EVALUATION OF POZZOLANIC REACTIVITY OF CALCINED KAOLINITE

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Abstract

The need to improve the sustainability and the need for innovation in the cement industry has brought to light the practice of using additives to the cement in order to decrease CO_2 emissions in industrial plants and increase the quality of cement in terms of durability and performance. Currently some additives have been employed as granulated blast furnace slag, limestone and pozzolan. The additives give mortar and concrete larger energy efficiency, gain in durability and resistance, contributing to buildings with slender structures and cheaper and durable maintenance. Besides natural pozzolan can be used artificial ones, as calcined clays, and over a range of amorphous aluminates and silicates waste, with highly reactive function as a binder material in the presence of water and calcium hydroxide. Calcined kaolinite clays were characterized using various techniques such as XRD, thermal analysis, and NMR observing ^{27}Al and ^{29}Si nuclei. The results showed that there is a structural modification of the samples, from crystalline to amorphous phases with the increasing of temperature in the calcination process. There is an improving in the reactivity of calcined clays by the range of 600ºC to 750ºC temperature in the reaction with calcium oxide, according to data from Chapelle test, indicating the possibility of using them as additives for cement and confirming their pozzolanic potential.

Keywords: *kaolin, pozzolan, calcined clays, cement additive*

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1. INTRODUCTION

The current Portland cement industry is undergoing major changes. The questioning of their contribution to climate change and the environment has led to increasing demand for environmentally friendly and economical alternative for its production, using a based on three basic pillars: greater energy efficiency, additions to cement and alternative fuels. Also notable is the need to make the final product, where the mortar and concrete, more durable and more resistant, contributing to buildings with slender structures and cheaper maintenance and durable.

In Brazil for decades the cement industry has been using partial additions replacement for Portland cement. This can be considered a way to reduce their environmental liabilities. The additives can be found of several types available in the Brazilian market: CPII - E cement with the addition of granulated blast furnace slag; CPII - F that receives the addition of limestone filler; CPII-Z which receives the addition of pozzolan [1]; CPIII with higher addition of granulated blast furnace slag [2]; and CPIV with higher addition of pozzolan [3]. The CPII-Z cement uses partial adding 6%-14% of pozzolan material and CPIV uses 15%-50%, both replacing clinker. These calcined particulate materials, added in part to the clinker substitution, have predominantly amorphous microstructure [1], [2].

Besides natural pozzolana one can use artificial pozzolans, as calcined clays. Brazil is rich in kaolinite clays that can be used as pozzolans after calcination at the appropriate temperature [4], [5].

Pozzolanic chemical reactivity can be evaluated by Chapelle test [6], [7]. The NBR 15.985 standard [6], published in Brazil and the technique NF P18513 [7] published in French at same time follow, the general guidelines described by Raverdy *et al.* [8] with the basic difference that these two normative texts use pozzolan: calcium oxide (CaO) 1:2 ratio to perform the test and expresses the results in mg of calcium hydroxide ($Ca(OH)_2$) fixed per gram of the sample.

In this work calcined kaolinite clays were characterized by various techniques such as X-ray diffraction (XRD), thermal analysis, magic angle spinning nuclear magnetic resonance (MAS-NMR), Blaine technique, BET analysis, for observing structural changes during the calcination process, correlated to formation of their meta-stable forms, improving the assessment of kaolinite clays and its reactive potential. Data were also studied and correlation between structural changes and pozzolanic reaction were compared using dedicated characterization techniques as MAS-NMR and Chapelle test.
The results showed that there is a structural modification of the samples with the calcination process of the kaolinite clay. There is an increasing from crystalline to amorphous phases, with the increasing in the temperature of calcination. Data compared between metakaolinite formation correlate to pozzolanic reaction showed a changing in the reactivity to a maximum at 700ºC calcined sample and the possibility of using them as addictive to cement.

