

# Thermal Activation of Two Complex Clays (Kaolinite-Pyrophyllite-Illite) from Tandilia System, Buenos Aires, Argentina

M.A. Trezza <sup>(✉)</sup>, A. Tironi, and E.F. Irassar

Facultad de Ingeniería (UNCPBA), CIFICEN (CONICET-CICPBA- UNCPBA),  
Av. del Valle 5737, B7400JWI Olavarría, Argentina

**Abstract.** The aim of this work is focused to identify natural resources with industrial potential to be used as supplementary cementitious materials (SCMs) in Portland blended cements. Two clays obtained from the quarries near to Barker in Tandilia System (Buenos Aires- Argentina) were studied. The geneses of these rocks are by a hydrothermal alteration and include the presence of pyrophyllite. Whole-rock were characterized by XRD and FTIR spectroscopy indicating that main clayed minerals are kaolinite ( $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ ), illite ( $\text{K}_{0.66}\text{Si}_{3.33}\text{Al}_{2.66}\text{O}_{10}(\text{OH})_2$ ) and pyrophyllite ( $\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2$ ) associated with feldspar. The thermal transformation was studied by differential thermal analysis and the phase changes were confirmed by XRD and FTIR. Samples of clays were calcined at different temperature (550 to 1050 °C), the electrical conductivity was measured and the dissolved silica in simulated pore water solution was quantified. The pozzolanic activity was measured by the compressive strength activity index, on blended cement mortars containing 25% by weight of calcined clays.

Results showed pozzolanic activity after 7 days and the compressive strength values exceed the rate of replacement for both clays. The high water demand of sample containing pyrophyllite can be attributed to the exfoliation that occurs during the water loss process.

## 1 Introduction

Calcined clays may be attractive as supplementary cementitious materials (SCMs) since clays are highly abundant and they are a rich source of alumina and silica which can drive the pozzolanic reaction in blended cement [1]. In the natural state, the clay minerals by their crystalline structure do not possess pozzolanic properties. However, they exhibit pozzolanic activity when are calcined at temperatures between 600 and 900 °C and are finely ground [2, 3]. Its use implies lower energy consumption and reduction in CO<sub>2</sub> emission.

Several studies have been carried out on different types of clays to know their thermal behavior and to analyze their potential use as pozzolanic addition in cement industry. The Pyrophyllite (P) clays have a structure that collapses above 1100 °C, accompanied by formation of amorphous SiO<sub>2</sub> and poorly ordered mullite. Li et al. [4] report that the amorphous SiO<sub>2</sub> in thermally treated P, is soluble in caustic soda solution. Illite (I) clays

conserve the order of their structure layers despite the thermally treatment, even after dehydroxylation [5]. Thermal activation of kaolinitic (K) clays produce metakaolinite (MK), amorphous phase that reacts with the calcium hydroxide (CH) generated during the hydration of Portland cement (PC) and contributes to its hydration.

Natural clays are complex systems as consequence the aim of this work is focused to identify natural resources with industrial potential to be used as SCMs in Portland blended cements. Two complex clays obtained from the quarries near to Barker in Tandilia System (Buenos Aires- Argentina) were studied. The geneses of these rocks are by a hydrothermal alteration and include the presence of K ( $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ ), I ( $\text{K}_{0.66}\text{Si}_{3.33}\text{Al}_{2.66}\text{O}_{10}(\text{OH})_2$ ) and P ( $\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2$ ) associated with feldspars. The thermal transformation of clays was studied at different temperature (550 to 1050 °C) and their potential activity as SCMs were determined in blended cement containing 25% by weight.

## 2 Materials and Methods

The studied clays were denominated PK1 and PK2. The crystalline phases were identified by X-ray diffraction (XRD) with a Phillips XPW 3710 diffractometer and quantified using the Rietveld method and PANalytical HighScore Plus software. The thermal stability of the phases present in the natural clay was determined by differential thermal analysis combined with thermo-gravimetric analysis (DTA/TG) using NETZSCH STA 409 thermobalance.

The natural clays were placed as a bed in a vessel and calcined in an ORL oven to the set temperature with a ramp of  $13\text{ }^\circ\text{C min}^{-1}$  and holding this value for 90 min. The temperatures selected, from DTA/TG results, were: 550, 650, 750 and 1050 °C. Calcined samples were grinding until the retained on 45  $\mu\text{m}$  sieve (# 325) was lower than 12%. The transformations of the crystalline phases present in the clays were studied by XRD and FT-IR spectroscopy using a Nicolet Magna 500 spectrophomter.

