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Physical-chemical, mineralogical and technological characterization of clays of Caxias/MA

Caracterização físico-química, mineralógica e tecnológica de argilas de Caxias/MA

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Resumo
Este trabalho visa caracterizar uma mistura de argilas utilizadas na fabricação de tijolos na região de Caxias/MA. Foram realizadas ensaios de composição química, difração de raios X, análise térmica (TG/DTG), análise granulométrica e plasticidade. Além disso, foram determinadas propriedades tecnológicas tais como absorção de água, porosidade aparente, densidade aparente e resistência à flexão. Corpos de prova (15x2,5x1,5 cm) foram moldadas por extrusão e queimadas a três temperaturas, 800, 900 e 1000°C. Em termos de mineralogia, as amostras são argilas caulinitícas e ilíticas. Os resultados mostraram que a formulação estudada é adequada para a aplicação em alvenaria de vedação. Assim, as amostras de argila têm potencial para várias aplicações (tijolos, telhas, entre outras) como matéria-prima para a indústria da cerâmica vermelha no estado do Maranhão.
Palavras-chave: Argila. Tijolo cerâmico. Cerâmica vermelha.

Abstract
This paper aims to characterize a mixture of clays used in the manufacture of bricks in the region of Caxias/MA. Chemical composition, X-ray diffraction, thermal analysis (TG/DTG), granulometric analysis and plasticity were performed. In addition, technological properties such as water absorption, apparent porosity, bulk density and flexural strength were determined. The specimens (15x2.5x1.5 cm) were shaped by extrusion and fired at three temperatures, 800, 900 and 1000°C. In terms of mineralogy, the samples are kaolinitic and illitic clays. The results showed that the formulation studied is suitable for the manufacture of masonry bricks. Hence, the clay samples have potential for several applications (bricks, tiles, among others) as raw material for the red ceramic industry in the state of Maranhão.
Keywords: Clay. Clay brick. Red ceramics.

1. Introduction

The main component of the structural ceramic mixture is clay. This raw material is easily found in nature, very abundant, with low extraction and processing costs. It is highly versatile in industrial applications, besides being, historically, the primary raw material used in the red ceramic industry (Acevedo et al., 2017; Ramos et al., 2019).

The clay deposits for red ceramics are distributed all over the state of Maranhão, but there is a concentration in the north-central portion of the state that coincides with the flood plains of the large rivers, such as Munim, Mearim and Itapecuru, which constitute the main source of clays (Bandeira, 2013).

The main production centers in the context of Maranhão are located in the cities of Itapecuru Mirim, Timon, Caxias, and Imperatriz (Mello et al., 2011). The city of Caxias is rich in clay mineral occurrences and has a high potential to be prominent in the production and supply of materials derived from this raw material for the local construction industry (Bandeira, 2013; Rocha et al., 2016).

The productive sector of the region is handmade, consisting of small to medium size companies (potteries). Some companies are investing in equipment such as kilns, extruder, and material transport systems using rails inside the facilities, as well as automatic drying systems, all this to improve production and the quality of the manufactured products (Sachs, 2017).

Mercury et al. (2012) characterized clays from São Luís (ASL), Rosário (ARO), Pinheiro (AP) and Mirinzal (AM). The results of mineralogical and chemical analyses show that the AM and AP clays are kaolinitic clays mixed with quartz and feldspar. In addition, the ARO and ASL clays are mixtures of kaolinite, quartz, feldspar, and illite.

Some special clays are found in the state. Rezende (1997) studied the occurrence of smectite/bentonite clays in the Parnaíba Basin. This mineral has a high cation exchange capacity and can be used in iron and manganese metallurgy as a binder in molding sands for foundry and the ceramic industry. Rodrigues et al. (2014) report the occurrence of a new palygorskite clay in the region of the city of Alcântara/MA. Paz et al. (2011) report the occurrence of new bentonite clay in the city of Formosa da Serra Negra, southern Maranhão, on the margins of the MA/006 highway, whose predominant mineral phase is montmorillonite.

