Cement & Concrete Composites 37 (2013) 319–327

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Assessment of pozzolanic activity of different calcined clays

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

ARTICLE INFO

Article history:
Received 20 August 2012
Received in revised form 3 January 2013
Accepted 4 January 2013
Available online 12 January 2013

Keywords:
Calcined clay
Kaolinite
Montmorillonite
Pozzolanic activity
Frattini test
Strength activity index
Saturated lime test
Electrical conductivity test
Metakaolin

ABSTRACT

The pozzolanic activity of calcined clays depends on the type and amount of clayed minerals, the nature and amount of impurities, the thermal treatment used for its activation and the specific surface obtained after calcination. In this paper, four test methods for assessment the pozzolanic activity on seven calcined clays (five kaolinites and two bentonites) were analyzed. Natural clays were calcined and investigated by two direct tests (Frattini and saturated lime) and two indirect tests (strength activity index and electrical conductivity). Frattini test and the strength activity index (SAI) were found to be the most accurate and reliable methods to assess pozzolanic activity over time. Frattini test evaluates accurately the calcium hydroxide (CH) consumption by pozzolanic reaction, and SAI test discriminates the real contribution of pozzolanic reaction to densification of microstructure. The electrical conductivity (EC) and the lime consumption (LC) tests evaluate the ability of pozzolanic material to fix CH during the first time of contact and their results are correlated with the specific surface of calcined clay.

1. Introduction

Pozzolans are defined as "a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties" (ASTM C 618 [1]). The pozzolanic reaction is slow, consumes calcium hydroxide (CH) and reduces the pore and grain size of the cementing system. *The pore size refinement* effect is related to the formation of additional C–S–H that fills up large capillary pores, thus improving the strength and the impermeability of *the system; while the grain size refinement* is caused by the reduction in the content and size of CH crystals improving the matrix and the transition-zone densification [2].

Today, the relative scarcity of traditional supplementary cementitious materials (SCMs) or their localization, whose transport causes a great economical and environmental impact, encourages the development of new supplementary materials, as well as the evaluation of pozzolanic activity [3,4]. Among the new SCM, the production of calcined clays is pointed out as a possible candidate to fill this gap [5]. Calcined clays from different location in the world have been largely studied [6–14].

Clay deposits contain a mixture of different clay minerals (kaolinite, illite, montmorillonite, palygorskite, and others) and a large proportion of impurities of non clay materials, such as quartz, calcite, feldspars, mica, anatase and sulphides [15]. After heat treatment, He et al. [16] concluded that kaolin and some montmorillonites had the highest pozzolanic activity, the rest of clay materials could be considered of low-pozzolanic activity. These clays are thermal activated when the heat treatment (550–900 °C) produces the dehydroxylation of argillaceous minerals to obtain amorphous aluminosilicate phases (AS_2, AS_4), preventing the formation of mullite precursor to AS_2. Amorphous phases react with CH in the presence of water producing a cementing compound like C–S–H and some hydrates of alumina bearing phase [10,17,18]. The proposed reactions are:

$$AS_2 + 3CH + 6H \rightarrow C\text{—}S\text{—}H + C_2ASH_8 \quad (1)$$

$$AS_4 + 5CH + 6H \rightarrow 3C\text{—}S\text{—}H + C_2ASH_8 \quad (2)$$

The optimum thermal treatment (temperature, residence time and cooling down) for activation of different clays is assessed measuring the pozzolanic activity of calcined material. According to Donatello et al. [19], the tests for the assessment of pozzolanic activity are divided into two groups: direct methods, which measure the CH consumptions by the pozzolanic reaction (chemical titration, XRD and TGA); and indirect methods, which measure a

---

* Corresponding author. Tel./fax: +54 2284 450 628.
E-mail address: firassar@fio.unicen.edu.ar (E.F. Irassar).

0958-9465/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.cemconcomp.2013.01.002

change of property related with the pozzolanic reaction (strength activity index – SAI, electrical conductivity, conduction calorimetry).

Among the chemical titration methods, the Frattini test is standardized and it can accurately define the pozzolanic activity of blended Portland cements measuring the CH consumption released during PC hydration. This test is very sensible to the chemical characteristic (silicic–aluminic or aluminic–silicic) of pozzolan and the alumina content of Portland cement used [20–22]. The saturated lime test also measures the amount of calcium consumption (LC) of pozzolan, but this test cannot provide reliable results [19]. With several variations in mixture proportions, the most popular standardized indirect test [23–25] is the SAI. It measures the contribution of pozzolanic reaction on densification of cementitious matrix, but also includes the packing effect that improves the compressive strength. Results of this type of tests depend on the water-to-binder ratio (w/b) for the same consistency and the proportion and the type (by volume or by mass) of replacement of cement by SCM that modifies the water content on mortar [26–28]. Pourkhorshidi et al. [28] recommend that SAI should be obtained on mortar with 20% natural pozzolan replacement at identical w/b, and Bentz et al. [29] state that the replacement of cement by SCM should be made by volume. A quick indirect test is based on measuring the change in electrical conductivity of pozzolan dispersed in saturated lime solution. It was developed by Luxan et al. [30], modified by Yu et al. [31] and Payá et al. [32]. Sinthaworn and Nimityongskul [33] proposed this measure using ordinary Portland cement (OPC) solution.

The correlation between the results of the different tests has been investigated for different types of SCM [19,33], but they are not exhaustively analyzed for different types of calcined clays. This type of SCM have a large amount of alumina in the glassy phases that reacts quickly with CH at ordinary temperatures to form aluminates phases, which have not cementitious properties that contributing to enhance the strength or to reduce the permeability. Also, they have a large specific surface causing fasts consumption of CH from solutions.

The objective of this study is to analyze the test methods to assess the pozzolanic activity of calcined clays from different origins. The pozzolanic activity of seven calcined clays was investigated by two direct (Frattini test and saturated lime test) and two indirect tests (SAI and electrical conductivity). Results are discussed according to the mineralogical composition of clay, the pozzolanic reaction and the amount of available CH in each test method.

2. Experimental

2.1. Materials and characterization

Seven natural clays (five kaolinites and two bentonites) from different regions of Argentina were used as raw materials. Table 1 presents the chemical composition of the samples performed by ICP-AES analysis in external laboratory (ALS, Argentine). Loss on ignition (LOI) was measured by oven drying natural clays at 105 °C to constant mass before calcining at 1000 °C for 1 h, cooling and re-weighing. All clays before the thermal treatment conform the chemical requirements stated in ASTM C 618 [1] (S + A + F > 70% and $SO_3 < 4\%$) for Class N pozzolan.

