Research paper

Potential use of Argentine kaolinitic clays as pozzolanic material

Alejandra Tironi [a,*], Monica A. Trezza [a], Alberto N. Scian [b], Edgardo F. Irassar [a]

[a] Facultad de Ingeniería, Universidad Nacional del Centro de la Provincia de Buenos Aires, B7400 JWI Olavarría, Argentina
[b] Centro de Tecnología de Recursos Minerales y Cerámica, CONICET La Plata — UNLP, Gonnet, Argentina

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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 $Ca(OH)_2$ 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 $Ca(OH)_2$ 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).

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

- K3 is a blend of kaolins from residual and primary deposits located at the Jurassic Marifil Fm (Chubut province), consisting of rhyolitic vulcanites. 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 overlaying 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 CuKα radiation at 40 kV and 20 mA. FTIR spectra were obtained using a Nicolet Magna 500 spectrophotometer that ranged from 4000 to 400 cm^{-1}. 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) (Kingery 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 dessicator 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
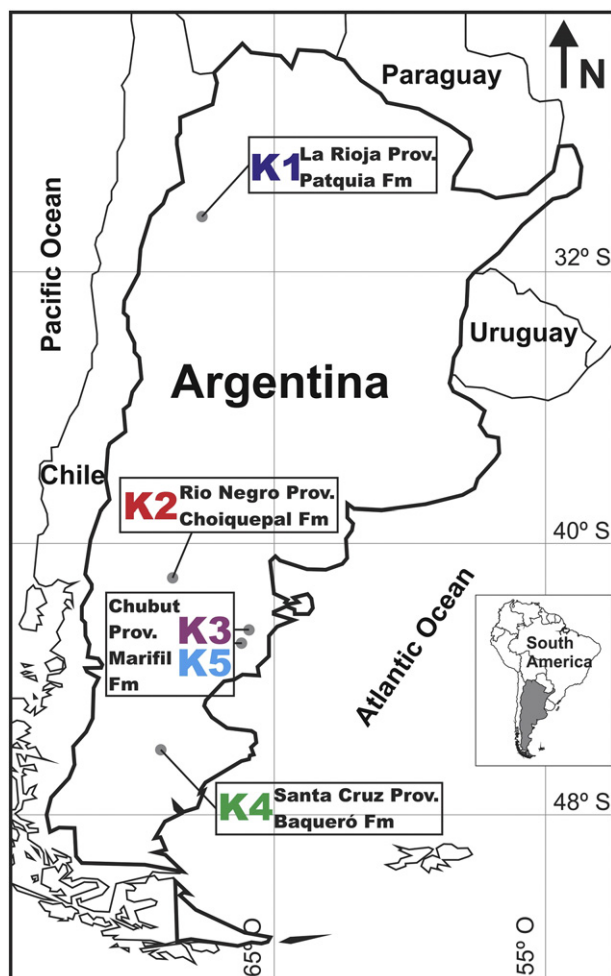
porosimeter (MIP) in the pore size radius from 3.7 to 7500 nm. Then, they were ground in a mortar type mill (Fritsch Pulverisette 2) until all mass passed through the 45 μm sieve (# 325). The specific surface obtained was measured using the Blaine method according to ASTM C 204-04 standard (Tironi et al., 2012).

2.3. Pozzolanic activity test methods

The two methods applied in order to prove the pozzolanic activity of calcined clays were the Frattini test (EN 196:5) and the strength activity index (SAI) calculated as the ratio of the compressive strength of blended cement to the strength of the Portland cement at 7, 28 and 90 days of hydration. For both tests, a normal portland cement (PC) was used. This PC is a strength class 40 (standard compressive strength > 40 MPa at 28 days), its Blaine specific surface was 383 m^2/kg and its mineralogical composition calculated using the Bogue's formula was C_3S = 47%, C_2S = 22%, C_3A = 8% and C_4AF = 9%.

The Frattini test was carried out according to the procedure described in EN 196:5 standard. The tested sample was a blend of 70% Portland cement (PC) and 30% by mass of ground calcined clay. This test compares the amount of Ca^{2+} (expressed as CaO) and hydroxyl ion (OH^-) contained in an aqueous solution that covers the hydrated sample at 40 °C for a given time (7 and 28 days) with the solubility isotherm for calcium hydroxide in an alkaline solution at the same temperature. Calcined clay is considered an active pozzolan (positive result) when the calcium hydroxide concentration in the sample solution is down the solubility isotherm curve.

Compressive strength was assessed on mortar 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. A mortar containing a blend of 30% by mass of ground quartz and 70% of PC was also studied. 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. Compressive strength was determined as the average of three specimens using universal testing machine Instron 4485 (Tironi et al., 2013).

Complementary, the presence of remaining $Ca(OH)_2$ in mortar at 28 and 90 days was checked by XRD. For this purpose, fragments of mortar after compressive test were immersed in acetone for 24 h and dried in oven at 40 °C overnight. Then, fragments were carefully crushed and screened through a 75 μm sieve (#200) in order to remove bulk sand particles. Afterwards, this material was ground and passed through a 45 μm sieve (#325) and analyzed by XRD.