Several clay deposits in the northeastern region have been characterized. Kaolinite and smectite clays from the Cariri region were studied. The study by Pinto et al. (2021) showed that the clay sample is suitable for application in roof tiles and hollow bricks. Almeida et al. (2020) demonstrated the potential deposits of kaolinite clays from the central region of Piauí (Oeiras/PI) for application in the local ceramic industry.

The knowledge of the characteristics of the raw materials contributes directly to the improvement of the properties of the final product and provides flexibility, reduction of production costs, and an increase in the product's added value (Silva et al., 2018). In this context, the objective of this paper is to characterize the physical-chemical, mineralogical, and technological properties of two clays from the city of Caxias/MA.

2. Methodology

The clay samples analyzed were from occurrences in the city of Caxias (4°52'45.6"S 43°22'44.6"W) located in the state of Maranhão, the northeastern region of Brazil, Figure 1. The clays collected were dried in an oven at 105°C for 24 h. Subsequently, they were submitted to the beneficiation process by grinding in hammer mills. After milling, the clays were passed through an ABNT sieve n° 200 (0.074 mm) and then were submitted to physical, chemical, and mineralogical characterizations.

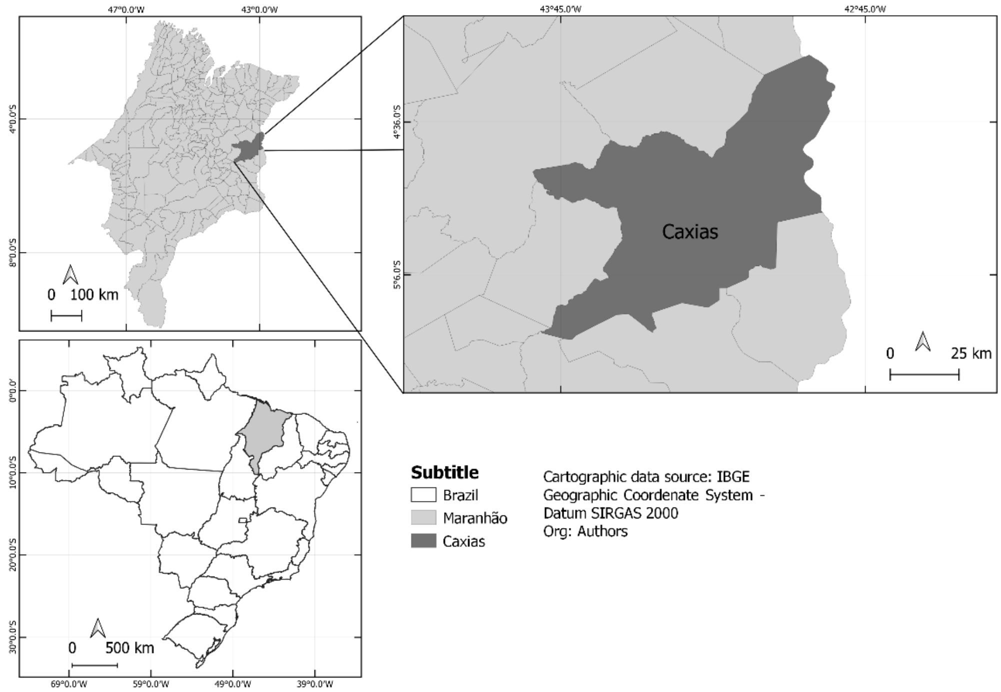

Figure 1 – Location map of Caxias, Maranhão, Brazil.

The samples of two clays, Figure 2, to make the specimens were collected in a ceramic industry in the city of Caxias/MA. A reddish clay (Clay A), and another yellowish-gray (Clay B). For the preparation of the specimens, the primary samples, after being collected, were dried in a laboratory oven at 105 °C for 24 hours. Afterwards, they were submitted to manual reduction of granulation in a 20 mesh (0,84 mm) ABNT sieve. The humidified mass with 20% water was stored in a sealed plastic container for 24 hours.

Figure 2 – Clays collected before and after processing.

The mixture studied is detailed in Table 1. The clays are in a 1:1 ratio because this is the formulation used in everyday working in the ceramic industry where they were collected. Therefore, this formulation will be the subject of study in F1. The specimens (15x2,5x1,5 cm) were shaped by extrusion and fired at three temperatures, 800, 900 and 1000°C, at a heating rate of 1,6°C/min. Each specimen weighed between 150 and 160g. Technological properties such as linear shrinkage, water absorption, apparent porosity, bulk densi-ty and flexural strength were determined.