Fig. 1 shows X-ray diffraction (XRD) spectra of all clays and the mineralogical species are identified. It shows that K1-clay is mainly composed by kaolinite (K) and a very low amount of quartz (Q). For K2, K3 and K4 clays, kaolinite and quartz were accompanied with a low amount of illite (I). K5-clay presents kaolinite, quartz, illite and alkali feldspars as anorthite (An) and orthoclase (O). For all the samples, XRD reveals a slight presence of anatase (A). For BN and BLP clays, montmorillonite was identified as the main clay-mineral, and the non-clay minerals were quartz and feldspar. The BLP-clay also reveals the presence of cristobalite, a polymorphism of SiO_2.

For K1–K5 clays, the content of kaolinite (K) was calculated as the weight loss from 500 to 700 °C determined by DTA–TG using a NETZCH STA 409C thermobalance and assuming a 13.76% of weight loss in pure kaolinite [34]. For bentonites, DTA–TG analysis shows the weight loss of absorbed water between the silicate sheets at low temperatures (100–200 °C) and the weight loss due to dehydroxylation of montmorillonite around 400–900 °C. The montmorillonite content was calculated comparing the mass losses obtained in the second temperature range with the weight loss of standard montmorillonite (≈4.1%) [35]. The kaolinite and montmorillonite content is reported in Table 1.

The crystallinity of the kaolinite phase was evaluated by the Hinckley index (HI) [36] and the results are reported in Table 1. This index indicates a less density of crystalline defect when it has a high value (HI > 0.5), while HI-values less than 0.5 indicate a disorder crystalline structure. When the studied clays are compared, kaolinite in K1-clay has the highest ordered structure, and kaolinite in K2-clay has the lower one.

The thermal treatment of clays was carried out in a laboratory programmable furnace using a fixed bed technique. The samples were heated from ambient temperature up to 700 °C, where they remained for 5 min. Subsequently, samples were cooled in the furnace until 450 °C and finally cooled down in desiccator at ambient temperature, obtaining MK1–MK5 and BLPc–BNc. After thermal treatment, the transformation of kaolinite to an amorphous material was checked by XRD, showing that the peaks corresponding to kaolinite disappear [37]. For bentonites, the displacement in the main basal spacing (d_{001} plane) from 13–14 Å of raw clays to 9.2–9.6 Å of calcined clays at 700 °C confirms the complete loss of interlayer water of the montmorillonite [38]. The total porosity of calcined clays was determined using a Carlo Erba 2000 mercury intrusion porosimeter (MIP) in the pore size radius from 3.7 to 7500 nm. The pH was determined by preparing a 10:1 liquid to solid ratio suspension using deionized water at 40 °C. It was shaken for 5 min and left for 3 h to equilibrate before measuring the pH [19]. The electrical conductivity of this suspension was also measured and reported in Table 1.

Finally, the calcined clays were ground in a mortar type mill (Fritsch Pulverisette 2) until fineness was lower than 45 μm. In this material, 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 was determined using the Blaine methods (ASTM C204-04 [39]) and the specific gravity was determined by pycnometry. These physical parameters are reported in Table 1.

2.2. Pozzolanic activity tests

The pozzolanic activity of calcined clays was measured by two direct methods (Frattini test and saturated lime test) and two indirect methods (strength activity index and the electrical conductivity). A brief description of these methods is presented here.

2.2.1. Strength activity index (SAI)

The compressive strength was assessed on mortars cubes ($25 \times 25 \times 25$ mm^3) made with standard sand (1:3) and constant water to binder ratio (w/b) of 0.50. Control mortar cubes were prepared using a normal Portland cement (PC) with a chemical composition reported in Table 1. The blended cement was composed by 30% w/w of calcined clay and 70% w/w of Portland cement. Complementary, an inactive pozzolan sample was prepared using 30% w/w of finely ground quartz as replacement of PC. The mortar

Table 1
Composition and properties of clays and Portland cement (PC).

Sample	K1	K2	K3	K4	K5	BLP	BN	PC
Chemical composition of raw clays, %								
SiO_2	45.90	51.40	59.40	65.70	74.80	63.90	54.80	19.93
Al_2O_3	37.00	31.03	27.10	21.10	14.80	12.60	15.75	5.54
Fe_2O_3	0.77	0.92	0.76	0.85	1.10	0.99	1.26	3.00
CaO	0.08	0.40	0.15	0.26	0.30	1.16	1.76	58.62
MgO	0.12	0.19	0.12	0.22	0.26	3.6	5.0	3.81
SO_3	–	–	–	–	–	–	–	3.22
Na_2O	0.06	0.36	0.14	0.07	0.92	1.52	3.01	0.70
K_2O	0.40	0.38	0.41	0.68	3.71	0.29	0.96	1.11
TiO_2	0.99	1.42	0.26	0.43	0.18	–	–	0.34
Loss on ignition	13.30	12.15	9.65	7.77	3.44	–	–	3.19
$SiO_2 + Al_2O_3 + Fe_2O_3$	83.7	83.4	87.3	87.7	90.7	77.5	71.8	–
Mineralogical composition of raw clays								
Kaolinite, %	98	65	56	44	19	–	–	–
Montmorillonite, %	–	–	–	–	–	54	59	–
Order index of kaolinite								
HI	1.19	0.36	0.47	0.74	0.98	–	–	–
Order/disorder	+O	+D	D	O	O	–	–	–
Physical properties of calcined clays								
Specific gravity, m^3/kg	2.38	2.41	2.17	2.54	2.49	1.84	2.16	3.10
Specific surface Blaine, m^2/kg	1461	2287	1865	981	1399	2327	1243	383
Total porosity, mm^3/g	91	403	348	285	254	284	162	–
pH	6.5	5.2	5.0	5.2	5.4	8.2	8.4	–
Electrical conductivity, mS	0.15	0.14	0.09	0.07	0.60	0.42	0.64	–
Particle size distribution								
d_{10}, μm	34.59	22.85	12.84	23.98	27.44	27.16	34.78	49.67
d_{50}, μm	7.30	6.35	3.99	6.32	5.61	4.93	9.43	15.37
d_{90}, μm	1.28	1.22	1.26	1.75	1.35	1.03	1.27	2.33

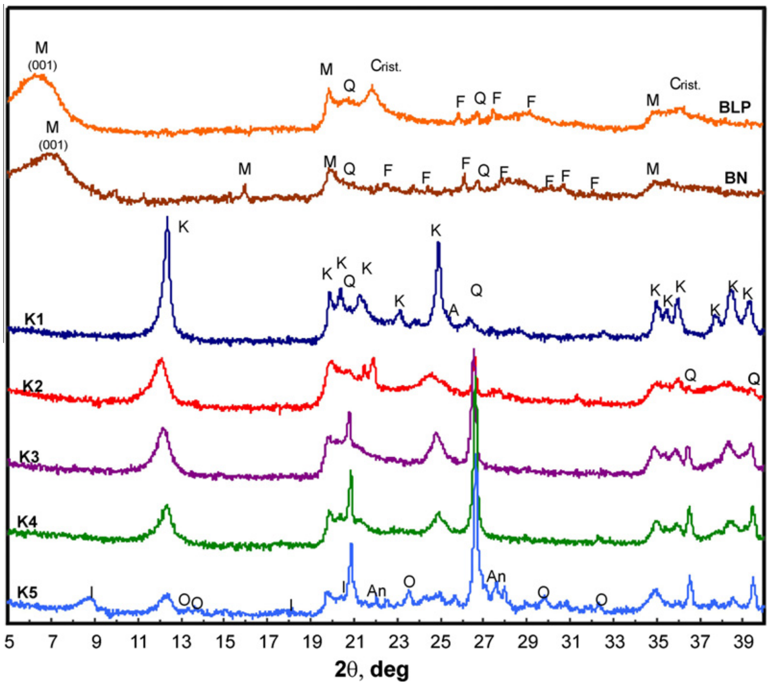

Fig. 1. XRD spectra for natural raw clays used. (K = kaolinite; Q = quartz; I = illite; An = anorthite; O = orthoclase; A = anatase; M = montmorillonite; Crist = cristobalite.)