3. Results

3.1. Chemical and mineralogical composition

The chemical composition and loss on ignition of raw clays are shown in Table 1. The mineralogical composition determined by XRD and the intensity of its main peak are presented in Table 2. Using these data, the kaolinite content and the major impurities are reported in Table 1. It can be observed that K1 and K2 have a high kaolinite content (Tironi et al., 2014b), K3 and K4 a moderate one, and K5 a poor kaolinite content. These results are compatible with the intensity of the bands corresponding to groups of kaolinite in the FTIR spectra (Tironi et al., 2012), the area of the endothermic peak between 400 and 700 °C determined by DTA and the weight loss determined by TG (Table 1).

3.2. Crystallinity of kaolinite phase

To analyze the crystallinity of kaolinite FWHM-001, FWHM-002, HI and R2 indexes were used. In previous study, these indexes were calculated for K1 and K2 (Tironi et al., 2014a). Amplified XRD patterns for this purpose are shown in Fig. 2. These crystalline indexes provide an

Table 1
Chemical analysis and loss on ignition; kaolinite and impurity contents; characteristic of DTA/TG-analysis of natural clay used and physical characteristics of calcined clays. Chemical and mineralogical compositions, and thermal analysis of the clays. Textural properties of the calcined clays.

Clay	K1	K2	K3	K4	K5
Chemical composition, %					
SiO_2	45.9	51.4	59.4	65.7	74.8
Al_2O_3	37.0	31.3	27.1	21.1	14.8
Fe_2O_3	0.77	0.92	0.76	0.85	1.10
CaO	0.08	0.40	0.15	0.26	0.30
MgO	0.12	0.19	0.12	0.22	0.26
Na_2O	0.06	0.36	0.14	0.07	0.92
K_2O	0.40	0.38	0.41	0.68	3.71
TiO_2	0.99	1.42	0.26	0.43	0.18
LOI	13.30	12.15	9.65	7.77	3.44
Mineralogical composition, %					
% kaolinite	94	76	65	48	16
% quartz	2	15	28	41	55
% illite	–	3	3	6	16
% feldspars	–	–	–	–	13
DTA–TG characteristics of decomposition of kaolinite					
TG — mass loss, %	13.49	9.00	7.70	6.11	2.59
DTA — start of peak, °C	450	300	350	450	450
DTA — end of peak, °C	700	700	680	650	650
DTA — center of peak, °C	577	548	573	559	533
DTA —area of peak	−5000	−3500	−2900	−1980	−850

Textural properties

Calcined clays	MK1	MK2	MK3	MK4	MK5
Specific surface Blaine, m^2/kg	1461	2287	1865	981	1399
Total pore volume, mm^3/g	91	403	348	285	254

approximation for real structure and they are strongly influenced by other minerals presented in natural clays (Aparicio and Galan, 1999).

FWHM-001 and FWHM-002 indexes are determined as the width at half height of the main peaks of kaolinite ((001) at 12.3° 2θ and (002) at 24.9° 2θ) (Fig. 2). Index values range from >0.4 (disordered) to <0.3 (ordered) (Aparicio and Galan, 1999). Both FWHM indexes are unaffected by quartz, but FWHM-001 is influenced by the presence of feldspars.

HI (Hinckley Index), the most widely used index, is the ratio of the height above background of the (11$\bar{0}$) (20.4° 2θ) and (11$\bar{1}$) (21.3° 2θ) peaks above the band of overlapping peaks occurring between 20 and 23° 2θ (A and B, respectively in Fig. 2) compared to the total height of the (11$\bar{0}$) above background (A_t in Fig. 2) (Hinckley, 1963; Kingery et al., 1976). Its value ranges from <0.5 (disordered) to 1.5 (ordered). HI is influenced by the presence of quartz (Aparicio and Galan, 1999) and it is sensitive to all crystalline defects of kaolinite (i.e., ±nb/3 translations, ±nπ/3 rotations, and random defects) (He et al., 2005).

R2 is calculated as the ratio between the sum of (1$\bar{3}$1) (38.5° 2θ) and (131) (39.3° 2θ) peak intensities and the counts in the valley between them (Fig. 2): R2 = (1/2(D + E) − F) / (1/3(D + E + F)). Reported values range from <0.7 (disordered) to 1.2 (ordered). The R2 is influenced by quartz (Aparicio and Galan, 1999) and its value decreases with the increase of defect density. Relative amounts of Al^{VI}, Al^V and Al^{IV} in MK vary with the defect density of the raw kaolinite. Hence, kaolinite with a lower random defect density is more stable during

Table 2
XRD results.

Clay	Kaolinite (K)	Quartz (Q)	Illite (I)	Anatase (A)	Feldspars (F)
K1	very strong	very weak	–	–	–
K2	strong	weak	very weak	very weak	–
K3	strong	medium	very weak	very weak	–
K4	medium	medium	very weak	very weak	–
K5	weak	very strong	weak	very weak	weak

