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Viability of using calcined clays, from industrial by-products, as pozzolans of high reactivity

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Abstract

The present work studies the use of clays like high reactivity metakaolin, as pozzolans for concrete. This study adopted two clay types: kaolinite and kaolin by-products from the paper industry. In this second clay, besides the possible technical advantages, the ecological benefit of the use of a by-product must be considered. Initially, the chemical and mineralogical characteristics of the clays were determined. After this, calcination and milling was carried out aiming at obtaining materials with pozzolanic activity. After milling took place in the clays kaolinite and in the by-products, with the best physical characteristics, lab tests were carried out to verify the pozzolanic activity of these materials with Portland cement and with lime. The results show a low performance of the kaolinite and a high performance of the by-products industrial. The low performance of the kaolinite was credited to the lack of homogeneity of the calcination, as the material was obtained after the calcination, and the low efficiency of its milling process.

Keywords: High-reactivity metakaolin; Industrial by-products; Pozzolanic activity; Calcined clay

1. Introduction

Although the studies on metakaolin in concrete are recent, its use as pozzolanic material precedes the use of cement, as the calcination of kaolinite clays were the main source of this kind of material. Romans used a pozzolanic material derived from the grinding of clay tiles and bricks where tuff and volcanic ashes were not available [1].

In order to develop pozzolanic activity, the kaolinite clay needs to be submitted to a process of calcination under temperatures between 500 and 800 °C, and subsequent grinding, which aims at decreasing its particle size. When and the grinding process reduces the particle size to values below 5 μm, excellent pozzolanic activity can be obtained, and it is called high reactivity metakaolin (HRMK) by some authors. This pozzolanic activity allows this material to replace part of the cement in the concrete, to increase its durability and resistance.

However, the production of HRMK may present problems due to the thermal treatment and the grinding process, as this material usually has a wide range of values due to the nature and the particle size of the clay. As a function of this variability, factors relating to calcination, such as temperature and burning time, and factors relating to grinding, such as grinding time and mill type, become very important when aiming at warranting the pozzolanicity of the clays calcined at low temperatures. This study aims at investigating the pozzolanic behavior of two kaolinite clays.

2. Experimental program

2.1. Materials

Two types of kaolinite clays were used in this study. The first, type I, is used as pozzolan for the manufacturing of cement in a factory located in the state of Pará (Brazil). For

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this study, it was obtained after the calcination process and before grinding. The other type of clay, type II, is a by-product of paper manufacturing, which uses kaolin as raw material. Samples of this by-products were collected and prepared by the paper mill, using the following steps: collection of the by-products pulp in a collection tank; decanting of the solid material using a aluminum sulfate solution; pressing of the decanted solution in a hurdy-gurdy type press filter (after this step, the solid particles of the by-products acquire the shape of thick plates of 50 cm × 50 cm × 5 cm, with about 30% humidity); drying of the plates in an oven at 110 °C until their consistency was rigid; and, finally, manual desegregation of the plates in smaller sizes.

2.2. Chemical characterization of the clays

The chemical characteristics of the materials were obtained by X-ray fluorescence. Regarding the material physical properties, the particle main diameter was measured by laser granulometry, and the specific surface was evaluated using surface area analyzer. The specific gravity was determined employing the methodology described in NBR 6474 [12]. It must be noted that the lower value obtained in loss on ignition of the type I material is due to the fact that it had already been submitted to calcination. As to the ratio Al_2O_3/SiO_2 for the used materials, it is observed that the values are close to the theoretical value (0.85) for the unitary cell of kaolinite, showing the predominance of the clay mineral in the investigated materials [2]. The mean diameter and specific surface of the type I material were not obtained due to the wide variation in particle size, with particles as large as 5 cm diameter. The variation in particle size results from the agglomeration of the kaolinite clay during the calcination process. The obtained values are presented in Table 1.