was mixed in a planetary orbital mixer for 5 min and the specimens molded and compacted according to the standard procedure. The specimens were cured in a moist cabinet for 24 h, and then demolded after 24 h and immersed in saturated lime water at 20 ± 1 °C until test age. At 7, 28 and 90 days, the compressive strength was determined as the average of three specimens using universal testing machine Instron 4485. Finally, the strength activity index (SAI = $A/B*100$) was calculated as the ratio of the compressive strength of blended cement mortar (A) to the strength of the Portland cement mortar (B) at the same age, as percentage. For this type of test, several standards (ASTM C 618 [1], EN 450-1 [23] and IRAM 1668 [40]) agree that pozzolan is active when SAI is greater than 75% at 28-days. Complementary, the XRD analysis was made on mortar samples at 28 days to check the presence of CH.

After the compressive test, fragments of mortar were immersed in acetone for 24 h and dried in oven at 40 °C overnight. Then, they 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.

2.2.2. Frattini test

Frattini test was carried out according to the procedure described by IRAM 1651:03 standard (a procedure similar to the old EN 196:5 standard [41]). In this method, test samples were prepared as 20 g of blended cement (70% PC and 30% by mass of ground calcined clay) and mixed with 100 ml of boiled distilled water. After preparation, samples were left for 7 and 28 days in a sealed plastic container in an oven at 40 °C. At test time, samples were vacuum filtered through a 8 μm nominal pore size filter paper and allowed to cool to ambient temperature in sealed Buchner funnels. The filtrate was analyzed for $[OH^-]$ by titration against dilute HCl with methyl orange indicator and for $[Ca^{2+}]$ by pH adjustment to 13, followed by titration with 0.025 M EDTA solution using Murexide indicator. This test compares the $[Ca^{2+}]$ and $[OH^-]$ contained in an aqueous solution that covers the hydrated sample at 40 °C for a given time (7 and 28 days) with the solubility curve for CH in an alkaline solution at the same temperature. Calcined clay is considered as active pozzolan when the $[Ca^{2+}]$, $[OH^-]$ in the solution is down the solubility isotherm.

2.2.3. Lime consumption test (LC)

In this test, the $Ca(OH)_2$ consumption in the saturated lime solution–clay suspension is analyzed at different ages [42]. Firstly, $Ca(OH)_2$ saturated solution was prepared at 40 ± 1 °C. Then the solution was filtered and fractionated in hermetic recipients containing 25 ml of saturated solution and 2.5 g of calcined clays were added. These suspensions were maintained at 40 ± 1 °C until 1, 7, 14 and 28 days. Then, the suspension was filtered and titrated using HCl 0.02 M to determine the [CH] in solution. Results of LC are expressed as the ratio between [CH] obtained from the solution in contact with calcined clay and the $[CH]_0$ at initial time.

2.2.4. Electrical conductivity test (EC)

It was determined using a similar procedure to those proposed by Luxan et al. [30] and modified by Yu et al. [31]. This test consists in monitoring, at regular intervals of time, the electrical conductivity of 20 ml of saturated solution of calcium hydroxide at 40 ± 1 °C after 2 g of calcined clays were added to the beaker. Electrical conductivity was measured using a Jeway 4010 conductivity meter. The EC values gradually decrease with the time when the added material is reactive due to the consumption of ions by the pozzolanic reaction [43].

Table 2
Compressive strength of mortars (CS in MPa) and strength activity index (SAI) at 7, 28 and 90 days.

Age (days)	PC	Q	MK1	MK2	MK3	MK4	MK5	BLPc	BNc
7									
CS	30.6	21.0	24.7	32.2	27.1	20.5	20.6	22.2	22.6
SAI		*0.69*	*0.81*	*1.05*	*0.89*	*0.67*	*0.67*	*0.73*	*0.74*
28									
CS	38.4	25.2	37.8	49.0	41.2	36.8	30.9	29.6	33.7
SAI		*0.65*	*0.98*	*1.28*	*1.07*	*0.96*	*0.80*	*0.77*	*0.88*
90									
CS	40.8	26.7	45.1	57.4	48.0	41.5	34.2	39.6	40.3
SAI		*0.65*	*1.11*	*1.41*	*1.18*	*1.02*	*0.84*	*0.97*	*0.99*

3. Results

The results of compressive strength (CS) of Portland cement and Portland blended cements and the strength activity index (SAI) are summarized in Table 2.

For 30% of replacement, the dilution effect is equivalent to an increase of the water to cement ratio from 0.5 to 0.71 [44] and it causes a reduction of CS. This effect can be measured in the mortar containing 30% of ground quartz (Q) and it causes a reduction of 31–35% in CS from 7 to 90 days. Then, Q mortar has a SAI lower than 0.70. When calcined clay is incorporated to blended cement, the increase of SAI above 0.70 will be attributed to the pozzolanic reaction of active phases with the CH released during the cement hydration.

At 7 days, it can be observed that the addition of calcined clays causes a reduction in the CS (SAI < 1.00), with the exception of MK2 (SAI = 1.05). For MK4, MK5, BNc and BLPc, the SAI was close to the SAI-value of Q-mortar and lower than 0.75, the SAI requirement established by ASTM C618 standard [1]. After 28 days, MK1, MK3 and MK2 have a SAI near or greater than 1.00, while the other four calcined clays presented a SAI < 1.00, but it was greater than 0.75 and all calcined clays can be considered as active pozzolan. At 90 days, MK1, MK2 and MK3 presented a SAI ≫ 1.00; MK4, BNc and BLPc have a SAI close to 1.00, and MK5 presents a SAI of 0.84, indicating that the contribution of pozzolanic reaction cannot compensate for the reduction of cementitious materials.

Results of Frattini test are presented in Fig. 2 as dot in the graph of $[Ca^{2+}]$ versus $[OH^-]$. In this graph the calcium isothermal curve demarcates the pozzolanic area below this curve and the non-pozzolanic area above it. This procedure assumes that no other source of Ca^{2+} is present in the system, as the leaching of calcium would invalidate this approach [19,45].