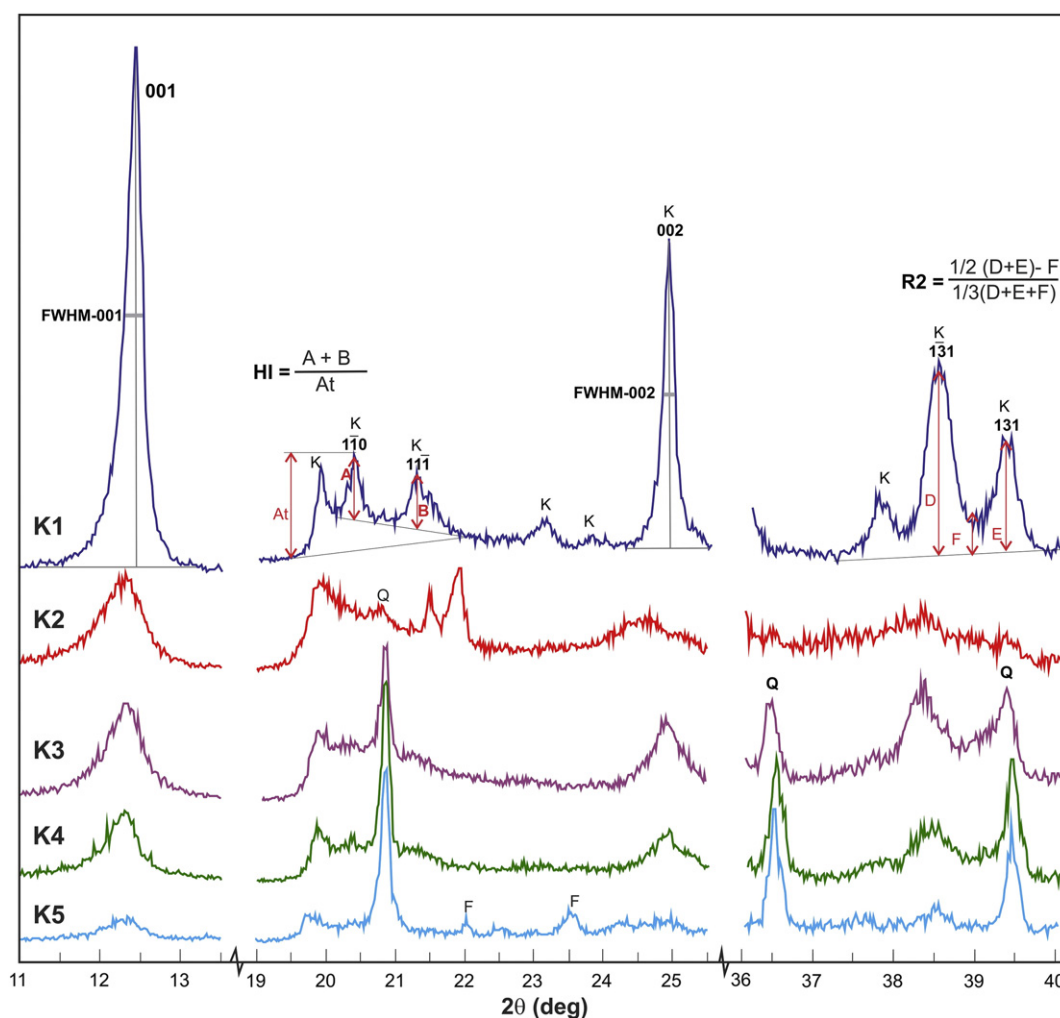/////: very strong, ////: strong, ///: medium, //:weak, /: very weak.

Fig. 2. Details of XRD patterns of kaolinitic clays used to calculate the XRD index: FWHM-001, FWHM-002, HI and R2.

dehydroxylation and derived in MK with a large amount of Al^V (He et al., 2005).

Fig. 3 shows the FTIR details corresponding to the stretching frequencies of the OH^- groups used to calculate the P_0 index as the ratio between the intensities of the bands at 3620 cm^{-1} and 3700 cm^{-1} (Murat, 1983; Bich et al., 2009). Kaolinite is well ordered when $P_0 > 1$ and it is not influenced by quartz or feldspars; however, illite presents a band related to OH^- group vibration near 3625 cm^{-1} (Wilson, 1987; Galos, 2011).

The results of five indexes are summarized in Table 3. All indexes classified K2 as the clay containing the most disordered structure or the lowest crystalline kaolinite. According to these indexes, K3 and K4 also present kaolinite with structural disorder. K2 and K4 were collected in sedimentary deposits, while K3 was collected in a primary deposit and wet processed. Most indexes determine that K1 and K5 samples contain ordered kaolinite. Both clays were collected from primary deposits. K5 has the least amount of kaolinite and a large proportion of feldspar as impurities (Table 1) that could affect the FWHM-001 index.

The morphology of natural clays obtained by SEM are showed in Fig. 4. K1 shows the typical microstructure of kaolinite, consisting of pseudo-hexagonal plates and clusters of plates (Tironi et al., 2014b). These plates are larger (>3 μm) and better-off compared with the other samples. Large kaolinite booklets are present and they are compact with low total pore volume as indicated by the results obtained by MIP and by the lower value measured of specific surface Blaine (Table 1), (Tironi et al, 2012). This sample presents a high degree of perfection in translational periodicity of clay, and an ordered structure

according to all indexes studied with a low empty space. In samples classified as disordered structure (K2 and K4), their microstructures present 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 and large specific surface (Table 1). Particularly, K3 has irregular boundaries and face to face arrangement attributable to the industrial processing cycle. In the case of K5, kaolinite particles agglomerate on the surface of other minerals with different grain morphologies.

3.3. Calcination effect

The calcination temperature selected (700 °C) was higher than the range corresponding to the complete dehydroxylation of kaolinite and lower than the temperature which avoided the mullite formation, according to DTA analysis (Table 1). For these samples, the initial temperature of kaolinite dehydroxylation ranges between 300 and 450 °C, the center of endothermic peaks appears at 533 °C for K5 to 577 °C for K1, and the maximum temperature for kaolinite dehydroxylation occurs between 650 and 700 °C (Table 1).