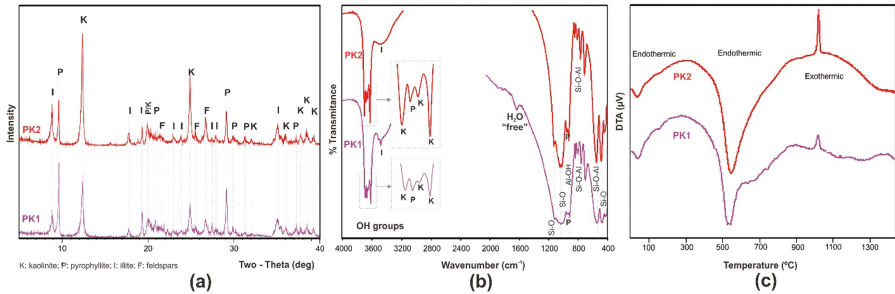
Pozzolanic activity of calcined clays was proved using electrical conductivity test (EC). The EC was measured using a Jenway 4010 conductivity meter at preestablished time intervals after that the different calcined clays were added to the beaker containing calcium hydroxide saturated solution. The test was performed at  $40 \pm 1\text{ }^\circ\text{C}$  [3]. The alkaline dissolution was carried out in order to quantifying the active silica of different calcined clays in strongly alkaline medium in which they would be found if be used as active additions to the PC. The quantification of dissolved  $\text{SiO}_2$  was performed with a colorimetric analytical method.

At the selected calcination temperature, calcined clays were prepared to elaborate blended cements (BC) with 25% w/w of replacement. Mortar (w/cm = 0.5 – sand: cement = 3:1) was elaborated, the flow was determined and the compressive strength (CS) of was measured on standard prisms at 7, 28 and 90 days. The strength activity index (SAI) was calculated as the ratio of the CS of blended cement to the strength of the plain cement at the same age.

### 3 Results

#### 3.1 Characterization of Clays

Both studied clays (PK1 y PK2) have a similarity chemical composition, with slight differences in the percentages of their main oxides. The crystalline phases were identified by XRD (Fig. 1a). The minerals present quantified by Rietveld method are: PK1: 25%P, 27%I, 40%K, 8%F; and PK2: 13%P, 33%I; 47%K, 7%F.



**Fig. 1.** (a) Diffractograms, (b) IR spectra and (c) DTA/TG of PK1 and PK2 clays

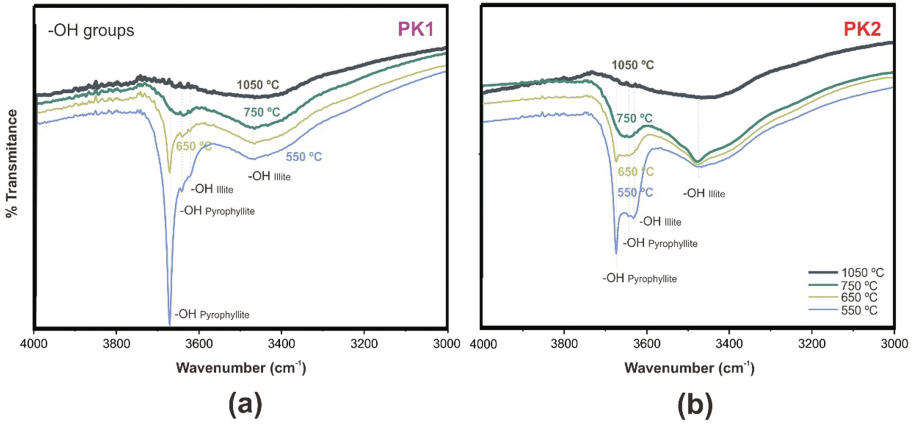
The highest I content quantified for PK2 by DRX-Rietveld is in agreement with the higher content of  $K_2O$  (3.65%), and the highest K content is in agreement with the higher content  $Al_2O_3$  (37.00%) in this clay. The FTIR spectra (Fig. 1-b) confirm the assignments made by DRX.

Both clays show similar DTA/TG curves (Fig. 1-c): a wide endothermic peak is observed between 550 and 600 °C, characteristic of the K-dehydroxylation and formation of metakaolinite (MK). In this area, the P-dehydroxylation [6] has also been reported. At approximately 990 °C, an acute exothermic peak corresponding to the formation of the crystalline premullite spinel phase appears. It was reported as typical peak in K-clay [7], as well as in P-clay [6]. The formation of crystalline phase decreases the amount of reactive amorphous phase, necessary to pozzolanic reaction.