At 7 and 28 days, results of pastes containing MK1, MK2, MK3 and MK4 are lying below the solubility line and near the *x*-axis, indicating that all Ca^{2+} released by cement hydration to solution was removed due to the progress of pozzolanic reaction. Results of MK5 at 7 days is lying near below the solubility line indicating its poor pozzolanic activity, and its result at 28 days is above the line due to the increase of $[OH^-]$ without $[Ca^{2+}]$ reduction. BNc and BLPc show good pozzolanic activity at 7 days, and the progress of pozzolanic reaction is observed for both calcined clays at 28 days (dots are located to the left and down in the pozzolanic area). BLPc shows a large reactivity at both ages, but it was lesser than those calcined clays containing MK. The result of Q is above the line corresponding to no pozzolanic activity. A control sample of 100% PC was also compared to ensure that this result lies on the

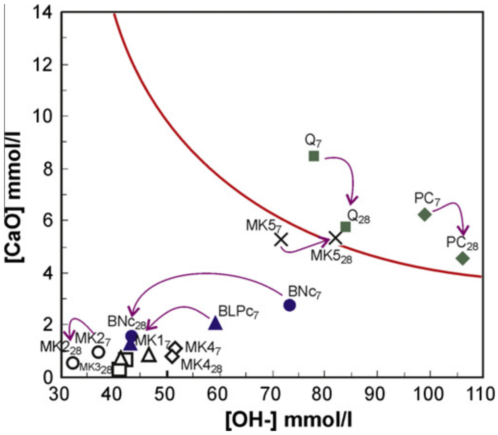

Fig. 2. Frattini test results for blended cement containing 30% of calcined clays tested after 7 and 28 days of curing at 40 °C.

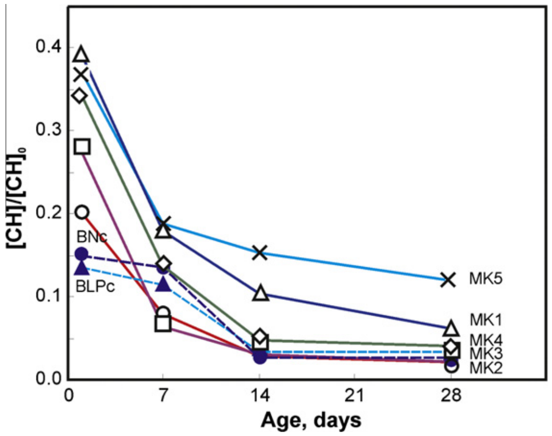

Fig. 3. Lime consumed test results for the calcined clays 1, 3, 7 and 28 days of at 40 °C.

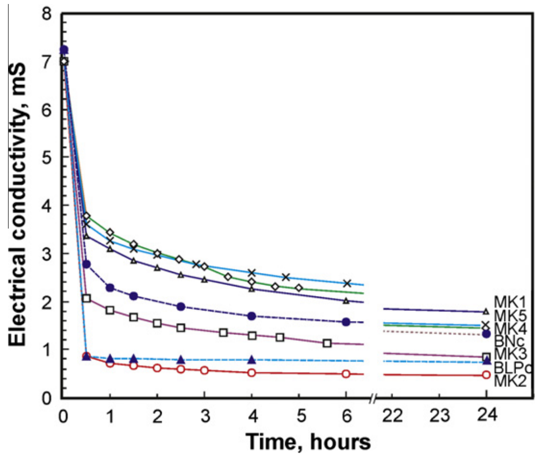

Fig. 4. Relationship between electrical conductivity and elapsed time of tested calcined clays.

saturation curve. With exception of MK5-clay, blended cements can be considered as pozzolanic cement according to the results of the Frattini test.

For the studied calcined clay, the lime consumption versus age is showed in Fig. 3. During the first day, the MK2 presents a significant LC indicating its high reactivity, while MK1 shows less LC instead of its high content of metakaolin. At 7 days, MK3 and MK2 consume more than 90% of CH in solution, while MK4 consumed 85%. Paradoxically, MK1 and MK5 contain the highest and lowest proportion of kaolinite and both calcined clays have the same LC at 7 days (approximately 80%). At 14 days, MK4 attains the same LC as MK2 and MK3; while the progress of the pozzolanic reaction of MK1 causes a drop in the remaining CH in solution. At the end of the test, MK2, MK3 and MK4 cause the depletion of more than 95% of $[CH]_0$ and MK1 has a 94% of LC. On the other hand, MK5 presents a slight LC from 14 to 28 days, indicating that the reactive phase in calcined clay has exhausted. For bentonites, the [CH] decreases drastically during the first day and more than 85% of $[CH]_0$ was fixed or consumed after 7 days. BLPc appears with higher LC than BNc, and later the LC was similar for both calcined bentonites.

For this test, all calcined clays, with exception of MK5, consume more than 90% of the available CH from the solution in 14 days. BLPc and BNc are presented as the most reactive pozzolans in this test at 28 days.

Fig. 4 shows the electrical conductivity (EC) of lime-water solution after addition of calcined clays recorded as a function of time. The EC drops drastically during the first 30 min, due to the fast reduction of Ca^{2+} and OH^- in the lime-water system [30] and it is attributed to the fixation of dissolved CH by calcined clay particles [31,46]. Later, the EC decreases slowly until approximately 8 h and finally its value remains approximately constant, except for MK4 and MK5 clays.

After 24 h, EC showed that MK2 is the more reactive pozzolan, followed by MK3, MK4, MK5 and finally MK1. For BLPc, the EC drops during the initial 30 min and then remains until 24 h. For BNc, the EC decreases slowly from 30 min until 6 h and then it remains.

4. Discussion

The *pozzolanic activity* of the calcined clays was ordered from the best to the worst in Table 3 according to the results obtained in each test method used. The criteria were the SAI-value, the CaO removed in the Frattini test calculated as the difference between the theoretical maximum [CaO] and the sample calcium concentration [CaO] expressed as a percentage of the theoretical maximum CaO removed [19], the LC-value and the EC-value of lime-clay suspension.

From the results of SAI and Frattini tests, the reactivity order of calcined clays was the same: MK2, MK3, MK1 and MK4. MK5 and both bentonites were classified as the worst in different order. For the LC and EC tests, results overvalue the pozzolanic activity for both bentonites, and there is an undervaluation of this property for MK1.

According to Massazza [47], the term '*pozzolanic activity*' covers all reactions occurring among the active constituents of pozzolan, lime (released by the Portland cement hydration) and water. This term includes two parameters: the maximum amount of lime that a pozzolan can combine and the rate at which such combination

Table 3
Classification of pozzolanic activity of calcined clays.