After thermal treatment, XRD-peaks of kaolinite disappear, remaining in the sample other crystalline phases, such as quartz, anatase, illite and feldspars. In the FTIR spectra, the complete dehydroxylation of kaolinite was confirmed by the lack of bands between 3500 and 3700 cm^{-1} (Tironi et al, 2012). The transformation of kaolinite into MK was also confirmed by the absence of Al–OH bands at 914 and 936 cm^{-1}
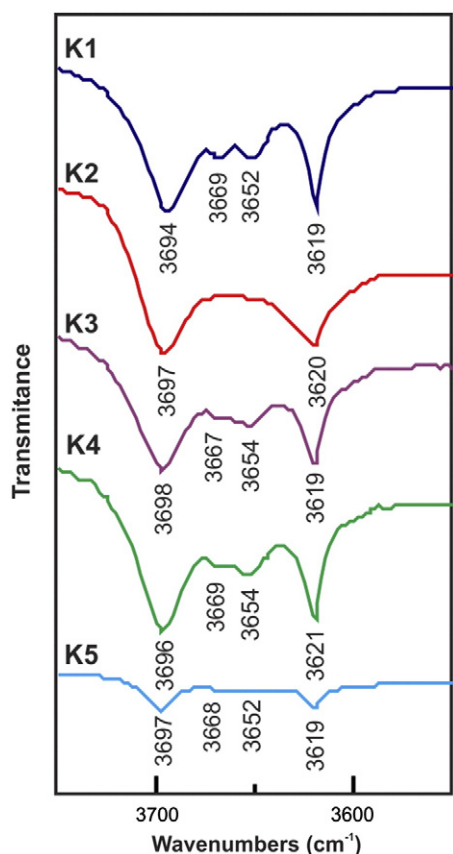
Fig. 3. Details of FTIR spectra corresponding to OH⁻ band used to calculate the P_0 index.

(Madejová, 2003; Chakchouk et al., 2009). The obtained calcined clays are labeled MK1 to MK5.

Thermal treatment does not modify drastically MK1 micrographs' morphology (Fig. 5); hexagonal plates are easily identified and the flakes are staked with a well-defined boundary. For MK2, the particles present poorly-defined crystals and their edges are undefined and present some bumps on the surface due to the formation of amorphous material (Fig. 5).

3.4. Pozzolanic activity

Table 4 reports the [CaO] and [OH⁻] measured in aqueous solution at 7 and 28 days using Frattini test (Tironi et al., 2012). For each sample, these values were compared with the solubility isotherm for calcium hydroxide in an alkaline solution at 40 °C. When the point is down the isotherm line, calcined clay has consumed some Ca(OH)₂ released during cement hydration. Results indicate that pastes containing MK1, MK2, MK3 and MK4 present a very good pozzolanic activity at 7 and 28 days (D, in Table 4). These clays consume almost the Ca(OH)₂ released by cement hydration. For MK1 and MK2, [OH⁻] decreases from 7 to 28 days. For paste containing MK5, the result is located below (B, in Table 4) the calcium isotherm at 7 days and it changes to an upper

Table 3
Crystallinity index of kaolinite.

Technical	Index	K1		K2		K3		K4		K5	
XRD	FWHM-001	0.21	+O	0.58	+D	0.44	D	0.43	D	0.42	D
	FWHM-002	0.20	O	0.64	+D	0.42	D	0.40	D	0.09	+O
	HI	1.19	+O	0.36	+D	0.47	D	0.74	O	0.98	O
	R2	1.16	+O	0.77	+D	0.82	D	0.82	D	1.14	O
FTIR	P₀	1.21	O	0.48	+D	0.81	D	0.90	D	1.69	+O

O: order, D: disorder, +O: high order, +D: high disorder.

(U, in Table 4) location at 28 days due to the alkalis released from clays, while [CaO] remains constant. Chemical composition of this clay shows a large proportion of alkalis as a consequence of the incomplete weathering of feldspars (Table 1).

The results of compressive strength were previously reported by Tironi et al. (2013). Data show that mortar with MK2 presents the highest strength at all test ages (32.2, 49.0, and 57.4 MPa at 7, 28, and 90 days, respectively); while MK3 has a very good performance (27.1, 41.2, and 48.0 MPa at 7, 28, and 90 days, respectively). MK1 and MK4 have a similar strength development despite their very different kaolinite content. Finally, MK5 shows a poor development of strength (20.6, 30.9, and 34.2 MPa at 7, 28, and 90 days, respectively). Fig. 6 shows the strength activity index (SAI) for calcined clays and quartz (Q) mortars. MK2 mortar presents a SAI greater than 1.0 at seven days resulting in a very reactive material, and later SAI-value increases up to 1.4 at 90 days. Mortars with MK1 and MK3 present SAI between 0.8 and 0.9 at 7 days and, thereafter, a value similar or greater than 1.0. For MK4 and MK5, SAI at 7 days has the same value than those of mortar with quartz indicating no contribution of these calcined clays to compressive strength. Thereafter, SAI of MK4 attains 1.0 at 28 and 90 days, while MK5 only develops a SAI near 0.8, indicating a poor progress of pozzolanic reaction, while SAI of mortar with quartz remains at 0.65.

