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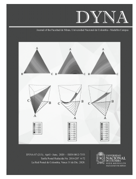

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Cement production with pozzolans from residual tropical soils formed from paragneiss with a high silicon oxide content

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Abstract
The manufacture of cement demands a lot of energy and gives off large amounts of CO_2. Calcined clays need less energy and emit water instead of CO_2, which has drawn attention to them, especially those rich in kaolinite. However, their use has been discouraged due to their location and high market price. Hence, the present study focuses on calcined clays with a low kaolinite content, specifically those derived from paragneiss. In Colombia they are located in weathering horizons with depths of up to 40 meters. The results showed contents of 20% Al_2O_3, less than 14% Fe_2O_3, more than 60% SiO_2, less than 40% kaolinite, 20% illite and more than 30% quartz. Calcined at 750 °C, they were used in mortars, obtaining SAI values of between 80 and 100% after 28 days, which, added to the results of Frattini tests, show that their use as a supplementary cementing material is feasible.

Keywords: supplementary cementing material; calcined clays: low kaolinite clay; Pozzolans; residual soils in cement manufacturing.

Producción de cemento con puzolanas de suelos tropicales residuales de paragneis con alto contenido de óxido de silicio

Resumen
La manufactura del cemento demanda mucha energía y aporta cantidades importantes de CO_2. Las arcillas calcinadas, demandan menos energía y emiten en vez de CO_2, agua a la atmósfera, convirtiéndolas en objeto de atención, fundamentalmente aquellas ricas en caolinita. No obstante, están siendo desincentivadas, por su ubicación y alto precio en el mercado. El presente estudio se enfocó hacia las arcillas de bajo contenido de caolinita, como las derivadas de paragneiss, encontrándose en Colombia, horizontes de meteorización con profundidades hasta 40 metros. Los resultados arrojaron contenidos de Al_2O_3 del 20%, Fe_2O_3 menores al 14%, SiO_2 mayores al 60%, contenidos de caolinita menores de 40%, illita 20% y cuarzo mayores al 30%. Siendo calcinadas a 750 °C, se emplearon en morteros, obteniendo valores de IAR a 28 días entre el 80 y 100%, que sumados a los resultados de ensayos Frattini, muestran que su uso como material cementante suplementario es factible.

Palabras clave: material cementante suplementario; arcillas calcinadas; arcilla de bajo contenido de caolinita; Puzolanas; suelos residuales en la fabricación de cemento.

1. Introduction

With the increase in the world's population, an increase in industry has occurred which has generated many problems including the rise in greenhouse gases. Cement manufacture has been implicated in substantially contributing to these emissions. The effects of the increase of the world's population and the need to supply energy for its social, food and housing requirements demand higher cement production to make concrete [1]. For this reason, it has been necessary to work to reduce emissions from cement manufacture and many alternatives have been studied [2]. However, currently, the most popular approach has focused on the use of supplementary cementitious material (SCM) such as fly ash, slag, rice husk ash, and activated clays called pozzolans. Pozzolans have traditionally been defined as ‘‘a siliceous or

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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 room temperatures to form compounds possessing cementitious properties''. Additionally, activated clays have the advantage of being widely available across the world.

The way in which clays act as SCMs is based on their reaction with portlandite which is produced in a traditional hydration reaction between cement and amorphous phases of clay. The clays are activated using different kinds of treatments such as thermal activation. As a result of this reaction, mineral phases are generated and produce a relative increase in compressive strength [3].

These kinds of materials are usually found as a mix of different clay minerals with non-clay minerals, quartz being the most common. There are many studies on the use of clays as SCMs, but these behave differently depending on the location of the deposits [3-5]. Kaolin is one of the most studied clays and much information is available on its application as an SCM, however, in Colombia there are few kaolin deposits, similar to other parts of the world where it is more usual to find materials consisting of a mix of many different mineral clays as was explained above [3]. Studies of kaolin have made initial progress as to understanding these kinds of materials' behavior, and so many of the parameters used for other clays have been taken from kaolin assays that have shown good results. For example, the greatest compressive strength has been obtained with calcined kaolin at 750 °C, so this temperature is usually used when testing other minerals. However, when other clays have been studied, they have behaved differently, which indicates that a clay's behavior heavily depends on what type of clay it is, the soil formation, and its response in terms of reactivity [6]. The most common type of clay is made up of a mix of different minerals, which could be defined as multicomponent clays. These are found in Colombia, where the most common soils are made up of more than 50% silicon oxide and have an iron content of between 4 and 12%. These soils have many particularities. First, higher silicon oxide contents mean that it is likely that the soil will contain siliceous or siliceous and aluminous materials. Second, these levels of iron oxide content generate an undesirable red color that can show in the cement—which is usually gray—but this can be improved by changing the calcination process' atmosphere to mitigate iron oxidation, using diverse strategies such as coal use. These kinds of clays are usually found in tropical countries like Colombia, and so it is important to study their potential as SCMs.