2. MATERIALS AND METHODS

Pozzolan material were obtained from sedimentary origin kaolinite clay with chemical composition determined by classical chemical analysis as follow: 51.77% SiO_2, 29.45% Al_2O_3; 2.22% Fe_2O_3; 2.87% K_2O; 1.38% TiO_2; Fire Loss 10.58% and other lesser extent. The material preparation occurred by manual grinding with a mortar until fully passing through sieve # 200mesh (65µm). The sample was calcined at various temperatures from 500°C, 550°C, 600°C, 650°C, 700°C, 750°C, 800°C and 850°C after two hours without heating ramp in a muffle furnace the material was cooled by forced ventilation to gain amorphousness.

X-ray diffraction was performed a Rigaku Windmax 1000 equipment, with 2° ramp, 1° slit. An acceleration voltage of 40 kV and a current of 20 mA were applied. The thermal analysis (TG / DTG / DTA) were performed using TA Instruments SDT 2960 equipment in an open alumina crucible, with Nitrogen 100mL/min purge, at a heating rate of 10°C/min. The ^{27}Al magic angle spinning (MAS) NMR spectra were obtained at the frequency of 156,38 MHz (14,1 Tesla) on a BRUKER Avance 600 spectrometer using 2.5mm probe with 25kHz spinning speed rotation, 5.5 µs 90° pulse, and 2 s repetition time. ^{29}Si MAS NMR spectra were obtained at the frequency of 79.49 MHz (9.4 Tesla) on a BRUKER 400 DSX spectrometer using 7mm probe with 6.5kHz spinning speed rotation, 3.1 µs 90° pulse, and 5-120 s repetition time. Blaine permeability was measured according to Brazilian standard NBR NM67 [10] and laser BET granulometric analysis [11] were performed on a Gemini V2.00 Micrometrics equipment on nitrogen atmosphere with 3s equilibration time and 711.945 mmHg sat. pressure. The pozzolanic reactivity analysis was performed with lime reaction according to the Chapelle test using 1:2 pozzolan-CaO ratio in 16 hours test at 90° C (± 5), with the result expressed as milligrams per gram of CaO fixed material.

3. RESULTS AND DISCUSSIONS

3.1 XRD Characterization

Figure 1 illustrates the XRD pattern of kaolinite and calcined kaolinite clays in different temperatures. The samples contain both crystalline (kaolinite, muscovite and quartz plus traces of potassium feldspar). The broad hump between 20 and 30° (at 2Θ values) indicates the presence of amorphous phases which increases with increasing calcination temperature, to a maximum at 700°C calcined sample.

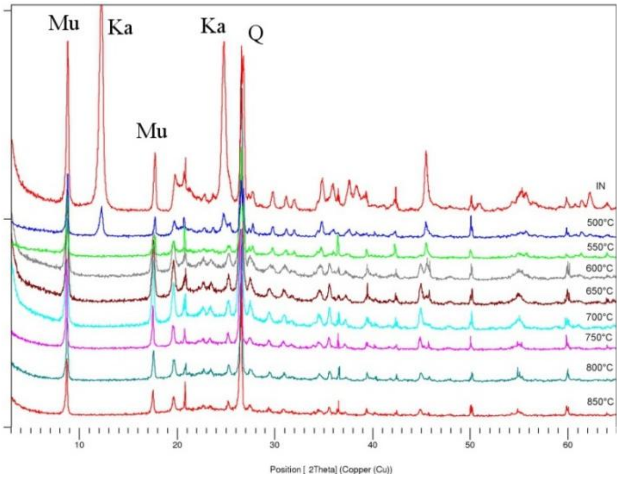

Fig. 1 - Overlapping diffraction patterns of fresh (IN) and raw material in various calcination temperatures. Highlight of major peaks: Mu = Muscovite, Ka = kaolinite and Q = quartz.

3.2 DTA Characterization

The DTA curves shown in Figure 2 shows an endothermic peak near 520ºC, due to the dehydroxylation of kaolinite in the natural sample and confirmed the presence of mineral compounds in the material [4], [9]. By 6.9% calculated hydroxyl group losses can be inferred that the kaolinite corresponds to approximately 50% in the sample. The dehydroxylation peak was also observed sample calcined at 500ºC. TG data showed that the material gain mass stability from 700°C calcined sample.