Table 1 - Proportion of the mixture.

Formulation	Clay A	Clay B
F1	50%	50%

The particle size distribution of the raw materials was measured according to ABNT NBR 7181/2016 (Soil - Particle size analysis) (ABNT, 2016b). Plasticity was determined according to ABNT standards NBR 7180/2016 (Soil-Plasticity limit determination)(ABNT, 2016a) and NBR 6459/2016 (Soil - Liquid limit determination) (ABNT, 2017b).

The chemical composition of the clays was determined by X-ray Fluorescence Spectroscopy (XFR) through the equipment allocated in the materials laboratory of PPGEM/IFPI, model Epsilon3-XL from Panalytical. To identify the crystalline phases of the raw materials, the samples were submitted to X-ray diffraction (XRD) in the SHIMADZU equipment, model XRD-6000, available at the Technology Center of the Federal University of Piauí/UFPI. The voltage used was 40kV/30mA and 2θ range of 5°-75° with scanning step of 0,02°. To quantify crystalline phases the program "QuantFases", developed at IFPI, was used (Silva, 2015). For thermal analysis, a thermogravimetric analyzer model SHIMADZU TGA-51H was used.

3. Results and discussion

In Figure 3, it is possible to identify that the clays present well distributed grain size. This wide distribution composed of fine, medium, and coarse grains is necessary to achieve a better grain packing factor (Netto, 2019). Both clays have a high fines content as more than 40% of the material has a particle size of less than 0,1 mm. The finer particle size, constituents of the clay fraction, can provide greater reactivity between the particles in the firing stage due to the fact that these particles have high specific surfaces (Dondi et al., 2014; Santos, 1989).

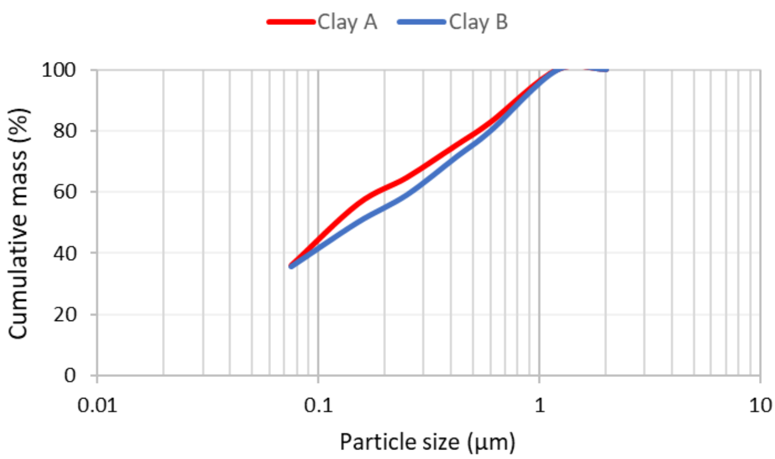

Figure 3 – Particle size distributions of clay samples.

The plasticity is a vitally important property in ceramic processing where clay has the role of agglomerating the non-plastic materials such as quartz, micas, feldspars (Netto, 2019). Table 2 presents data of liquid limit (LL), plasticity limit (LP) and plasticity index (IP) of raw materials and formulations. IP values above 10% are within an acceptable range for the production of bricks and tiles (Dondi, 2006). Caputo (2017) classifies soils into weakly plastic (IP≤7), medium plastic (7<IP<15), and highly plastic (IP≥15). Clay B showed lower plasticity than clay A, which can be attributed to the higher SiO_2 content (Silva et al., 2017).

Table 2 - Chemical composition of clays (% by weight).

Sample	LL (%)	LP (%)	IP (%)	Classification
Clay A	38.05	22.01	16.04	Highly plastic
Clay B	25.97	16.23	9.75	Medium plastic

Table 3 presents the results of the chemical characterization of the raw materials. The analysis indicates that the clays are mostly composed of SiO_2 and Al_2O_3, together they correspond to 83.27% and 89.94% of the mass of clay A and B, respectively. SiO_2 is the preponderant element in the constitution of clays and is found as quartz grains (Muñoz et al., 2016). In addition, it favors workability, decreases drying time and drying/firing shrinkage (Nicolite, 2017).