2.3. Thermal treatment of the clays

As previously described, type I clay was obtained after the calcination process. Therefore, in this material, this step of the production of high reactivity metakaolin was suppressed. Fig. 1 shows the X-rays diffraction of type I material, where the predominance of a single type of mineral clay, kaolinite, is observed. The low intensity of the amorphicity halo demonstrates that it contains crystalline phases. This result, combined with the high residual loss on ignition observed in Table 1, may have been caused by the lack of homogeneity of the calcination process, which may impair its pozzolanic activity.

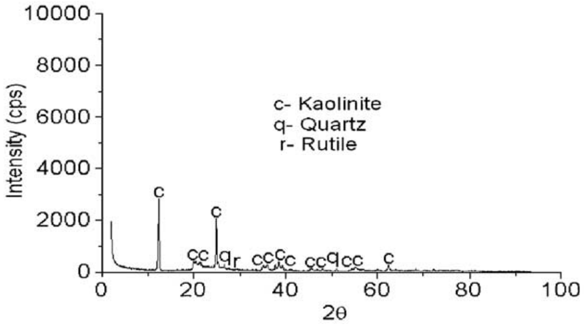

Fig. 1. X-rays diffractograms of kaolinite clay type I.

Table 1
Chemical and physical characteristics of materials

Characteristics		Clay type I	Clay type II
Chemical	Silicon dioxide (SiO_2)	46.00%	42.19%
	Aluminum oxide (Al_2O_3)	40.00%	39.24%
	Ferric oxide (Fe_2O_3)	1.30%	1.88%
	Calcium oxide (CaO)	0.77%	0.02%
	Sodium oxide (Na_2O)	0.13%	0.02%
	Magnesium oxide (MgO)	0.00%	0.20%
	Titanium oxide (TiO_2)	2.51%	1.49%
	Potassium oxide (K_2O)	0.00%	0.02%
	Phosphorus oxide (P_2O_5)	0.10%	0.21%
	Sulfur trioxide (SO_3)	0.02%	0.00%
	Loss on ignition	9.6%	14.80%
	Al_2O_3/SiO_2	0.87	0.93
Physical	Specific gravity	2.52 g/cm^3	2.40 g/cm^3
	Mean diameter	Not measured	1.85 μm
	Specific surface	Not measured	17.510 m^2/kg

As to type II material, as it was still in clods, it was first ground in a roll mill, aiming at turning it into powder in order to make the calcination process more homogenous. After grinding was completed, the material was calcined by thermal shock. Calcination temperature was 750 °C and the mass of the calcined material was approximately 0.23 kg. This calcination temperature was based on literature using the same by-products industrial [3].

Before calcination, a preliminary study, aiming at verifying the optimum time for this process for the quantity of material used, was carried out. Three calcination times were used (30, 45 and 60 min), and it was found, using X-ray diffraction, that 60 min provided the best results in terms of amorphicity of the material, as shown in Fig. 2. As expected, a lower value of residual loss on ignition of the calcined material was also obtained with a calcination time of 60 min. In all X-rays diffraction, the predominance of the mineral clay kaolinite was again observed.

In order to confirm the results of the calcination process, as well as to verify if the calcination time of 60 min caused the re-crystallization of the internal structure, thermogravimetry (TG) and differential thermal analysis (DTA) were performed. The results of these tests are shown in Fig. 3. The comparison between the results obtained before and after the calcination for 60 min shows that the peak of the endothermic reaction was virtually extinct, demonstrating again the efficacy of the calcination process, i.e., the change in the phase of the material. As to the peak of the exothermal reaction, it remained unchanged in both situations, demonstrating that, during the calcination process, the materials did not re-crystallize, which may have caused a decrease in their pozzolanic activity. The need to verify the exothermal peak is justified by the possibility that, according to COOK [13], re-crystallization may occur when