Fig. 7 shows the XRD patterns for mortars at 28 and 90 days. For mortars with MK2, the main peaks of Ca(OH)₂ (CH: 18,08° and 34,01° 2θ) are absent at both test ages, confirming that Ca(OH)₂ was consumed by pozzolanic reaction. For mortars with MK1 and MK3, Ca(OH)₂ peaks are very weak at 28 days, disappearing at 90 days. Well defined Ca(OH)₂ peaks are present for MK4 mortar at 28 days and their intensity decreases at 90 days. Finally, MK5 mortar presents a well defined Ca(OH)₂ peak at 28 and 90 days, indicating the poor pozzolanic reaction. In all mortars containing calcined clays, the intensity of Ca(OH)₂ peaks was lower than that corresponding to PC mortar and the mortar containing 30% of ground quartz (Q). This reduction is due to the dilution effect and it was greater for mortars with calcined clay due to pozzolanic reaction (Kastis et al., 2006). In agreement with the literature (Murat, 1983; Morsy and Shebl, 2007), CAH and CASH phases found in these mortars were strätlingite (Str: C_2ASH_8), ettringite (Ett: $C_4AS_3H_{32}$), monosulfoaluminate (MS: $C_4A\underline{S}H_{12}$), tetracalcium aluminate hydrate (C_4AH_{13}), and monocarboaluminate (MC).

4. Discussion

The potential performance of kaolinitic clays as pozzolanic addition to Portland cement depends on several factors related to the characteristics of the raw materials, the thermal process used, the cement, and the test used.

According to Murat (1983), the mineralogical characteristics of raw materials (amount of kaolinite, crystallization state of clays, nature and amount of impurities, and the grain size) can modify the hydration reaction of MK obtained by calcination. Shvarzman et al. (2003) identified the amorphous phase content and the degree of dehydroxylation obtained from thermal treatment as the main parameters of calcined clays' pozzolanity. Other parameters such as specific surface area and total pore volume will also be taken into account. Pozzolanic activity also depends on the mineralogical composition of Portland cement, the content of Ca(OH)₂ in the cement paste, the percentage of calcined clay replacement, the water to cementing material ratio and the curing temperature used in the test for pozzolanic assessment (Kaloumenou et al., 1999; Rahhal and Talero, 2005).

The amount of reactive phase in calcined clays is related to kaolinite content in raw clay and there is a linear relationship between the weight loss from TG analysis and the amorphous phase content (Shvarzman et al, 2003) when the thermal treatment produces the complete dehydroxylation. Then, 0.86 g of MK is obtained out of each g of kaolinite.

Table 5 shows a summary of the calculated MK content in cement blended with 30% of substitution. It is seen that MK as a pozzolan ranges
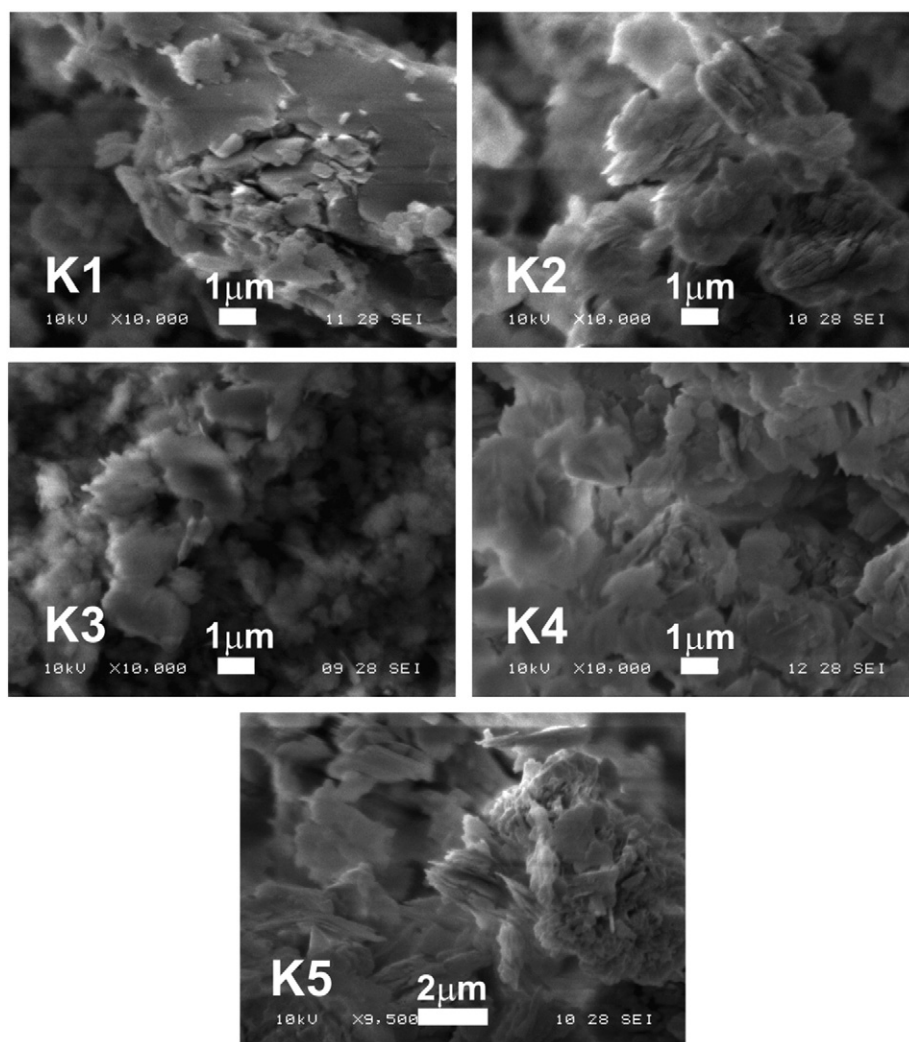
Fig. 4. SEM micrographs of kaolinitic clays K1 and K2 (Tironi et al., 2014b); K3, K4, and K5. All the samples are observed at the same magnification scale (1 μm bar).