Table 3 - Chemical composition of clays (% by weight).

Raw material	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	MgO	MnO	LoI
Clay A	65.65	17.62	7.60	0.65	5.26	1.34	1.27	0.09	7.58
Clay B	72.04	17.90	3.65	-	3.85	1.29	0.67	0.50	6.91

The second most common component in clays is Al_2O_3, which during the firing process, reacts and forms mullite, and this structure is of great importance to promote an increase in chemical and mechanical strengths (Muñoz et al., 2016). The high iron oxide (Fe_2O_3) content of Clay A explains its reddish color, generally this occurs from values above 4% of this oxide (Dondi et al., 2014).

The presence of fluxing oxides such as CaO, MgO, K_2O and Fe_2O_3 contributes to the firing stage by promoting the formation of liquid phase necessary for particle consolidation, decreasing porosity and increasing linear firing shrinkage (Almeida et al., 2020; Cipriano & Ferraz, 2019; Racanelli et al., 2020). The high K_2O content of the clays under study favors densification and provides mechanical strength to red ceramics (Nicolite, 2017; Silva et al., 2018). The loss on ignition (LoI) of clays is due to the elimination of water from the clay minerals, followed by the dehydration of hydroxides and oxidation of organic matter (Racanelli et al., 2020).

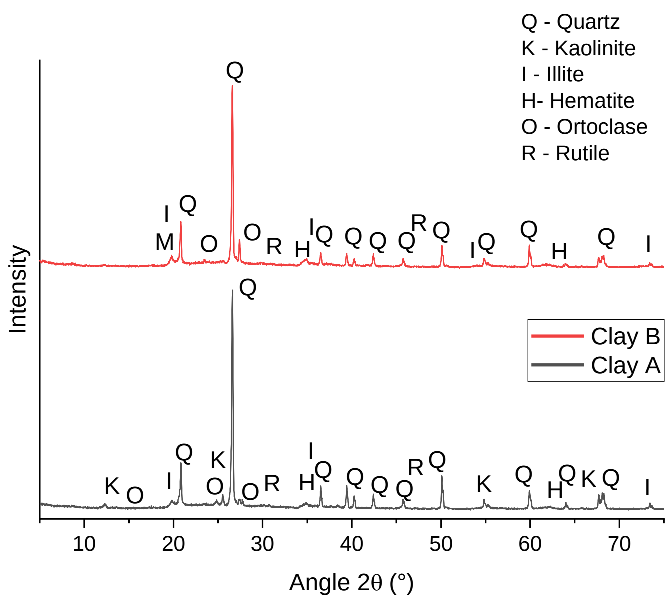

Figure 4 – X-ray diffraction pattern of the clays.

The x-ray diffractograms of the clay samples are illustrated in Figure 4. The samples presented the following crystalline phases: quartz (SiO_2), kaolinite ($Al_2(Si_2O_5)(OH)_4$), illite ($KAl_2Si_3AlO_{10}OH_2$) orthoclase ($KAlSi_3O_8$), hematite (Fe_2O_3) and rutile (TiO_2). The kaolinite is an important component of a ceramic mass, because it helps in the conformation improving the workability of the masses (Silva et al., 2018). The quartz present in the clay is a component that acts as a non-plastic and inert raw material during the firing process (Racanelli et al., 2020). Orthoclase is the main raw material used as flux and provides great benefits to the ceramic mixture (Almeida et al., 2020). Therefore, the mineralogical analysis is in agreement with the chemical analysis.

Table 4 - Quantitative mineral analysis using the software QuantFases.

Raw material	Quartz	Kaolinite	Illite	Hematite	Orthoclase	Rutile	Others	Quartz
Clay A	37.08	6.06	36.25	7.60	11.47	1.34	0.20	37.08
Clay B	47.53	-	46.29	3.40	-	1.04	1.74	47.53

Table 4 shows the quantitative analysis of the crystalline phases was done using software developed at IFPI, QuantFases (Silva, 2015). Figure 5 and 6 shows the TG/DTG curves of the raw materials. In both clays, the derivative peaks (in red) around 100°C are a result of free water leaving. The second peak around 550°C is the result of molecular water leaving (dehydroxylation), in other words, the OH- ions present in the crystal structure of kaolinite begin to be eliminated in the form of water vapor (OH- + OH- → H2O + O2-) (Emmerich & Steudel, 2016; Netto, 2019).