Globally, teams of recognized researchers—including Tironi et al. [3] and Alujas et al. [5]—have studied low-grade clays and their thermal activation as a supplementary cement material. Both evaluated their pozzolanic activity. Tironi et al. [6] evaluated the potential pozzolanic activity of five Argentine caolinitic clays, calcined in a fixed bed furnace at temperatures of up to 700 ºC for 5 minutes, and then characterized using FTIR, ATG-ATD, SEM and DRX. Results yielded from samples were classified according to kaolin content—high Kaolin content (>50%), moderate content (30-50%) and poor (30%)—concluding that Metakaolin (MK) exhibits good pozzolanic activity, except the sample of MK from ordered kaolinite. In addition, Alujas et al. [5], after studying five low-grade clay deposits of different primary origin, determined that the pozzolanic reactivity of calcined clays depends on the content of potentially reactive material (directly related to the content of Al_2O_3 and SiO_2) and the degree of structural disorder achieved during thermal activation, although they found that clay minerals from the Kaolin group (Al_2O_3 * 39.50%, OH^- * 13.95%) have the highest pozzolanic reactivity, while 2:1 clay minerals (Al_2O_3 * 28.50%; OH^- * 5.00%) exhibit moderately high pozzolanic reactivity, which points to the association of reactivity with the Al_2O_3, SiO_2 and OH^- content in the structural clay samples. Clay samples with high pozzolanic reactivity, where Kaolinite is the dominant clay mineral, are grouped in 1:1, while the samples of this study are 2:1, in correspondence with their content of montmorillonite clays [5].

The aim of present study is to evaluate the potential of multicomponent clays with high silicon oxide content from Colombia as SCMs, and characterize their chemical and physical make-up. With this is mind, chemical, mineralogical, and thermal analyses were undertaken on activated clays using a thermal treatment and their response was measured in terms of compressive strength.

2. Materials and methods

2.1. Raw materials

128 samples of residual soils formed from metamorphic rock were taken according to macroscopic criteria and were characterized and evaluated as Pozzolans. The parental rock contained around 43.3% quartz of 0.1-0.6 mm in size, garnet (2.3%), tourmaline (1%), epidote (1%), 20.2% subhedral biotite and 10.4% muscovite crystals of 0.1-0.5 mm in size, microcline crystals (3.4%) and albite (12.1%), anhedrals and subhedrals of around 0.1-0.6 mm in size, with sericitation, argilization and other accessory minerals such as apatite (1%) and zircon (1%) (Figs. 1-3).

2.2 Characterization of materials

The physical, chemical and mineralogical characterization of 128 clay samples were carried out using

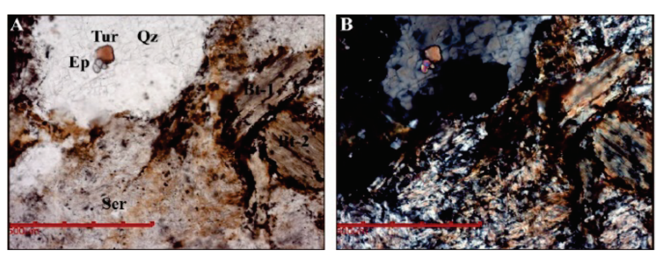

Figure 1. Biotite (Bt), epidote (Ep), quartz (Qz), sericite (Ser) and Tourmaline (Tur). A) NII - B) NX.
Source: The Authors.

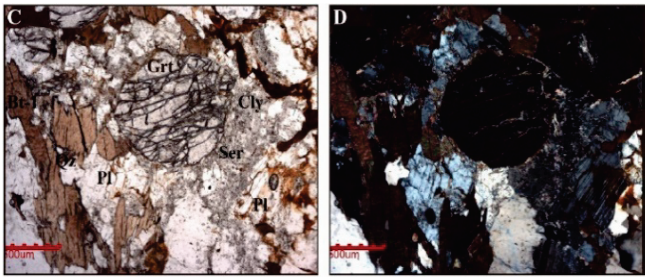

Figure 2. Plagioclase (Pl), clays (Cly), garnet (Grt). C) NII - D) NX.
Source: The Authors.