Test		SAI		Frattini		Lime consumption		EC residual		
Age, days		7 d	28 d	7 d	28 d	7 d	28 d	1 h	4 h	24 h
Pozzolanic activity	*Best*	MK2	MK2	MK2	MK2	MK2	BNc	MK2	MK2	MK2
		MK3	MK3	MK3	MK3	MK3	BLPc	BLPc	BLPc	BLPc
		MK1	MK1	MK1	MK1	BLPc	MK2	MK3	MK3	MK3
		MK4	MK4	MK4	MK4	BNc	MK3	BNc	BNc	BNc
		BNc	BNc	BLPc	BLPc	MK4	MK4	MK1	MK1	MK4
		BLPc	MK5	BNc	BNc	MK1	MK1	MK5	MK4	MK5
	Worst	MK5	BLPc	MK5	MK5	MK5	MK5	MK4	MK5	MK1

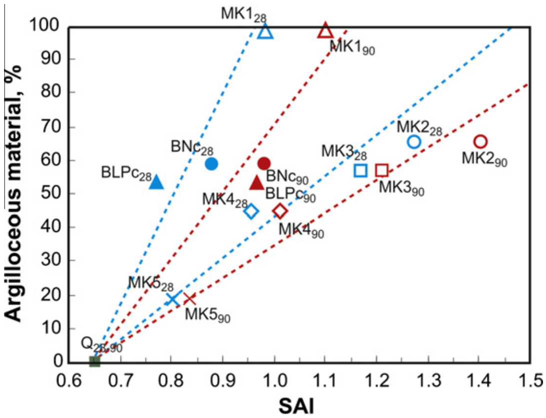

Fig. 5. Relation between the SAI and the percentage of argillaceous minerals in the clay.

occurs. The overall amount of combined lime depends essentially on the nature, the quality and quantity of the active phases present in the calcined clays. It also depends on some factors determined by the test method used (the lime/pozzolan ratio in the mix and the length of curing). On the other hand, the lime combination rate depends on the specific surface area of pozzolan, the water/solid ratio and the temperature of curing.

The nature and quality of the active phases obtained from different natural clays produce different capabilities to combine with CH. For kaolinitic clays, the reactivity of obtained metakaolin (AS_2) depends on the geological nature (primary or secondary source), the order/disorder and the amount of kaolin in raw clay, the calcinations conditions (temperature, residence time) and the fineness of the final product [8]. For complete pozzolanic reaction, 1 g of metakaolin could combine with a maximum of 1 g CH to form C–S–H (I), C_2ASH_8 (strätlingite), and some quantities of C_4AH_{13} and C_3ASH_6 (hydrogarnet) [17]. For the bentonites, the reactivity of the alumina-silicate phase obtained after calcinations depends on the type of montmorillonite (Ca-montmorillonite had higher pozzolanic activity than Na-montmorillonite); the temperature of calcination and the reduction of specific surface after calcinations [9,14]. This active phase (AS_4) reacts with CH to give C–S–H as the main product of pozzolanic reaction [9]. The stechiometric calculation gives that 1 g CH is combined with 0.9 g of calcined montmorillonite. Small quantities of moncarboaluminate and Mg–Al-silicate are found as reaction products, too.

Fig. 5 illustrates the relation between the percentage of argillaceous minerals in the raw clay and the SAI at 28 and 90 days. At 28 days, there is a poor correlation between SAI and the clay mineral content because the rate of pozzolanic reaction varies widely between the calcined clays analyzed. At later ages (90 days), the SAI is more dependent on the clay mineral content rather than the clay mineral type, as described by Habert et al. [15], because the degree of pozzolanic reaction is equilibrated during prolonged curing time. For kaolinites, the pozzolanic activity measured by SAI is proportional to the content of clayed mineral phases and inversely proportional to the content of inert or crystalline phases (quartz, feldspar, etc.), with exception of the MK1 that presents another quality of MK. This clay has a large content of kaolinite, but its structure is judged as highly ordered causing an active phase with low porosity and low specific surface after thermal treatment that reduces the rate of reaction. On the other hand, the high reactivity of MK2 is attributed to the great disorder in the kaolinite structure that causes a large porosity and a large specific surface of calcined clay (see Table 1). Then, the crystallinity of kaolinite, a structural factor, plays an important role in the pozzolanic activity, causing different rates of reaction of the active phase. The bad correlation between SAI and clay content for K1 could be attributed to a large proportion of metakaolin still unreacted. The different reactivity of MK1 and MK2 was also observed in the Frattini test at 7 days, the CH consumption in the LC and EC tests.

For calcined bentonites, the reaction of active phase with lime is slower than the corresponding to the metakaolin, causing low contribution to compressive strength at 7 and 28 days. Later, a significant contribution is observed at 90 days.

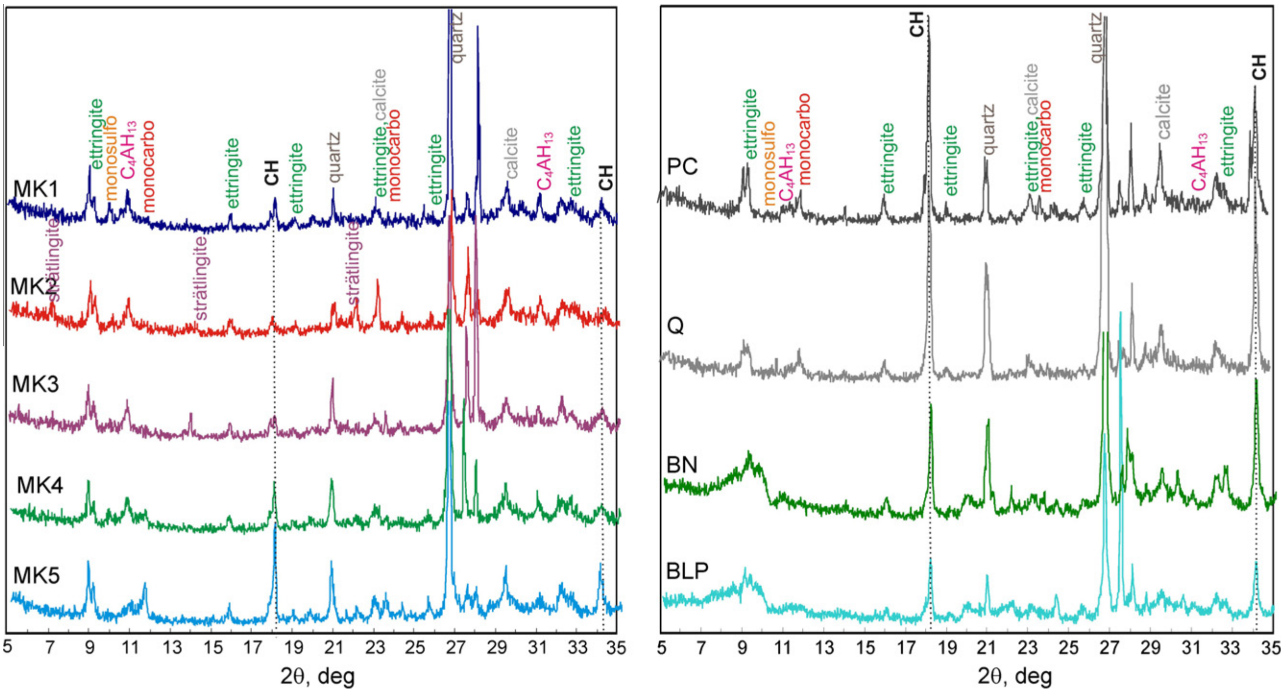

Fig. 6. XRD pattern of samples obtained from mortars after compressive strength test at 28 days.