#### 3.2 Calcined Clays

Based on DTA/TG results, four calcination temperatures were evaluated: 550, 650, 750 and 1050 °C. Figure 2 show the FTIR characteristic OH-stretching region of calcined clays. As observed by DTA/TG at temperatures between 550 and 600 °C, the K-dehydroxylation was produced to obtained amorphous phase MK. The four bands of OH-stretching corresponding to K disappear at 550 °C. The sharp and narrow band of OH-stretching corresponding to P at  $3675\text{ cm}^{-1}$ , decreases greatly with the increase of calcination temperature. It indicates than large amount OH groups of P are removed and disappear over 1000 °C when the dehydroxylation is completed. The mean intensity band centred at  $3630\text{ cm}^{-1}$  and the shoulder at  $3469\text{ cm}^{-1}$  assigned to the stretching of

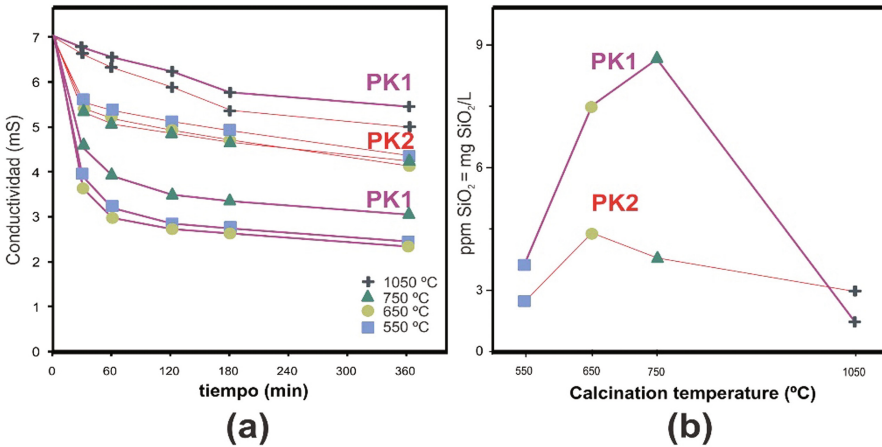
the OH groups of I, also decreases with the dehydroxylation process, and the formation of amorphous phase.



**Fig. 2.** FT-IR spectra (4000-3000 cm<sup>-1</sup>) of calcined clays PK1 and PK2.

At temperatures over 550 °C, partial dehydroxylation of the I occurs but this does not affect its crystalline structure and the reduction of the intensity of the basal planes in X-ray diffractograms is seen [5]. It is also observed by XRD that the peak-intensity of I and P decreases with the increase of temperature.

Figure 3a shows the EC as a function of time for the calcined clay–calcium hydroxide solution. During the first 30 min, PK1 calcined at 550, 650 and 750 °C reduce its EC more than calcined PK2. This behaviour indicates the high interaction of this calcined clay with Ca(OH)<sub>2</sub>. The reactivity of PK1 is similar between 550 and 650 °C, but it decreases at 750 °C. The reactivity of PK2 does not change between 550 to 750 °C. Both



**Fig. 3.** (a) EC (mS), (b) silica dissolved (mg/l) of calcined clays

calcined clays have low reactivity at 1050 °C, according to the formation of crystalline phase determined by DTA/TG and the consequent decrease of amorphous phase.

The amount of silica dissolved in ppm ( $\text{mgSiO}_2/\text{l}$  solution) in alkaline solution is associated with the amorphization achieved by the heat treatment. Crystalline phases such as quartz and mullite are insoluble in alkaline solution [8]. For PK1 clay, with a higher content of P, where the Si/Al ratio is higher than for K and I, the dissolved  $\text{SiO}_2$  content increases significantly with the increase of temperature up to 750 °C (Fig. 3b), where the amount of P decreases. This dissolution decreases if the calcination is done at 1050 °C, at which temperature, as observed by DTA/TG, the premullite [4] has crystallized. The clay PK2 has the same behavior but with more moderate dissolution.

Silica and alumina reactive contribute to the pozzolanic reactivity in the calcined clays. The higher reactivity of the calcined PK1, with least percentage of K can be attributed to the P and I contribution. PK2 with high illite content shows less pozzolanic activity. At 1050 °C, part of the amorphous phase obtained during the dehydroxylation crystallizes and reduces the amount of amorphous reactive phase.

### 3.3 Blended Cement

Considering that complete dehydroxylation of the major phases and the biggest silica soluble content (Fig. 3b) occurs between 550 and 650 °C, the selected temperature for calcination was 600 °C to produce the SCMs. The physical characteristics of the calcined and grinding clays were: PK1-600 (Blaine 879  $\text{m}^2/\text{kg}$ , RoS 45  $\mu\text{m}$  11.2%, density 2.54), PK2-600 (Blaine 786  $\text{m}^2/\text{kg}$ , # 45  $\mu\text{m}$  6.4%, density 2.49). The properties of blended cement mortars with PK1-600 and PK2-600 are reported in Table 1. The mortar flow of blended cement is significantly lower (42 and 63%) than that of the control mortar (122%). This behaviour may be due to the fact that the addition particles that replace the cement particles have large specific surface that requires more water to wetting.