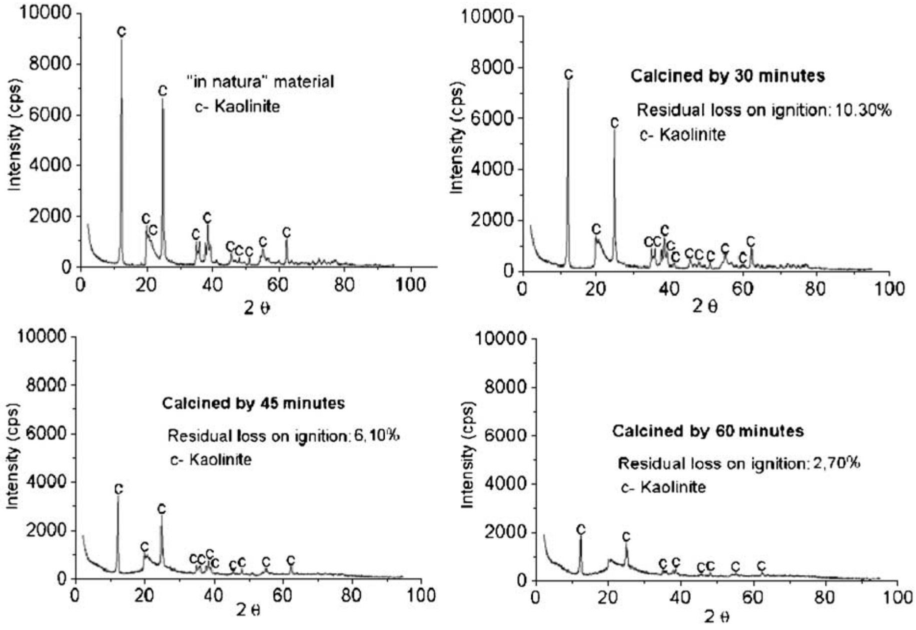

Fig. 2. X-rays diffractograms of kaolinite clay type II, after different times of calcination.

the clay is exposed to a high temperature for long periods, even if this temperature is below the clay re-crystallization point (970 °C). The results of the TG curve presented small variations regarding mass loss as compared to results of X-ray diffraction, referred to the "in natura" material and after 60 min of calcination, as shown in Figs. 2 and 3.

2.4. Grinding of the material resulting from calcination

This step aims at producing an average diameter of 3 μm. To measure the particle size, the same equipment (laser granulometer) was used for all carried out tests. According to literature [4–6], fine particle size is one difference between metakaolin and high reactivity metakaolin. In the case of type I clay, even after the determination of possible deficiencies in the calcination process, grinding was carried out at first by the use of vertical ball mills with different grinding times. However, none of these times resulted in particle sizes producing a highly reactive pozzolan.

Aiming at a better grinding efficiency, the pre-sieving of the material in a 4.8 mm mesh was used. However, this procedure did not produce the expected results, only a small improvement in the ground material as compared to the material obtained with no pre-sieving. Next, pre-sieving in a 2.4 mm mesh was attempted, but it also did not produce the expected results, despite showing a small improvement in the ground material as compared to the material obtained with the pre-sieving with the 4.8 mm mesh.

Aiming at solving the inefficiency of the grinding process, other types of mills, as well as a combination of mills, were used. In all grinding tests, the material resulting from pre-sieving with a 2.4 mm mesh was utilized. However, none of the mills produced the desired particle size.

As the expected range of particle sizes ($\phi_{50\%} \cong 3$ μm) was not obtained, the material that presented the best results after the grinding process was sieved in a 75 μm (n. 200) mesh, which allowed the verification of pozzolanic activity in the