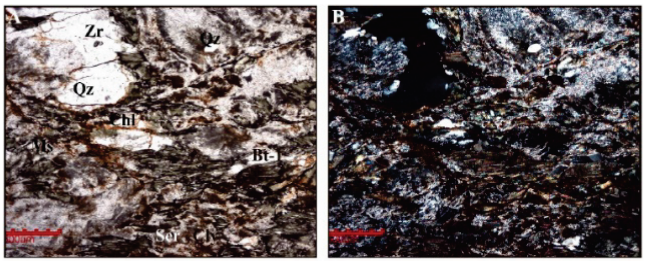

Figure 3. Interchange of Chlorite in Biotite. A) NII - B) NX.
Source: The Authors.

Table 1.
Mix of patrons for calibration curve preparation.

Standard	% Kaolinite	% Montmorillonite	% Mica
1	0	0	0
2	25	0.4	1.8
3	40	0.5	4
4	48	1	6
5	55	1.2	7.8
6	60	5	9
7	70	8	14
8	98	20	60

Source: The Authors.

density, specific surface area, X-ray fluorescence (XRF), X-ray diffraction (XRD), and thermogravimetry analysis TGA.

For the X-ray fluorescence studies, fused Pearl in Malvern Panalytical's Axios FAST was used. Diffraction analysis was carried out in an aCubiX3 range XRD from Malvern Panalytical, with an X'celerator detector and an X-ray tube anode made of copper at 6-70° (° 2theta), a step size of 0.015 (° 2Theta) and a step time of 0.5 sec. For the mineralogical analysis and quantification, a calibration curve using pure minerals of quartz, mica and kaolinite according to the reflections in plane ($00l$) was made in a mixture, and is shown in Table 1.

The thermogravimetric study was carried out in a TA instruments SDT series Q600, into which 30 mg of the sample was introduced, where it was heated to 900 °C at a rate of 10 °C/min in a nitrogen atmosphere.

Density was measured in Micromeritics' AccuPyc II 1340 Series helium pycnometer, with three measurements per sample. A Micromeritics Gemini V pore size analyzer was used to measure specific surface areas using the Brunauer-Emmett-Teller (BET) method with nitrogen.

2.3. Preparation of Pozzolans

To calcine the clays in this study, the common calcination temperature for kaolinite was used, and so clays were calcined at 750 °C for 30 minutes. Coal at 1.5 % was used, as previous essays have shown that this can reduce red coloration. Afterwards, the clays were milled until 10% was retained in a 325-sieve to simulate the size distribution of cement. The strength activity index (SAI) was used as a measurement of reactivity, and the ASTM C 311 method was employed. Finally, Frattini tests were carried out on the same mixes that were used for SAI, after 7 and then 28 days, following the UNE EN 196-5 standard [7], for the evaluation of the pozzolanic reactivity of the calcined clays.

3. Results and discussion

3.1 Characterization

The chemical composition of clays when crude and calcined is presented in Fig. 4.

The principal oxides were measured, and it was found that the silicon oxide in clays was around 60%, aluminum oxide 23% and iron oxide presented values of close to 10%. In the raw state, the loss of ignition was around 10%, and so these chemical compositions comply with the requirement for pozzolanic materials as stated in ASTC C618. When these values are compared with values found in the clay in its calcined state, there were no large differences in the variables' median values, except for loss of ignition, which was close to zero after calcination. The values of silicon oxide and aluminum oxide were similar to contents reported in other studies that tested materials as possible clinker replacements such as that of Rashwan et al., who found that metagrabbo was made up of 48% silicon oxide and 15% aluminum [8]. In another study, Avet et al. evaluated the amount of reacted metakaolin in different calcined clay blends [9].

The mineralogical composition of samples is shown in Fig. 5. Like the chemical analysis, mineralogical analysis, where possible, observes the effect of the elimination of volatile compounds on the concentration of minerals. The analysis principally looks at quartz content, but also reveals

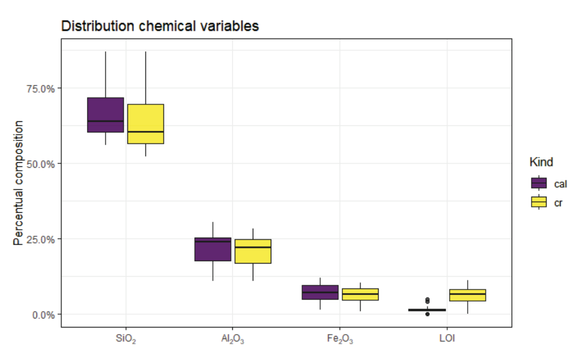

Figure 4. Chemical composition in oxides for raw (cr-yellow) and calcined (cal-purple) state clays with high silicon oxide content.
Source: The Authors.