from 4 to 28% w/w in blended cement. On the other hand, finely divided quartz and other impurities in calcined clays play the role of filler in the blended cement (Rahhal and Talero, 2005). When filler is incorporated to cement, three main physical effects are observed on cement hydration (Cyr et al., 2005): (a) the dilution effect, which is equivalent to an increase in the water–cement ratio, is inversely proportional to the replacement level; (b) the effect of the particle size distribution is related to grains interpose between cement grains, separating and dispersing

the reactive grains; and (c) fine grains act as nucleation centers for $Ca(OH)_2$ and other crystalline hydrates, accelerating the dissolution process and stimulating the hydration of cement.

According to the impurity content in calcined clays, the amount of filler in mortars ranges from 2 to 26% w/w with particle sizes lesser than 45 μm. Depending on the amount of impurities, the stimulation of cement hydration and the MK pozzolanic reaction cannot compensate for the adverse effect of dilution that causes an increase of water/
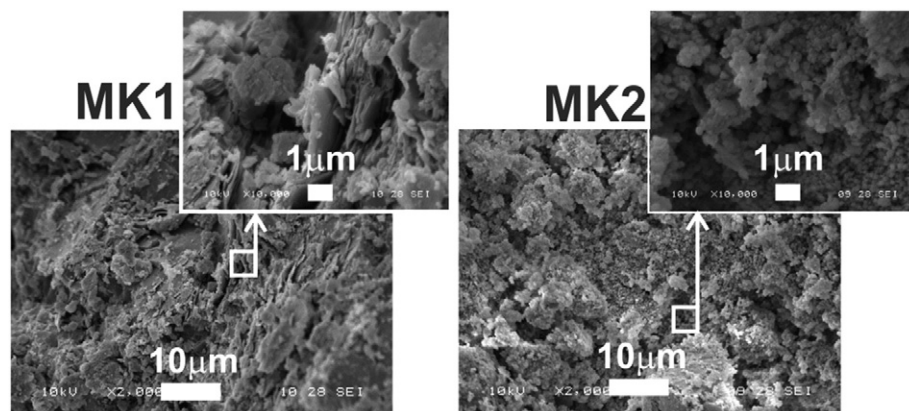

Fig. 5. SEM micrographs of calcined clays MK1 and MK2. Both samples are observed with two magnification scales: 10 μm bar, and 1 μm bar.

Table 4
Results of Frattini test at 7 and 28 days.

Days		MK1	MK2	MK3	MK4	MK5
7	[OH$^-$]	46.31	37.13	42.23	51.61	71.60
	[CaO]	0.95	0.96	0.68	1.10	5.26
	Result	D	D	D	D	B
28	[OH$^-$]	41.21	32.03	41.00	51.00	82.01
	[CaO]	0.74	0.55	0.32	0.79	5.31
	Result	D	D	D	D	U

D (Down), B (below) and U (Up) the solubility isotherm for calcium hydroxide in an alkaline solution at 40 °C.

(cement + MK) from 0.51 to 0.67 for MK1 to MK5 (Table 5). It can cause the loss of relative compressive strength due to the increase of capillary porosity of mortars at later ages (28 and 90 days). Feldspars, as impurities, appear when the alteration degree of the parent rocks is incomplete and they can lead to alkali releases during the hydration, as occurs in the sample MK5 of the Frattini test causing an increase of [OH$^-$] from 7 to 28 days.

In blended cements, the reaction of MK could be limited by the insufficient amount of Ca(OH)$_2$ released during the hydration of PC. Typically, the maximum amount of Ca(OH)$_2$ released is in the range of 16–28% w/w, depending on the C$_3$S/C$_2$S ratio, for complete hydration. Cement used produces 0.20 g of Ca(HO)$_2$ by g of cement. Thereafter, blended cement containing 70% of Portland cement has 0.14% w/w (0.20 ∗ 0.70) of Ca(OH)$_2$ when it attains complete hydration.

According to Murat (1983), the pozzolanic reaction between MK and Ca(OH)$_2$ produces C – S – H, C$_2$ASH$_8$ (Str), and very small quantities of C$_4$AH$_{13}$ and C$_3$ASH$_6$ (hydrogarnet). Assuming C – S – H and Str as products of the MK-lime reaction, 3 mol of Ca(OH)$_2$ (74.1 ∗ 3 = 222.3 g) is needed to react with 1 mol of MK (222.2 g); in other words, the reaction is a g of MK by g of CH. The formation of C$_4$AH$_{13}$ and C$_3$ASH$_6$ requires a large amount of Ca(OH)$_2$ by 1 g of MK.