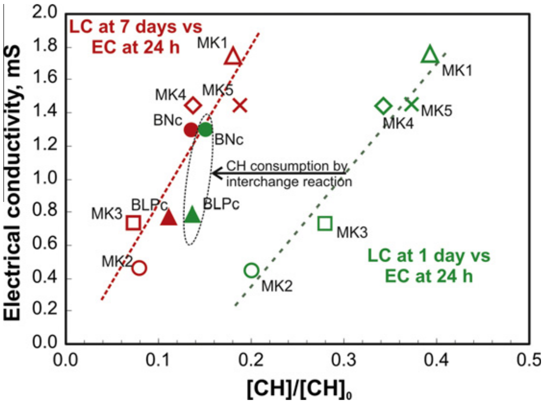

Fig. 7. Correlation between the fraction calcium hydroxide remaining in the saturated lime test LC and residual EC at 1 day.

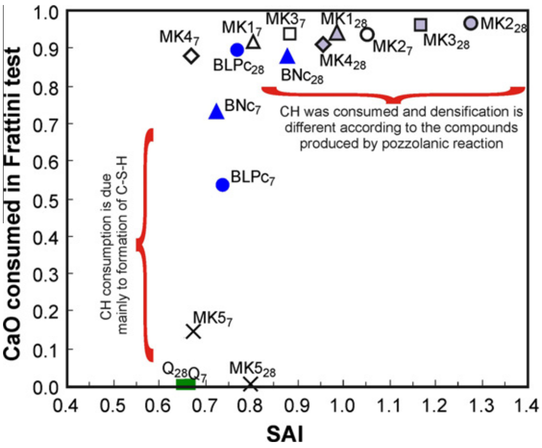

Fig. 8. Fraction of CaO consumed in the Frattini test and the strength activity index (SAI) at 7 and 28 days.

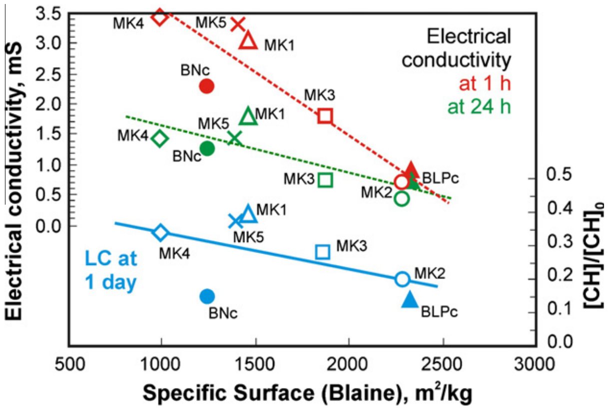

Fig. 9. Correlation between pozzolanic activity using the saturated lime test (1 day) or the electric conductivity (1 and 24 h) and the (Blaine) specific surface of calcined clays.

The pozzolanic reaction of calcined clays can be limited by the insufficient amount of CH in the system. For SAI and Frattini tests, the CH is supplied by the hydration of PC. Depending on the C_3S/C_2S ratio, the maximum amount of CH released by complete hydration of PC is in the range of 16–28% w/w. Cement used produces 0.20 g of CH by g of cement (20% w/w). Thereafter, blended cement containing 70% of PC has 0.14% w/w ($0.20*0.70$) of CH when it attains to complete hydration giving 0.58 g of CH by g of calcined clay. This ratio indicates that all CH will be consumed when the raw clays contain approximately 50% activated calcined argillaceous minerals in the sample. Fig. 6 reports the XRD of mortars at 28 days. It can be observed that kaolin containing more than 45% of kaolinite produce calcined clay (MK1 to MK4) that are capable of combining most of the available CH within 28 days, whereas MK5 are uncapable of chemically binding the CH provided by cement hydration. For bentonites, the CH peaks are identified in both mortars at 28 days and the peak intensity is too high for BN clay, indicating that some part was still uncombined after 28 days.

For the LC and EC tests, the CH to calcined clay ratio is 0.014 w/w. This ratio is too low and very reactive calcined clay (MK2) consumes rapidly more than 80% of CH present in saturated lime solution at 1 day, causing the drop of EC. On the other hand, MK1 consumes 60% of CH of solution producing high residual EC. There is a linear relationship between LC and EC at 1 day (Fig. 7) for the same type of argillaceous mineral. The large CH consumption in bentonites without EC drop could be attributed to an interchange ion reaction of Ca^{+2} by Na^{+}, which is equilibrated at 7 days causing a linear good correlation between the LC result at 7 days and the EC result at 24 h.

Results of Frattini, LC and EC tests show that CH was largely consumed. Then, these tests could fail to classify the order of calcined clay reactivity in relationship with the SAI test that measures the densification of microstructure, which produces the cementing compounds generated by the pozzolanic reaction. The composition of calcined clays, especially the content of reactive alumina, is responsible for the quick consumption of CH [19]. Kaolinitic calcined clays have appreciable quantities of reactive alumina favoring the formation of calcium aluminate phases (C_2ASH_8, C_4AH_{13} and C_3AH_6–C_2ASH_6) detected by XRD analysis (see Fig. 6). The reactive alumina also tends to substitute for silica in the structure of C–S–H, thus increasing the Al/Ca ratio of the C–S–H. In this case, the hydrated phase is often referred to as C–A–S–H [48].

The *rate of pozzolanic reaction* depends on the water/solid ratio (w/s) and the temperature [6], which are different in the SAI and Frattini tests. For Frattini test, the w/s increases ten times and the temperature rises from 20 to 40 °C, and both factors increase the consumption of CH. The pozzolanic reaction is slower in paste (reduced w/s) than in dispersion solution and it is still incomplete after many years. It is due to the severe drop in the mobility of chemical species that governs the later pozzolanic reaction in the paste and could stop it progresses [47].