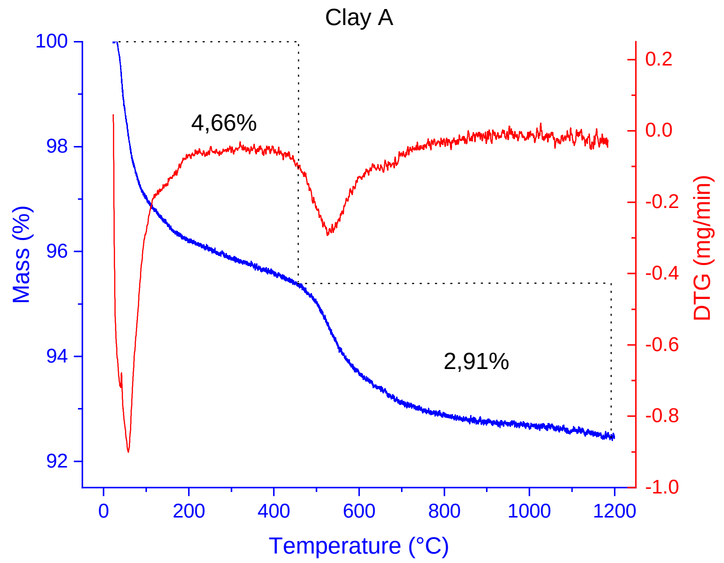

Figure 5 – TG/DTG results of clay A.

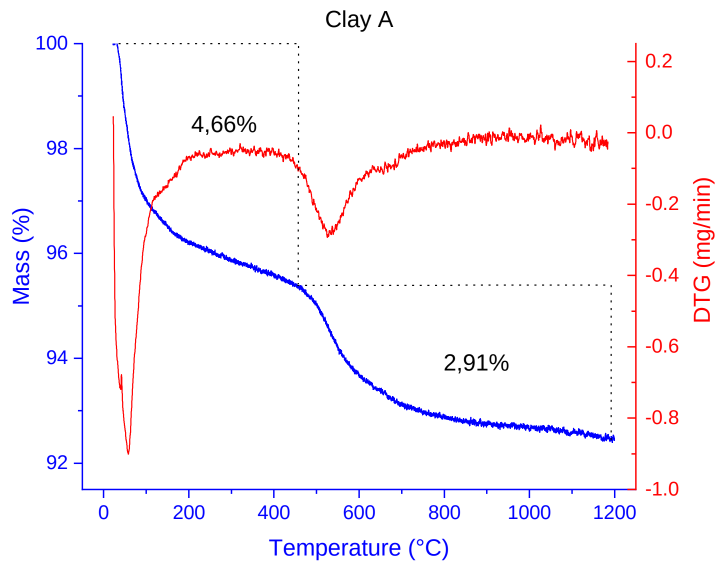

Figure 6 – TG/DTG results of clay B.

Water absorption is the property that reveals the amount of water that a ceramic piece can absorb in contact with moisture (Netto, 2019). The values ranged from 12.31% to 16.97%, Figure 7. Therefore, all values are below the maximum limits for making bricks (22%) and tiles (20%), and above the minimum of 8% (ABNT, 2017a). A correlation between the values is perceptible, whose coefficient of determination (R^2) is 0.99. Therefore, it is an inversely proportional relationship. In other words, the lower the water absorption, the higher the flexural strength.

Santos (1989) recommends the following parameters for flexural strength: at least 6.5 MPa for the manufacture of tiles; 5.5 MPa for hollow bricks and, at least 2 MPa for masonry bricks (without structural function). Hence, the manufacture of masonry bricks is possible at all temperatures. From 900°C, it is possible to manufacture hollow bricks, and at 1000°C, there is a minimum resistance for the manufacture of ceramic tiles.