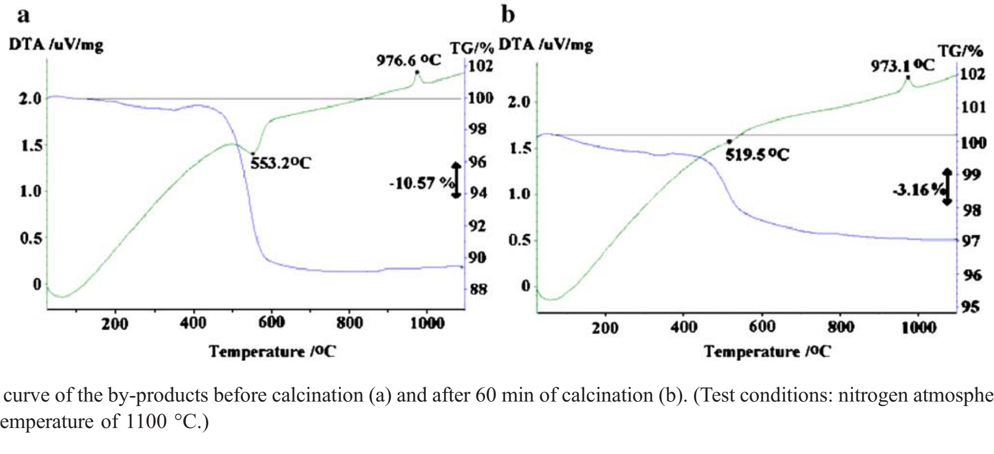

Fig. 3. TG and DTA curve of the by-products before calcination (a) and after 60 min of calcination (b). (Test conditions: nitrogen atmosphere, heating rate of 10 °C/min, maximum temperature of 1100 °C.)

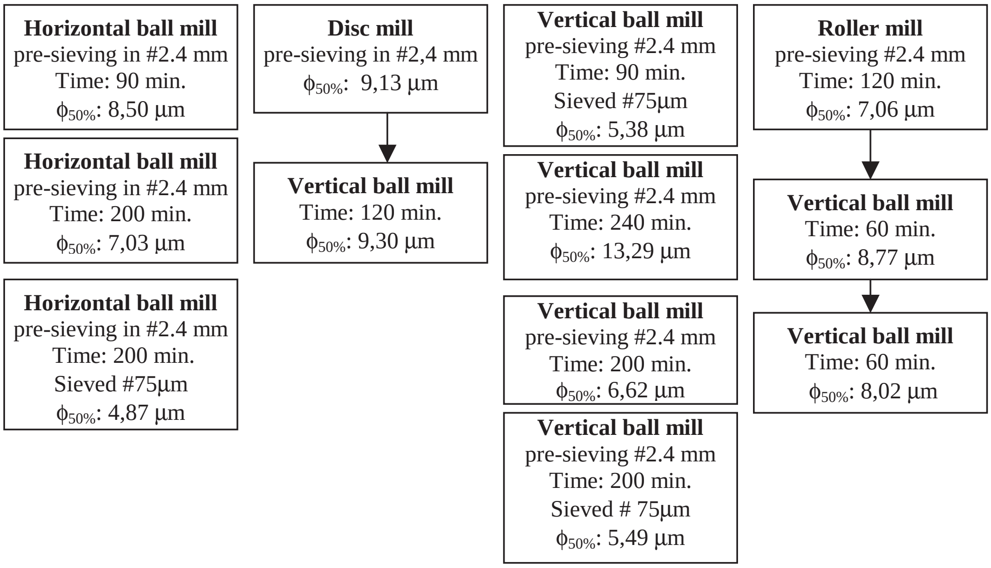

Fig. 4. Schematic illustration of the series of milling used for grinding.

tests with lime and with Portland cement. Fig. 4 shows a summary of the attempts to obtain the desired average particle size.

Each chart presents the type of mill, the mesh used in pre-sieving, grinding time, when the n. 200 mesh was used, and the mean diameter ($\phi_{50\%}$) obtained in the process. Due to the results obtained in this step with the type I clay, it was defined that the following process would be employed to prepare the material to be used in the pozzolanic activity tests: pre-sieving in a 2.4 mm mesh, grinding in a vertical ball mill for 200 min and sieving in a n. 200 mesh. This choice was not based exclusively on the material smaller mean diameter (549 μm), but also on the better distribution of grains, obtained from the particle size curve.