**Table 1.** Flow, compressive strength (CS) and strength activity index (SAI).

	Flow (%)	7 days		28 days		90 days	
		CS(MPa)	SAI	CS(MPa)	SAI	CS(MPa)	SAI
PC	122	34.5	1.00	46.6	1.00	53.8	1.00
PK1-BC	42	31.4	0.90	48.5	1.04	50.8	0.94
PK2-BC	63	29.4	0.85	48.0	1.03	50.0	0.93

For PK1-600 and PK2-600, the CS at 7 days is lower than the corresponding to plain cement but it overcomes the dilution effect due to stimulation of cement hydration and the pozzolanic reaction. The high reactivity of PK1 produces a quick contribution to CS, but the CS at later ages (28 and 90 days) attains similar values for both calcined clays attributed to the develop of pozzolanic reaction. The SAI attain a value near to 1 for both blended cements at 28 days.

## 4 Conclusions

The thermal treatment on two complex clays (kaolinite-pyrophyllite-illite) from the Tandilia system is characterized by: *dehydration* at low temperature, the *dehydroxylation* of clayed phases from 500 to 600 °C, and the *crystallization* of premullite at 990 °C. The collapse of structure of pyrophyllite occurs when the calcination temperature exceeds 750 °C as occurred with the illite phase despite the complete dehydroxylation.

In alkaline solution, complex calcined clays showed increasing percentages of soluble silica when calcination temperature increases from 550 to 750 °C and it was more marked in the PK1. At 1050 °C, the dissolved silica decreases significantly due to the formation of premullite.

For these complex clays, the recommend calcination temperature was 600 °C, considering the high pozzolanic reactivity of these complex calcined clays occurs between 550 and 650°C.

For these clays, mortar flow decreases significantly when 25% by weight of replacement was used and the compressive strength shows a slight reduction at 7 days and a great contribution at later ages reaching to SAI close to 1 at 28 days.

## References

1. Ambroise, J., Murat, M., Pera, J.: Hydration reaction and hardening of calcined clays and related minerals. V: extension of the research and general conclusions. *Cem. Concr. Res.* **15**, 261–268 (1985). doi:[10.1016/0008-8846\(85\)90037-7](https://doi.org/10.1016/0008-8846(85)90037-7)
2. Tironi, A., Trezza, M.A., Scian, A.N., Irassar, E.F.: Kaolinitic calcined clays: factors affecting its performance as pozzolans. *Constr. Build. Mater.* **28**, 276–281 (2012). doi:[10.1016/j.conbuildmat.2011.08.064](https://doi.org/10.1016/j.conbuildmat.2011.08.064)
3. Tironi, A., Trezza, M.A., Scian, A.N., Irassar, E.F.: Assessment of pozzolanic activity of different calcined clays. *Cem. Concr. Comp.* **37**, 319–327 (2013). doi:[10.1016/j.cemconcomp.2013.01.002](https://doi.org/10.1016/j.cemconcomp.2013.01.002)
4. Li, G., Zeng, J., Luo, J., Liu, M., Jing, T., Qiu, G.: Thermal transformation of pyrophyllite and alkali dissolution behavior of silicon. *Appl. Clay Sci.* **99**, 282–288 (2014). doi:[10.1016/j.clay.2014.07.011](https://doi.org/10.1016/j.clay.2014.07.011)
5. Fernández, R., Martirena, F., Scrivener, K.L.: The origin of the pozzolanic activity of calcined clay minerals: a comparison between kaolinite, illite and montmorillonite. *Cem. Concr. Res.* **41**, 113–122 (2011). doi:[10.1016/j.cemconres.2010.09.013](https://doi.org/10.1016/j.cemconres.2010.09.013)
6. Mukhopadhyay, T.K., Ghatak, S., Maiti, H.S.: Pyrophyllite as raw material for ceramic applications in the perspective of its pyro-chemical properties. *Ceram. Int.* **36**, 909–916 (2010). doi:[10.1016/j.ceramint.2009.10.026](https://doi.org/10.1016/j.ceramint.2009.10.026)
7. Sanchez Soto, P.J., Justo Erbez, A., de Haro, M.C.J., Pérez Rodriguez, J.L., Raigón Pichardo, M., Pascual Cosp, J.: Caracterización y propiedades cerámicas de una pizarra aluminica que contiene pirofilita. *Bol. Soc. Esp. Cerám. Vidrio* **33**, 199–205 (1994)
8. Jiang, T., Li, G., Qiu, G., Fan, X., Huang, Z.: Thermal activation and alkali dissolution of silicon from illite. *Appl. Clay Sci.* **40**, 81–89 (2008). doi:[10.1016/j.clay.2007.008.002](https://doi.org/10.1016/j.clay.2007.008.002)