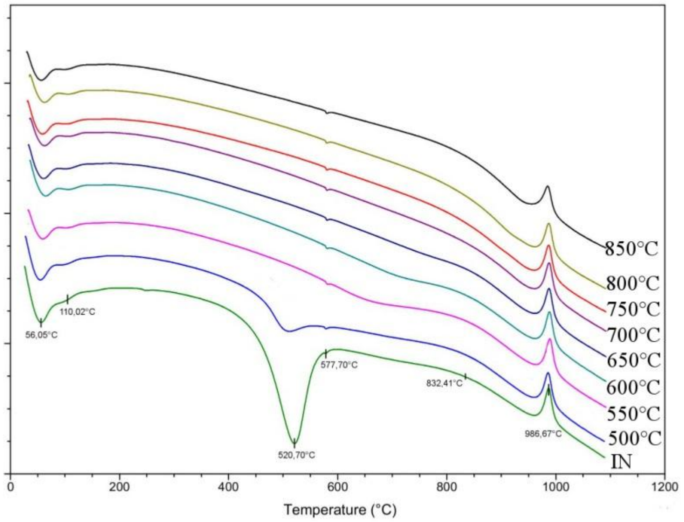

Fig. 2 - Differential thermal analysis curves at different temperatures of calcination.

3.3 Blaine, BET characterization

The particles of the kaolinite clay in nature, manually grounded, are largely formed by spheroids with small dimensions and high specific surface area of 19.530 cm^2/g as measured by Blaine method and the value of 166.200cm^2/g analyzed by BET as showed in Table 1. Both techniques showed that sample calcined at 550°C has a significant loss of surface area by agglomeration of particles. When analyzed by Blaine technique, sample calcined at 600°C showed the tendency of particles to stabilize in spheroid shape, however, the BET technique showed that these particles undergo changes in its internal structure by opening the layers and leaving more exposed surface for reactivity. It is important to observe that temperatures above 600°C are related to the early loss of oxygen bridges and disruption of the alumina layer by changing the coordination of aluminum.

At 650°C the specific surface area returns to the value of 162.000cm^2 indicating a reorganization of the internal structure of the particle which makes the area similar to that material calcined at 550°C. The tendency of gradual increase in specific surface area from temperature between 650°C and 750°C analyzed by the BET technique showed area gain by increasing the amount of amorphous keeping the size and shape of spheroid particles.

At 750°C calcination temperature the BET determination of surface area was slightly larger and the one measured by Blaine was slightly smaller than the calcination at 700°C, resulting in more particles agglutinated, and more amorphous.

Considering the results obtained from the two techniques, they indicate a reduction of surface area from clay calcined at 800°C, both the external and internal area of the spheroids sample.

Table 1 – Specific surface area of the samples.

Sample	Blaine Technique	BET Technique
in nature	19,550	166,200
550°C	17,701	161,100
600°C	17,160	175,000
650°C	17,020	161,800
700°C	17,170	165,200
750°C	16,850	171,100
800°C	16,360	170,700

3.4 Nuclear Magnetic Resonance

The ^{29}Si MAS-NMR spectra of kaolinite clay calcined in different temperatures are shown in Figure 3. Spectra showed a peak shift from 90ppm to 105ppm with the increasing of calcination temperature, which could be related to structural changes from high crystalline to high amorphous phases by increasing the number of Q_4(3Al) structure to Q_4(1Al) and Q_4(4Si). Sample calcined at 500ºC showed a peak at -91.5ppm due to kaolinite structure still present in the sample. This signal has less intensity from sample calcined 550ºC. Sample calcined at 800ºC and 850ºC showed peaks at -100ppm and -105ppm due probably to the formation of Q_4(1Al) e Q_4(0Al)(4Si) structure in the samples.