Besides the grindings presented in Fig. 4, other attempts, including changing grinding time, were made, but they also did not produce the expected results. Interestingly, during all grinding processes, a poor particle size distribution was observed in the resulting material, and this was reflected in the particle size curve. This suggests that, even though the material seemed to be easily ground, the failure to obtain the expected results may be due to the fact that the mills were not suitable for the material. In Fig. 4, the arrows indicate the grinding sequence. Surprisingly, it should be noted, from this figure, that after the roller mill grinding for 120 min, the mean diameter observed was 706 um, and after the material is ground for 60 min, in the vertical ball mill, the measured mean diameter increased to 877 um. These results possibly indicate lack of homogeneity of the process.

As expected, there was an agglomeration of the particles of the type II clay after calcination, resulting in a mean diameter ($\phi_{50\%}$) of 9 μm. Therefore, it needed to be ground to obtain a mean diameter of $\phi_{50\%} \cong 3$ μm. The grinding process started while the material was still hot, i.e., immediately after the calcination process. The material was ground in a vertical ball mill for 60 min. The decision to grind the material immediately after calcination aimed at a better efficiency of the process due to the lack of humidity in the material resulting from calcination. This grinding was not sufficient as it resulted in a $\phi_{50\%}=496$ μm, indicating

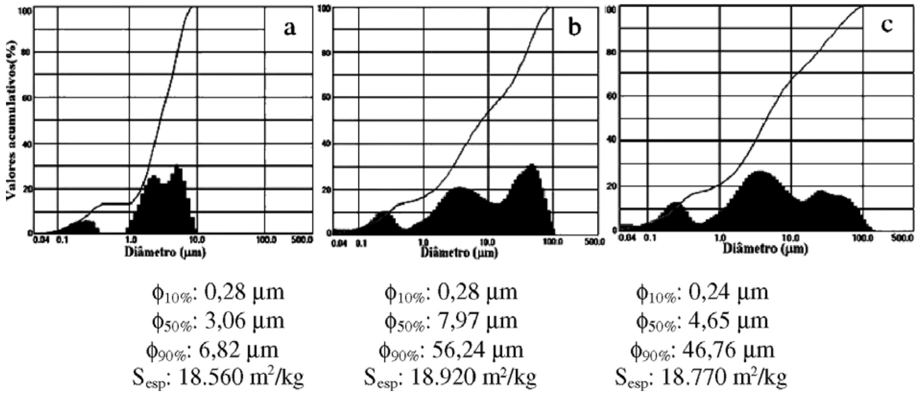

Fig. 5. Particle size distribution curves, mean diameter and specific surface obtained in the study aiming at defining extra grinding time. a) 90 min grinding: 60 min initial time plus 30 min extra time. b) 120 min grinding: 60 min initial time plus 60 min extra time. c) 180 min grinding: 60 min initial time plus 120 min extra time.

Table 2
Comparison of chemical and physical characteristics of the produced material, with the regulatory requirements

Properties	IS 1344 [7]	ASTM C 618 [8]	NBR 12653 [9]	Clay type I	Clay type II
$SiO_2+AL_2O_3+Fe_2O_3$	70% (min.)	70% (min.)	70% (min.)	87.3%	91.56%
SiO_2	40% (min.)	–	–	46.0%	45.80%
Mean diameter	–	–	–	5.49 μm	4.65 μm
Diameter>45 μm	12% (max.)	34% (max.)	34% (max.)	2.00%	10.59%
Specific surface (m^2/kg)	320 (min.)	–	–	–	18.770
Loss on ignition	5% (max.)	10% (max.)	10% (max.)	9.6%	2.7[a]

[a] Residual loss on ignition.

the need of another study to define extra grinding time in order to obtain the desired particle size. This study involved three different grinding times (30, 60, and 120 min). Before grinding, the material was dried in an oven at 100 °C to increase the efficiency of the grinding process.

In this study, a very irregular behavior was observed in the results, showing, similarly as to type I clay grinding, a great heterogeneity of particles of the ground material. This situation is presented in Fig. 5, which shows the particle size curve, the mean diameter and the specific surface for the three grinding times.