In the Frattini test, the amount of Ca(OH)$_2$ released by cement is lower than the reactant mass needed for hydration of MK present in blended cement containing MK1, MK2 and MK3, and a large portion of MK remains unreacted. In MK4, the amount of Ca(OH)$_2$ released is slightly higher than that needed for complete reaction of MK. On the other hand, the amount of Ca(OH)$_2$ is four times larger than the amount needed for the complete hydration of MK in MK5 blended cement. The amount of MK and Ca(OH)$_2$ unreacted in the mortars is shown in Table 5.

For mortar specimens at 90 days, it is clear that Ca(OH)$_2$ has been consumed and their peaks are absent in XRD for MK1, MK2 and MK3 blended cements; hydrated gehlenite (strätlingite) appears as well defined hydration products. For these blended cements, the amount of

MK is sufficient to react slowly and to obtain a similar compressive strength to that of PC mortar (SAI ≥ 1 at 90 days). The amount of reactive material in MK4 blended cement is slightly lower than the available Ca(OH)$_2$ in paste, causing the progressive reduction of Ca(OH)$_2$ peaks and the increase of SAI to 1 at 90 days. For MK5 blended cement, the amount of MK is too low in relation to the Ca(OH)$_2$ amount, whose peaks appear in XRD pattern while the relative compressive strength (SAI < 1) decreases due to a large increase of water to cementitious material ratio.

Regarding the previous works, French researchers (Ambroise et al., 1985; Ambroise et al., 1992) concluded that clays containing only 20–30% kaolinite can also be converted to pozzolan, since both tested soils have 30% of illite. Greek experience (Kakali et al., 2001; Badogiannis et al., 2005) reports similar strength development, setting times and hydration compounds of blended cements containing a commercial metakaolin of high purity and those containing poor Greek kaolins (38–52% kaolinite) thermally activated. These kaolinitic clays contain alunite in their mineralogical composition. Two poor kaolin sands from Slovakia (26 and 36% of kaolinite accompanied by illite and muscovite) after temperature transformation provide a pozzolan that, blended with Portland cement (20 to 40% w/w), can produce a similar compressive strength at 90 days and the depletion of most part of Ca(OH)$_2$ (Krajci et al., 2007). The activation of three Sardinian kaolin clays containing 31 to 46% of kaolinite and quartz as main impurity produces a pozzolan that causes the complete lime consumption after 180 days (Cara et al., 2006).

To conclude, the stoichiometry calculation shows that 30% w/w replacement of calcined clay containing 47% of MK (51% kaolinite in raw clays) will consume all Ca(OH)$_2$ released during the complete hydration of this Portland cement. Finally, it is possible to obtain a good pozzolan, when a suitable heat treatment and grinding are applied to clays containing more than 50% of kaolinite. The problem of this approach is that compressive strength obtained for different clays with the same MK content did not provide similar results. It is known that the pozzolanic activity of MK is strongly related to the crystallinity of the original kaolinite (Murat, 1983; Badogiannis et al., 2005; Bich et al., 2009).

Results of Frattini and compressive strength tests demonstrated that for high kaolinite content (K1 and K2), MK obtained from poorly crystalline kaolinite (MK2 obtained from K2) developed a higher and faster pozzolanic reaction, while MK obtained from kaolinitic clay with a well ordered structure has a slow reaction (MK1 obtained from K1). French researchers (Murat, 1983; Ambroise et al., 1985) found that poorly-crystallized kaolinite leads to more effective pozzolanic cement when evaluated from mechanical parameters. The crystallinity was evaluated through XRD FWHM-002 index, IR bands at 3620 and 3700 cm^{-1}, DTA slope ratio and SEM observation. From Greek experience (Kakali et al., 2001), it can be observed that well ordered kaolinite (FHWM-002 index and IR bands) was transformed into less reactive MK. On the other hand, the crystallinity (FHWM-002 index) of the kaolinite phase appears to play a secondary role in the Ca(OH)$_2$ consumption of calcined Sardinia clays (Cara et al., 2006). The selection of indexes to evaluate the crystallinity depends on the impurities present in the raw kaolinitic clays.

From Table 1, it can also be observed that the calcined kaolinitic clay MK2 obtained from K2 poorly crystallized has a larger specific surface Blaine than calcined kaolinitic clay MK1 obtained from well crystallized K1. In addition, MK2 has a large volume of pores in radio size ranging from 20 to 100 nm, as previously reported (Tironi et al, 2012). The rate of pozzolanic reaction is increased by high total pore volume and a large specific surface, resulting in a large consumption of Ca(OH)$_2$ at 7 days in Frattini test and a high compressive strength at 7 days.

Finally, the potential pozzolanic activity of calcined raw materials depends on the kaolinite content, the crystallinity and the specific surface obtained after calcination. Hence, blended cement containing MK1 and MK4 has a similar compressive strength development despite the lowest kaolinite content in the K4 clay. This behavior can be
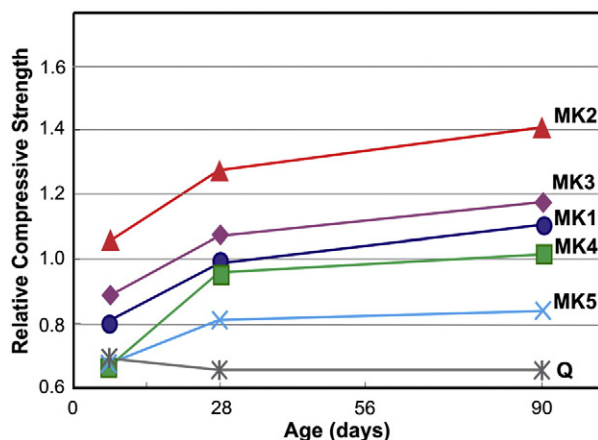