In the Frattini test, the acceleration of pozzolanic reaction produces the complete consumption of CH after 7 days for MK1 to MK4. Then, the location of the point in the graph does not change at 28 days. For bentonites, there is a progress in CH consumption from 7 to 28 days. For this situation, the complete consumption of CH in MK1–MK4 and two bentonites resulted in no significant correlation between results from this test and SAI (Fig. 8), contrary to the report by Donatello et al. [19]. The compressive strength depends on the nature and compactness of the hydration product formed, especially C–S–H, during the pozzolanic reaction. For MK calcined clays, the alumina phases formed ($C_3A{\cdot}CH{\cdot}H_{12}$) consume a large proportion of CH (crystal size refinement) with poor contribution to compressive strength [6,49], while the compressive strength development (SAI 0.67–0.80 for MK3 and MK4) depends mainly on the pore size refinement caused by the pore filling due to C–S–H or C–A–S–H formation [2]. The alumina phase assembling depends on the variation of CH/Al ratio during time [49] and the curing temperature [42]. For BLPc and BNc, the aluminum phases are less likely to form (see Fig. 7) and the main product of pozzolanic reaction is the C–S–H.

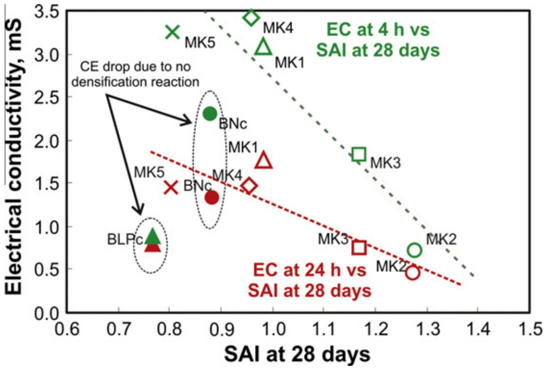

Fig. 10. Correlation between electrical conductivity measured at 4 and 24 h and the SAI test at 28 days.

LC and residual EC measure the short-term activity of calcined clays and this property essentially depends on the specific surface area of pozzolan. For these tests, cement hydration is not involved and the pozzolanic reaction occurs in solution. Fig. 9 shows the relationship between the specific surface of calcined clay and the LC at 1 day or the EC at 1, 4 and 24 h. It can be observed that the CH was quite consumed when the specific surface of calcined clay increases. The reaction rate of MK2 is higher than MK1; this different behavior can be attributed certainly to the higher specific surface, which favors a higher initial rate of lime combination or fixation. For calcined bentonites, the high specific surface and the cation exchange capacity could be sufficient to remove most of the calcium from the solution in a few hours. However, the compounds formed do not contribute to compressive strength and the initial SAI is low. Fig. 10 shows the correlation between the SAI at 28 days and the residual EC (24 h). A linear relationship between both measures for the same type of clays can be seen. This suggests that there is a different contribution to cementing compounds of MK and bentonites.

Finally, the results of pozzolanic activity test depend on the nature, crystallinity and content of reactive alumino–silica glass in the calcined clay, the type and mineralogical composition of cement used and the level of cement replacement. To define the pozzolanic activity of calcined clays, authors recommend the use a combination of the Frattini test to evaluate accurately the CH consumption in blended cement and the SAI tests to discriminate the real contribution of pozzolanic reaction to the microstructure densification that cause the improve of strength.

5. Conclusions

From the results obtained in the evaluation of the pozzolanic activity of calcined clays for replacement in cement, the following conclusions can be drawn:

- The Frattini test (direct) and the strength activity index (indirect) were found to be the most accurate and reliable methods to assess pozzolanic reaction of calcined clays to be used in blended cements The Frattini test monitors the CH content, giving a good indication of the pozzolanic character of the blended cement formulated with calcined clays containing different argillaceous minerals.
- The pozzolanic reaction of calcined bentonites as substitute of cement favors the formation of silicate phases, while this reaction for calcined kaolines produces the formation of early AFm phases ($C_3A\cdot CH\cdot H_{12}$) and later the presence of strätlingite (C_2ASH_8). This aluminic character of the pozzolanic reaction consumes a large proportion of CH during Frattini, LC and EC tests and can lead to overvalue the pozzolanic activity of calcined clay in relationship with the SAI results that show the engineering performance of the blended cement.
- The very large specific surface of calcined clays (980–2300 m^2/kg) causes a great influence on the short-term pozzolanic activity, while the long-term activity is related to the chemical and mineralogical composition of the amorphous phases present in the calcined clays. Then, the electrical conductivity and the lime consumption tests evaluate the ability of pozzolanic material to fix CH during the first time of contact. Both properties show a good relationship with the specific surface of calcined clay, which is capable of exhausting the CH quickly. At later ages other factors, such as densification and pore size reduction produced by pozzolanic reaction also became important in the evolution of SAI. The mechanical strength is controlled by the microstructure of the hydration products, rather than the amount of reacted CH. Microstructural differences in the hydration products associated with the pozzolanic reaction depend on the predominant argillaceous mineral present in the clay.
- The compressive strength can be maintained and even increased from 28 days by substituting 30% of the cement in mortars by calcined clays containing a large proportion of impurities (more than 40% of quartz). There is a good correlation between the pozzolanic activity measured as the compressive strength of mortars and the content of argillaceous mineral in the clays.

References

[1] ASTM C618. Standard specification for fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland cement concrete. American Society for Testing and Materials. West Conshohocken(PA, USA): ASTM International; 2003.
[2] Mehta PK, Monteiro PJM. Concrete: microstructure properties and materials. USA: McGraw-Hill; 2006.
[3] Damineli BL, Kemeid FM, Aguiar PS, John VM. Measuring the eco-efficiency of cement use. Cem Concr Compos 2010;32(8):555–62.
[4] Pacheco Torgal F, Jalali S. Eco-efficient construction and building materials. London Limited: Springer Verlag; 2011 [chapter 5].
[5] Sabir BB, Wild S, Bai J. Metakaolin and calcined clays as pozzolans for concrete: a review. Cem Concr Compos 2001;23(6):441–54.
[6] Ambroise J, Murat M, Pera J. Hydration reaction and hardening of calcined clays and related minerals. IV Experimental conditions for strength improvement on metakaolinite minicylinders. Cem Concr Res 1985;15(1):83–8.
[7] Bich Ch, Ambroise J, Péra J. Influence of degree of dehydroxylation on the pozzolanic activity of metakaolin. Appl Clay Sci 2009;44(3–4):194–200.
[8] He C, Makovicky E, Osbaeck B. Thermal stability and pozzolanic activity of calcined kaolin. Appl Clay Sci 1994;9(3):165–87.
[9] He C, Makovicky E, Osbaeck B. Thermal treatment and pozzolanic activity of Na- and Ca-montmorillonite. Appl Clay Sci 1996;10(5):351–68.
[10] Samet B, Mnif T, Chaabouni M. Use of a kaolinitic clay as a pozzolanic material for cements: formulation of blended cement. Cem Concr Compos 2007;29(10):741–9.
[11] Badogiannis E, Kakali G, Dimopoulou G, Chaniotakis E, Tsivilis S. Metakaolin as a main cement constituent. Exploitation of poor Greek kaolins. Cem Concr Compos 2005;27(2):197–203.
[12] Vejmelková E, Keppert M, Rovnaníková P, Keršner Z, Černý R. Application of burnt clay shale as pozzolan addition to lime mortar. Cem Concr Compos 2012;34(4):486–92.
[13] Castillo R, Fernández R, Antoni M, Scrivener K, Alujas A, Martirena JF. Activation of low grade clays at high temperatures. Rev Ing Construcción 2010;25(3):329–52.
[14] Fernandez R, Martirena F, Scrivener KL. The origin of the pozzolanic activity of calcined clay minerals: a comparison between kaolinite, illite and montmorillonite. Cem Concr Res 2011;41(1):113–22.
[15] Habert G, Choupay N, Escadeillas G, Guillaume D, Montel JM. Clay content of argillites: influence on cement based mortars. Appl Clay Sci 2009;43(3–4):322–30.
[16] He C, Osbaeck B, Makovichy E. Pozzolanic reaction of six principal clay minerals: activation reactivity assessments and technological effects. Cem Concr Res 1995;25(8):1691–702.
[17] Murat M. Hydration reaction and hardening of calcined clays and related minerals. I. Preliminary investigation on metakaolinite. Cem Concr Res 1983;13(2):259–66.