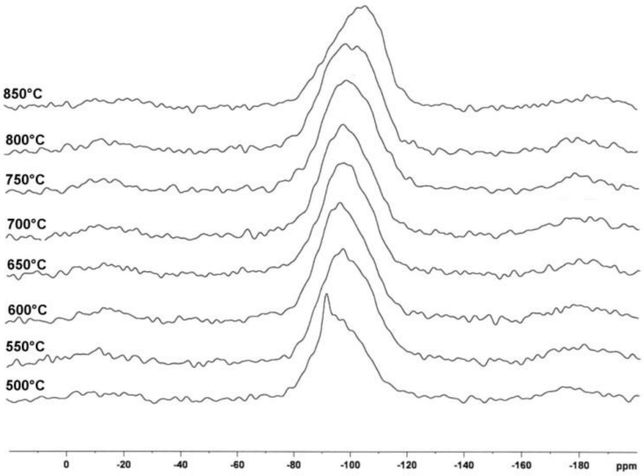

Fig. 3 - Evolution of the ^{29}Si MAS-NMR spectra in calcined samples at different temperatures.

Observing the ^{27}Al MAS NMR spectra showed in Figure 4 it can be observed a significant change in coordination of the Aluminum sites in the samples, according to the increasing of calcinations temperature. The sample calcined at 500ºC presents a sharp peak at approximately 0ppm, referred to the kaolinite phase still present in the clay. This peak is characteristic of octahedral Al (Al(VI)). When the kaolinite is calcined to higher temperatures the intensity of this peak decreases and two lines in approximately 30 and 60ppm increases indicating respectively an increase in aluminum-V (Al(V)) and aluminum-IV (Al(IV)) sites. Calcined samples at 700°C and 750°C showed the highest Al(V) peaks (slightly higher at 700° C) over Al(IV) and Al(VI).

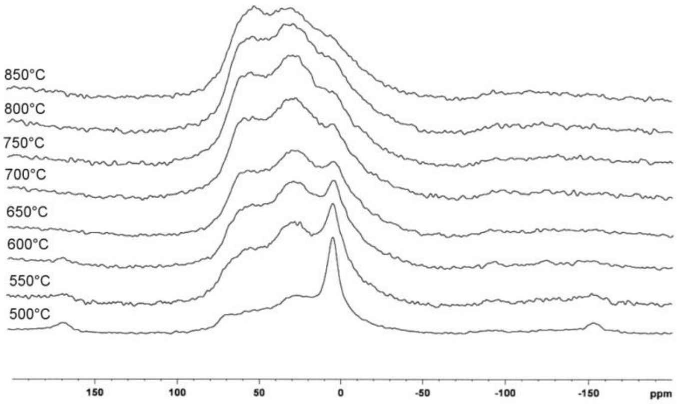

Fig. 4 – Evolution of the ^{27}Al MAS-NMR spectra of calcined samples in different temperatures.

The evolution of the transformation observed in the ^{27}Al and ^{29}Si MAS-NMR spectra suggests that silicates are freed from their connections sheet of alumina with increasing temperature to a maximum of 700°C, when it begins larger change in chemical shift in ^{29}Si spectra and a small decrease in the proportion Al(V), corresponding to structural modification of metakaolin back to promote higher condensed silicate network with less aluminum contained links between aluminates and silicates.

3.5 Chapelle test

The results of the tests performed with standard NBR 15895 [6] in the calcined samples showed a level of reactivity between 650°C and 750°C, with a tendency to peak at 700°C, as shown in Figure 5. It is possible to observe that there is a smooth trend pointing to 700°Cin the assay, like more reactive material.

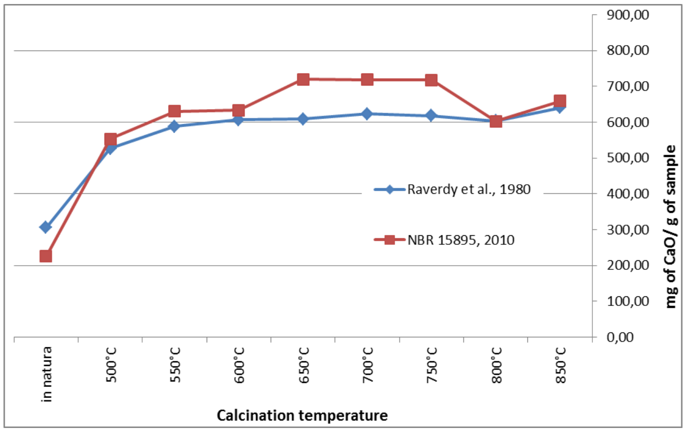

Fig. 5 - Results of the Chapelle test performed as Raverdy et al. [8] and NBR 15 985 [6].