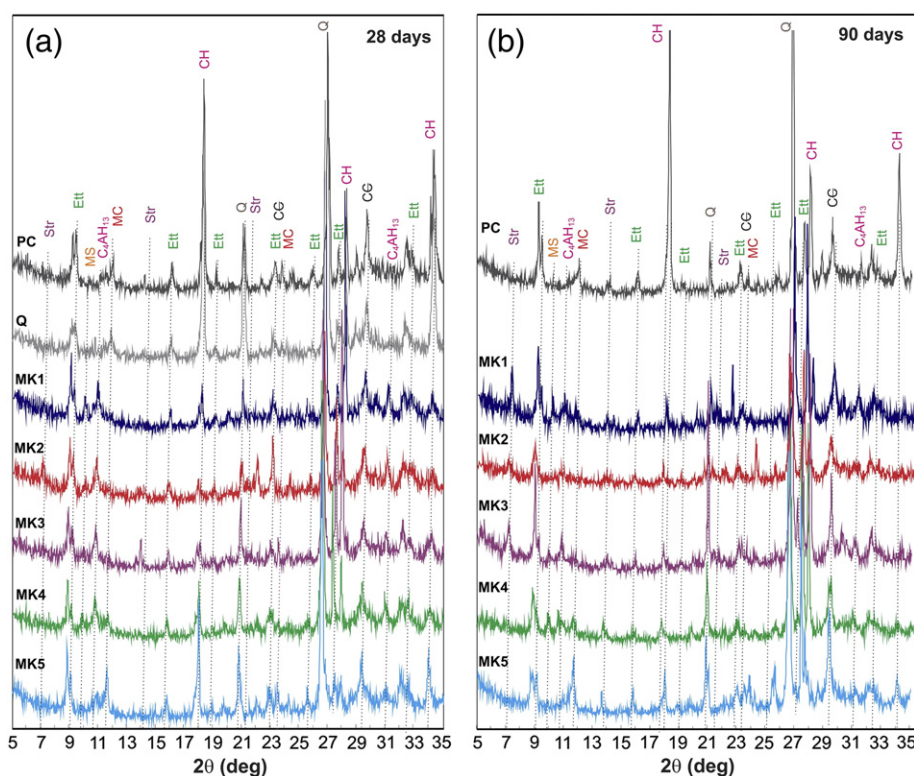**Fig. 6.** Evolution of strength activity index (SAI).

Fig. 7. XRD patterns for different mortars at (a) 28 days and (b) 90 days. CH: calcium hydroxide; Q: quartz; Str: strätlingite; Ett: ettringite; MS: monosulfoaluminate; C_4AH_{13}: tetracalcium aluminate hydrate; MC: monocarboaluminate; C: calcite.

attributed to the more disordered kaolinite of K4 compared with ordered kaolinite of K1.

5. Conclusions

The assessment of pozzolanic activity of five kaolinitic clays from very different locations of Argentine after heat treatment at 700 °C until complete dehydroxylation was performed; and the conclusions are:

- The pozzolanic activity of kaolinitic calcined clays (30% w/w), evaluated by the Frattini test and the compressive strength index, seems to be more dependent on the crystalline order of original kaolinite rather than on kaolinite content when raw clay contains more than 50% of kaolinite. Calcined kaolinitic clay obtained from poorly crystallized kaolinite has a larger specific surface and greater pozzolanic activity.
- Compressive strength development of blended cement containing calcined clays with high metakaolin content is more dependent on the crystalline order of original kaolinite rather than on the kaolinite content in raw clay. Calcined clay obtained from kaolinitic clay with high content of disordered kaolinite (K2) produces a blended cement with a compressive strength higher than that of Portland cement at all age strength activity index (SAI) > 1.00; while SAI of blended cement

with calcined clay obtained from clay with high content of ordered kaolinite (K1) tends to be 1.00 at 28 days.
- The crystallinity of kaolinite in raw clays can be evaluated by a combination of P_0 index using FTIR and an appropriate index using XRD. The selection of indexes calculated from XRD pattern (FWHM-001, FWHM-002, Hinckley and R2) depends on impurities present in the raw clays. Clays used for this study containing disordered kaolinite were collected in sedimentary deposits or in primary deposits and wet processed; while those with an ordered structure had their origin in primary deposit.

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Table 5
Calculation of MK and impurity contents in blended cement, Ca(OH)$_2$ and MK unreacted after complete hydration; and effective water to cementing material ratio.

Calcined clay	% MK	% impurities	Unreacted MK for 30 g calcined clays, g	Unreacted Ca(OH)$_2$ for 30 g calcined clays, g	Water/ (cement + MK)	Water/ (cement + MK$_{reacted}$)
MK1	27.9	2.1	13.8	–	0.51	0.59
MK2	21.9	8.1	7.8	–	0.54	0.59
MK3	18.5	11.5	4.3	–	0.57	0.59
MK4	13.3	16.7	–	0.8	0.60	0.60
MK5	4.2	25.8	–	9.9	0.67	0.67
Q	0.0	30.0	–	14.2	0.71	0.71

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