Due to this behavior, an extra grinding time of 120 min was used. This decision was based on the better distribution of particle size in this material, which should promote better packing as minor variations were found among the grinding times, and no conclusive results were obtained as to mean diameter ($\phi_{50\%}$) and specific surface (S_{esp}). With the utilization of the 120-min extra grinding time, the total grinding time reached 180 min. It must be noted that both in the first and in the second grinding, the variables load/material ratio = 5, mill rotation = 43 rpm, and load size (ball diameter) remained constant.

At the end of the process of pozzolan production, a comparison of the values obtained with type I and type II clays referring to physical and chemical characteristics, with the requirements of the American, Indian and Brazilian standards, is shown in Table 2.

2.5. Pozzolanic activity of the resulting material

These tests employed NBR 5751[1] [10] and NBR 5752[2] [11] for pozzolanic activity with lime and Portland cement, respectively. Table 3 presents a comparison of the results obtained using the NBR 12653 [9] requirements. The low pozzolanic activity of the Type I clay may be due to the lack of homogenization during the calcination process, which did not produce total amorphization of the material, and to the low grinding efficiency, as seen above. On the other hand, the material resulting from type II clay produced excellent pozzolanic activity values. Another factor which may have influenced the lower performance of the type I clay, as compared to the type II clay, is the higher content of reactive chemical compounds present in the latter, such as SiO_2, Al_2O_3 and Fe_2O_3.

Despite the excellent results of the pozzolanicity tests obtained for type II clay, the amount of water required for the mortar was 23% higher than the reference mortar, higher than the maximum value required by NBR 12653 [9] for the use of calcined clays. These results must be attributed to the high fineness of the material, requiring more water to obtain the mortar consistency defined by the regulation (225 ± 5 mm). The excessive need of water clearly made the results worse. Therefore, type II clay was submitted to another pozzolanic activity test using a superplasticizer additive instead of water in order to obtain the same consistency of the reference mortar. In this tests a 200% content of superplasticizer was employed. This resulted in a pozzolanic activity of 140.71% at 28 days, showing again the high pozzolanicity of this material, and also ratifies the need to use plasticizer and superplasticizer additives with this pozzolan in order to obtain better performance.

3. Final considerations

The results obtained in this study show the feasibility of obtaining high reactivity pozzolans derived from kaolinite clays, if the parameters related to their chemical composition, and to their calcination and grinding processes are taken into account. The use of the pozzolan derived from by-products industrial promoted an increase of 40% in the mechanical resistance of the mortar produced with the replacement of 35% of the cement by this high reactivity metakaolin as compared to the reference mortar. Both mortars had the same water/(cement + HRMK) ratio. These results clearly show the potential of this material to obtain high strength concrete with lower cement use.

This type of pozzolan, when derived from paper manufacturing by-products, besides its technical characteristics, also has the advantage of being another option to utilize a material that causes great environmental impact.

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[1] The pozzolanic activity with lime is evaluated through a compressive test of a mortar sample (made with sand, lime and metakaolin). If the sample compressive strength is above 6 MPa (value prescribed in NBR 12653 [9]), pozzolanic activity is confirmed.

[2] The pozzolanic activity with Portland cement is evaluated comparing the compressive strength of two samples: one consisting of a standard mix of cement and sand, and the other, having a 35% substitution of cement by pozzolan.

Table 3
Pozzolanic activity results

Materials	Test	Standard	Age (days)	Water-to-cement ratio	Results	Standard requirement NBR 12653 [9]
Clay type I	Pozzolanic activity with lime	NBR 5751 [10]	7	0.72	8.30 MPa	≥6.00 MPa
	Pozzolanic activity with Portland cement	NBR 5752 [11]	28	0.59	74.00%	≥75.00%
Clay type II	Pozzolanic activity with lime	NBR 5751 [10]	7	0.84	16.00 MPa	≥6.00 MPa
	Pozzolanic activity with Portland cement	NBR 5752 [11]	28	0.74	94.15%	≥75.00%

However, it is important to emphasize that new tests will be carried out in order to verify the performance of metakaolin regarding durability issues.

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