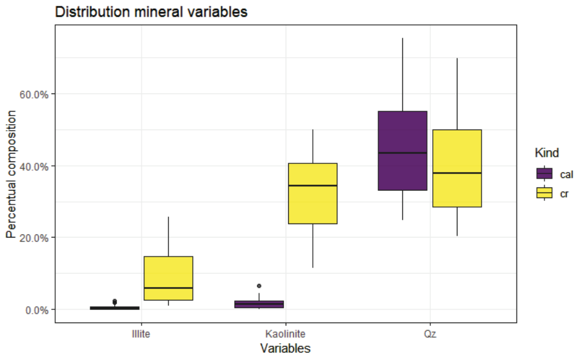

Figure 5. Composition of principal minerals for the evaluated raw (cr-yellow) and calcined clays (cal-purple).
Source: The Authors.

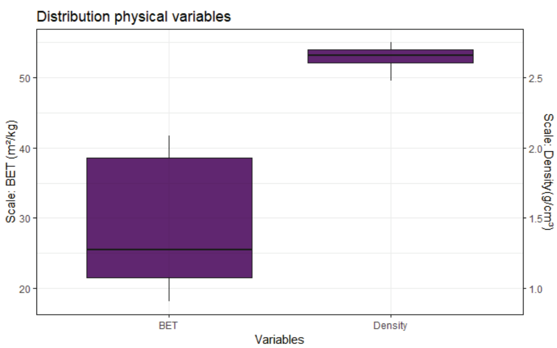

Figure 6. Density and Specific surface area (BET) for calcined clays with high silicon oxide content.
Source: The Authors.

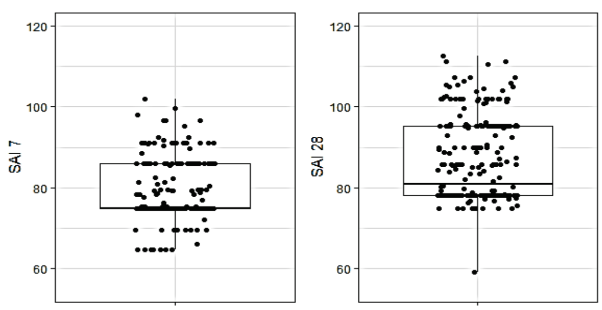

Figure 7. SAI values for calcined clays with high silicon oxide content at 7 and 28 days.
Source: The Authors.

that minerals such as kaolinite and illite tend to be reduced to zero after calcination. Kaolinite content in the samples was below 40% which is unusual in these kinds of studies because high kaolinite content has been associated with good pozzolanic activity [10-12]. For example, in studies such as that carried out by Castillo et al., clays with low kaolinite content were used for thermal activation and the kaolinite was decanted in order to increase its concentration [13]. However, this process is not relevant to the focus of this study. Other factors can also affect pozzolanic activity, such as the physical effects of specific surface areas and densities [14]. Thus, these variables were measured in the calcined clays and are shown in Fig. 6.

Density was measured to be around 2.7 g/cm^3 and specific surface area was around 26 m^2/kg, both values are similar to those found by Fernandez et al. in different kinds of clays such as montmorillonite, illite, and kaolinite [12].

SAI values are show in Fig. 7.

The strength activity index (SAI) used in the ASTM C 311 method indicates that values of SAI larger than 75% at 7 or 28 days indicate a pozzolanic material. In Fig. 7 it is possible to see that most of the SAI values obtained after 7 and 28 days of curing are greater than 75%, so it can be confirmed that almost all the samples evaluated behave like pozzolans. At 7 days, 75% of the samples exceed the limit, while at 28 days, 85% surpass it. The pozzolanic activity of these clays increases the longer the curing time, which can be clearly seen by comparing the number of samples that have a SAI greater than 100% at 7 and 28 days. Thus, it can be stated that it is possible to obtain materials with very good pozzolanicity (SAI greater than 100%) from clays from residual soils formed from paragneiss with kaolinite contents of below 40% or with a high silicon oxide content associated with a high quartz content.

