6	0.04	0.006	2.48	1.00	0.005
28	22.4	0.05	0.002	8.75	0.98	0.096
90	22.7	0.10	0.003	9.56	0.99	0.077

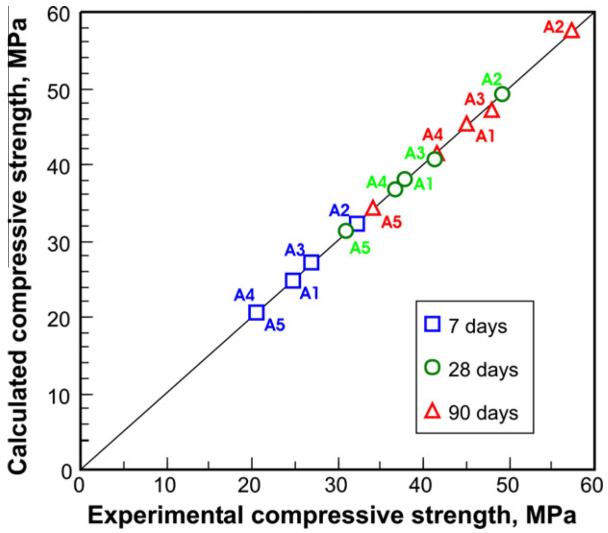

Fig. 6. Compressive strength obtained experimental and calculated by Eq. (1).

respectively. Finally, the contribution of order/disorder of clay structure on the CS when P_0 change from 1.10 to 0.50 will be approximately 3.0 MPa at 7 days and 9.0 MPa at 28 days.

4. Conclusions

Five local kaolinitic clays have been characterized. After submitted to a heat treatments their pozzolanic activity was investigated by several methods and the following conclusions can be drawn:

It was shown that the effectiveness of mineral addition as pozzolana on the Portland Cement clinkers is reached by thermal activation of the mineral at 700 °C on clays with at least 45% of kaolinite in its composition.

Calcined clays with high content of kaolin can present a very different pore size distribution and specific surface, modifying the kinetic and reactivity of the pozzolanic material obtained. Based on the Frattini and electrical conductivity tests, raw clays containing high and medium kaolinite content and disordered structure appear as the most reactive mineral addition after heat treatment. These calcined clays have a large specific surface and a large volume of pores in radio size ranging from 20 to 100 nm.

Compressive strength of blended cement with 30% of calcined clay with medium and high kaolinite content (A1–A4) reaches or surpasses the level of compressive strength of plain Portland cement mortar at 28 days.

At different ages, the compressive strength depends on the amorphous material derived from kaolinite content in clays, the structural order/disorder and physical factors that determine the rate of pozzolanic reaction. Contribution of these factors on compressive strength is time-dependent. Specific surface of calcined clay has a large influence at early ages, then the effect of structural disorder is more important and, finally the kaolinite content has greater weight in the model at later ages. All these parameters are condensed in an equation that model the overall system.

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