[18] Fernández R, Nebreda B, Vigil de la Villa R, García R, Frías M. Mineralogical and chemical evolution of hydrated phases in the pozzolanic reaction of calcined paper sludge. Cem Concr Compos 2010;32(10):775–82.

[19] Donatello S, Tyrer M, Cheeseman CR. Comparison of test methods to assess pozzolanic activity. Cem Concr Compos 2010;32(2):121–7.

[20] Rahhal V, Talero R. Calorimetry of Portland cement with silica fume, diatomite and quartz additions. Constr Build Mater 2009;23(11):3367–74.

[21] Talero R, Rahhal V. Calorimetric comparison of Portland cements containing silica fume and metakaolin. J Therm Anal Calorim 2009;96(2):383–93.

[22] Trusilewicz L, Fernández-Martínez F, Rahhal V, Talero R. TEM and SAED characterization of metakaolin. Pozzolanic activity. J Am Ceram Soc 2012;95(9):2989–96.

[23] EN-450-1 Fly ash for concrete. Definition, specifications and conformity criteria, European Committee for Standardization; 2005.

[24] ASTM C311. Standard test methods for sampling and testing fly ash or natural pozzolans for use as a mineral admixture in Portland-cement concrete. American Society for Testing and Materials. West Conshohocken (PA, USA): ASTM International; 2003.

[25] IRAM 1654. Pozzolans: general test methods. Instituto Argentino de Racionalización de Materiales, Buenos Aires, Argentina; 2001.

[26] Gava GP, Prudencio LR. Pozzolanic activity tests as a measure of pozzolans' performance. Part 1. Mag Concr Res 2007;59(10):729–34.

[27] Gava GP, Prudencio LR. Pozzolanic activity tests as a measure of pozzolans' performance. Part 2. Mag Concr Res 2007;59(10):735–41.

[28] Pourkhorshidi AR, Najimi M, Parhizkar T, Jafarpour F, Hillemeier B. Applicability of the standard specifications of ASTM C 618 for evaluation of natural pozzolans. Cem Concr Compos 2010;32(10):94–800.

[29] Bentz DP, Durán-Herrera A, Gálvez-Moreno D. Comparison of ASTM C311 strength activity index testing versus testing based on constant volumetric proportions. J ASTM Int 2011;9(1):1–21.

[30] Luxan MP, Madruga M, Saavedra J. Rapid evaluation of pozzolanic activity of natural products by conductivity measurement. Cem Concr Res 1989;19(1):63–8.

[31] Yu Q, Sawayama K, Sugita S, Shoya M, Isojima Y. The reaction between rice husk ash and $Ca(OH)_2$ solution and the nature of its product. Cem Concr Res 1999;29(1):37–43.

[32] Payá J, Borrachero MV, Monzó J, Peris-Mora E, Amahjour F. Cem Concr Res 2001;31(1):41–9.

[33] Sinthaworn S, Nimityongskul P. Quick monitoring of pozzolanic reactivity of waste ashes. Waste Manage 2009;29(2):1526–31.

[34] Shvarzman A, Kovler K, Grader GS, Shter GE. The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite. Cem Concr Res 2003;33(3):405–16.

[35] Wilson MJ. A Handbook of determinative methods in clay mineralogy. USA: Chapman and Hall Publ.; 1987.

[36] Aparicio P, Galan E. Mineralogical interference on kaolinite crystallinity index measurements. Clays Clay Miner 1999;47:12–27.

[37] Tironi A, Trezza MA, Scian AN, Irassar EF. Kaolinitic calcined clays: factors affecting its performance as pozzolans. Constr Build Mater 2012;28(1):276–81.

[38] Tironi A, Trezza M, Irassar EF, Scian A. Thermal activation of bentonites for their use as pozzolan. Rev Construcción 2012;11(1):44–53.

[39] American Society for Testing and Materials (ASTM) C 204-04. Standard test method for fineness of Portland cement by air permeability apparatus.

[40] IRAM 1668. Pozzolans: characteristic and sampling. Instituto Argentino de Racionalización de Materiales, 2001.

[41] EN 196-5. Standard methods for testing cement. Part 5: Pozzolanicity test for pozzolanic cements. European Committee for Standardization; 1988.

[42] Frías M, Sánchez de Rojas MI, Cabrera J. The effect that the pozzolanic reaction of metakaolin has on the heat evolution in metakaolin–cement mortars. Cem Concr Res 2000;30(2):209–16.

[43] Sinthaworn S, Nimityongskul P. Effects of temperature and alkaline solution on electrical conductivity measurements of pozzolanic activity. Cem Concr Compos 2011;33(5):622–7.

[44] Cyr M, Lawrence P, Ringot E. Mineral admixtures in mortars: quantification of the physical effects of inert materials on short-term hydration. Cem Concr Res 2005;35(4):719–30.

[45] Garcia R, Vigil de la Villa R, Vegas I, Frías M, Sánchez de Rojas MI. The pozzolanic properties of paper sludge waste. Constr Build Mater 2008;22(7):1484–90.

[46] Mohamed SM, Sayed SS. Effect of silica fume and metakaoline pozzolana on the performance of blended cement pastes against fire. Ceramics – Silikáty 2007;51(1):40–4.

[47] Massazza F. Pozzolana and pozzolanic cements. In: Hewllet, editor. Lea's chemistry of cement and concrete. 4th ed.; 2003, p. 471–635, [chapter 10]

[48] Fernández López R. Calcined clayey soils as a potential replacement for cement in developing countries. Thèse no. 4302, École Polytechnique Fédérale de Lausanne, Suisse; 2009.

[49] de Silva PS, Glasser FP. Phase relations in the system $CaO–Al_2O_3–SiO_2–H_2O$ relevant to metakaolin – calcium hydroxide hydration. Cem Concr Res 1993;23(3):627–39.