The Frattini test is a chemical method, the results of which are shown in Fig. 8, and indicate that most of the data obtained at both 7 and 28 days for the clays calcined at 750 °C is located below the saturation curve (pozzolanic region). Due to this, the tests show pozzolanic reactivity to be positive. Additionally, the uncalcined clays (room temperature), both at 7 and 28 days, are above the saturation curve, and so the result is negative. This allows us to conclude that these clays develop pozzolanic properties only when calcined.

The test obtained two vectors which are shown in Fig. 8, and each implicitly retains a relationship with the calcination temperature. The vector obtained under natural conditions, that is, at room temperature, is above the Frattini saturation curve, from which it can be concluded that raw gneissic clay cannot be categorized as pozzolan under these conditions. However, when the other vector is studied, it can be seen that the consumption of [CaO] and [OH$^-$] tends to increase considerably, causing the vector to appear below the saturation curve, thus the vectors resulting from 750 °C conditions show that thermally activated gneissic clay can be determined to be pozzolan.

Hollanders et al. evaluated the pozzolanic activity of pure clays of kaolinitic, illite, and smectite and found that kaolinite clays presented the highest values for pozzolanic activity at a lower temperature than the two other types of clay evaluated and that are globally well known [15]. It is, however, interesting to note that the clays with poor kaolinite content or that were found to be mixed with other materials presented good SAI values. This was also evidenced by Yanguatin et al., who evaluated the pozzolanic activity of excavated waste clays, and found satisfactory results that indicated that the best pozzolanic activity was found in materials with high kaolinite content [16]. Uchima et al. obtained good results that showed pozzolanic activity in biomass and kaolinitic clay [17].

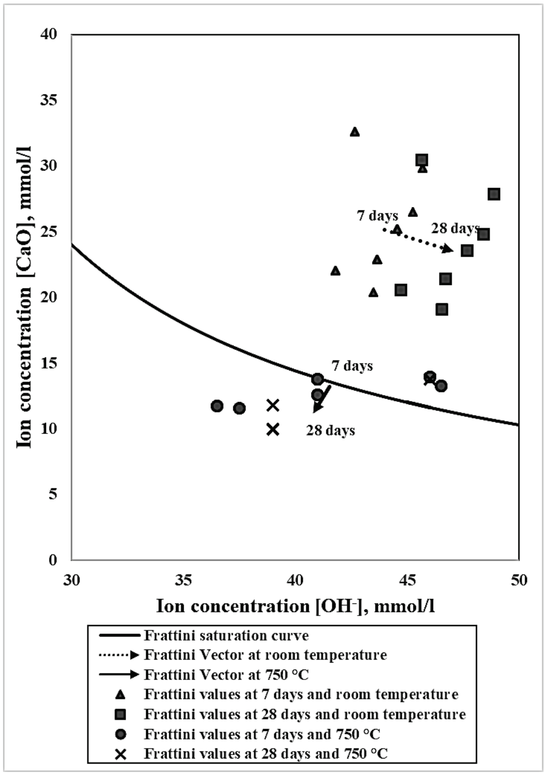

Figure 8. Frattini test results for cements with calcined clays, evaluated at 7 and 28 days at 750 °C.
Source: The Authors.

The present study could suggest that illite and kaolinite could have a synergic effect because a study carried out by Msinjili et al. that compared illite and kaolinite clays as supplementary cementitious materials concluded that all of these kinds of materials have pozzolanic activity but differ in the temperature at which they activate [18]. It is important to note that in this study, it was possible that the illite had a disordered structure—a normal characteristic of this mineral [19]—and so activated with kaolinite in the same temperature range.

On the other hand, when the correlations between SAI and the characterization variables were evaluated, it was found that the only characterization that had a relationship higher than 75% was kaolinite content. It is important to note, however, that although many researchers have studied the relationship between SAI and kaolinite [16,3,6,17], it was also relevant to the present study, although these kinds of materials showed low values of kaolinite and had a high quartz content, which could suggest that these kinds of materials' pozzolanic activity are related to the clay content more than the kaolinite content, which has been suggested by Msinjili et al., referring to the pozzolanic activity of illite clays [18].

4. Conclusions

Multicomponent clays with a high silicon oxide content are abundant in nature, however, silicon oxide is related to a high quartz content which is not reactive. So, although good pozzolanic reactivity has been associated with high kaolinite content, materials with a kaolinite content of below 40%—such as those evaluated in this study—showed good pozzolanic activity which was comparable to that found for pure kaolins. This pozzolanic effect could be related to the mineral clay content.

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