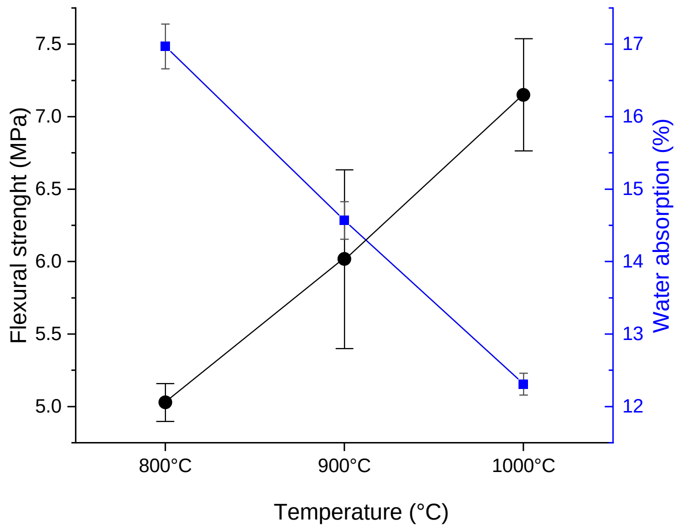

Figure 7 – Flexural strenght versus water absorption.

The apparent porosity determines the amount of open pores in the specimens and is closely linked to water absorption (Gencel et al., 2020). This technological property showed analogous behavior to that of water absorption. The values ranged between 21.05% and 25.92%, Figure 8. The bulk density is a property that is directly related to the physical-mechanical properties of bricks. In addition, the sharp increase in specific mass is noticeable between 800 and 900°C. The increase in sintering temperature provides a better packing of the particles, which contributes to the closing of the pores. This effect favors the densification of the specimen (Racanelli et al., 2020). A correlation between the values is perceptible, whose R^2 coefficient is 0.76.

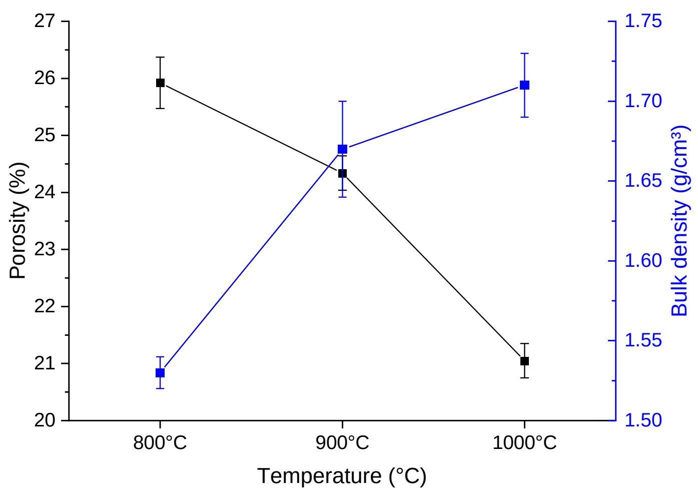

Figure 8 – Porosity versus bulk density.

Figure 9 shows the macro-structural analysis, which is necessary to determine the possible visible cracks and fissures and to analyze the coloration of the sample (Almeida et al., 2020). The figures show the specimens from leaving the oven at 105°C to firing at 1000°C. Red coloration of the specimens is observed, which confirms the presence of iron in the chemical composition (iron oxide) and the crystalline phases (hematite). Moreover, as the firing temperature increased, the shade tended to become redder. Finally, the specimens did not present cracks or defects resulting from firing.

Figure 9 – Color of the specimens after firing.

4. Conclusion

The characterization of two clays from Caxias/MA was performed. The samples in their mineralogical composition have kaolinite, illite, quartz, orthoclase, hematite, and rutile. The clay samples have high silica contents associated with low alumina contents that constitute a characteristic material for red ceramic manufacturing. SiO_2, Al_2O_3, and Fe_2O_3 are the main oxides in the studied clay samples.

The technological properties reveal that the formulation studied can be applied to the production of masonry bricks. And at 1000°C, the results indicate the possibility of producing ceramic tiles. Thus, the clay deposit has the potential to become a raw material for the clay ceramics industry in the state of Maranhão.

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