In a preliminary study Sanz *et al.* [12] raised a suspicion of correspondence between reactivity observed and Al(V) sites in the samples. With the quantification of this Al(V) by integrating the peak areas it was observed that this species has a significant evolution from the calcination at 600°C and increases up to 43.7% of the total aluminum in the sample when calcination is carried out at 700°C, with a lightly decreasing for 750°C calcined sample. The sample to 800°C temperature suggests that this modification of the structure of the sheet silicates more sharply diminished reactivity of the change in the coordination of the aluminum

Figure 6 showed a direct and proportional correlation between the amounts of aluminum V obtained by ^{27}Al MAS-NMR spectra with pozzolanic reactivity of metakaolin obtained by Chapelle tests for each calcined sample. It was observed that the evolution calcination temperature of the kaolinite sample correspond to a proportionally larger amount of the reactive aluminum V sites. These data indicate a high correlation between the NMR techniques with Chapelle test.

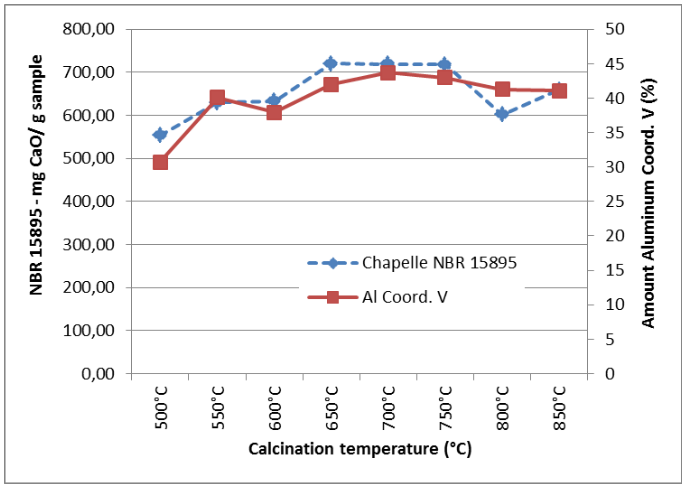

Fig. 6 – Correlation between pozzolanic reaction observed by Chapelle test and percentage of Al(V) obtained by ^{27}Al MAS-NMR experiment.

CONCLUSIONS

All correlated techniques showed that there is a level of pozzolanic reactions between the samples calcined at temperatures between 600°C and 750°C with a higher reactivity closely related to the specific area measured by Blaine method. In this range of temperature of calcination there is smaller coalescence of material as showed by Blaine specific area. The evolution in the calcination temperature produces larger particles, mainly in the range above 45μm, as characterized by laser particle size. The changes highlighted by technique BET / Blaine collaborate to better understand the behavior of particles, not only with respect to their specific area, but also with respect to the same format throughout the various calcination temperatures.

The pozzolanic reactivity measured by Chapelle test using pozzolan: CaO 1:2 ratio as described by the current NBR 15.985 was more appropriate than the 1:1 ratio originally proposed by Raverdy et al in 1980, and actual Chapelle tests showed the presence of a level of reactivity between the samples calcined at temperatures between 650°C and 750°C with the tendency of higher reactivity at 700°C.

^{29}Si and ^{27}Al MAS-NMR techniques of the calcined samples showed that there is a structural modification of the samples, from crystalline to amorphous phases with the increasing of temperature in the calcination process. Which means a change in silicon and aluminum coordination sites and this is related to the reactivity of the samples, as compared with Chapelle tests. The higher amount of Al(V) showed a higher reactivity of the calcined samples, with the release of the silicates sheet for reactivity.

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