Availability of raw materials in the state of Piauí for the production of ceramic coating

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Abstract

The main raw material for the production of ceramic materials is clay, it can be found in large quantities throughout Brazil, in addition to having a simple processing method in the preparation of the mass of ceramic tiles using mixtures of kaolinitic clays (not very plastic) and illitic (plastic) clays, this mixture favors by developing a series of functions such as: light-burning color; act as binders and plasticizers; facilitate fluidity, due to its melting properties, provide a good burning density and excellent mechanical resistance.

This work addresses the main basic white-burning raw materials used in the production of ceramic tiles: quartz, kaolin, talc and limestone and their influence on the ceramic mass. All raw materials mentioned are available in the State of Piauí. For this, a bibliographic review of a descriptive, basic and qualitative nature was carried out on the theme and with the results, it was possible to identify the existence of white-burning raw materials in the State of Piauí that can be used in the production of ceramic coating.

Keywords: Raw material; Coating ceramics; Clays.

1. Introduction

The ceramic sector plays an extremely important role in the country's economy. According to studies carried out by ANFACER (National Association of Ceramic Manufacturers for Coatings, Sanitary Ware and the like), Brazil is one of the main players in the world market for ceramic tiles. Occupying the third place in production and the second place in consumption in the world and besides being the sixth in the ranking of exports. With productive concentrations in the south, southeast and northeast (ANFACER, 2018).

Thus, the ceramics industry ended up attracting high investments in training, installation costs and applied technology. Ceramic materials exhibit a wide range of properties, comprise all non-metallic inorganic materials, usually obtained after heat treatment at high temperatures, are the basis of cheap raw materials and are widely used in several areas of knowledge. Its main raw material for the production of ceramic materials is clay, which becomes very plastic and easy to mold when moistened, and can be found in a large quantity throughout the Brazilian territory (SANCHES, 2012).

As the name implies, ceramic tiles or ceramic tiles are used to cover floors, countertops, walls, pools and even ceilings inside and outside the environment. When used as floor coverings, they are called floors. When used as a wall covering, they are called tiles, tiles, tiles. (OLIVEIRA and HOTZA, 2015). The ceramic tile sector generally uses other types of classification, such as: floors and coverings (depending on how they are used) on the floor or on the wall; white or red burning ceramic plates, depending on the color after firing (SANCHEZ et al., 1996).

One of the main reasons why the Brazilian ceramics industry has grown rapidly is due to the excess of natural raw materials. That is why it is important to choose the raw materials, the formulation of the ceramic mass, the compaction of the product and the burning conditions, as they determine the physical and chemical transformations occurred during the manufacture of a ceramic product, thus influencing its final properties (OLIVEIRA, 2011).

Currently, ceramics is considered an intense object of research, considering the use of its physical and chemical properties of a large number of materials. Studies have shown that another region that has shown development in this sector, due precisely to the wide variety of raw materials in the area and the developing consumer market is the Brazilian Northeast.

In Piauí, the ceramic tile industry is a segment that has been experiencing difficulties, as there are some factors that hinder this manufacturing, such as a high cost of raw materials, which makes production expensive, a significant loss of production and in In particular, the lack of knowledge about other raw materials that can be applied to the ceramic mass. Thus, there is an abundance of products that are

considered of inferior quality when compared to products from other regions and available in the Piauiense market (SOARES, 2008).

Another important factor is the lack of technological support, as well as the lack of research that makes it difficult to improve the quality of the coating ceramics produced in Piauí. As a result, these products end up becoming less competitive and with low market value. With the improvement of the ceramic quality manufactured in Piauí using raw materials specific to the State, it would end up becoming a viable economic alternative, as it would develop the existing industry, thus generating investments in the sector and jobs and income for the State (SOARES, 2010).

Therefore, this work addresses the main basic white-burning raw materials used in the production of white-based ceramic tiles: quartz, kaolin, talc, limestone, showing their availability in the State of Piauí and their influence on the mass.

1.1 Raw materials

The term "raw material" refers to all materials that are incorporated into the product during the manufacturing process. Ceramic raw materials can generally be divided into: plastics, which are clay minerals, ie clays and kaolin and non-plastics, which are fluxes, quartz and talc. Both have important functions throughout the ceramic production process. In the conformation phase, plastic raw materials are essential, as they confer important characteristics, such as plasticity and mechanical resistance, while in the thermal processing phase, non-plastics act, which confer characteristics such as, structure and color (MOTTA et al., 1998).

Clay materials are highly fine materials, so they can provide a mixture with high cohesion and processability, making these products with excellent plasticity and ease in the process of coating execution (RECENA, 2017).

According to Santos (2009), the main function of fluxes is to make the existing impurities more fusible. Limestone, dolomite, feldspar, manganese oxide and iron oxide are the main fluxes in the manufacture of coatings. In the blast furnace, these fluxes burn silica.

In the production of ceramic tiles, there is not a single raw material, as with bricks and ceramic tiles, because to form a good formula, with good stability and good meltdown, it is necessary to mix several raw materials with different chemical properties. Heck, (1996, p.21) affirms "it is essential to maintain the homogeneity of the batch and to meet the specifications, in order to avoid variations in tonality and variations in the melting point of the composition".

The selection of raw materials that make up the ceramic mass must have the required characteristics of the product and the basic criteria of the characteristics inherent to the manufacturing process, which depend on the chemical and mineral composition of each raw material used (SOUZA et al., 2000).

Knowledge of the chemical composition (presence of main oxides) and mineralogy (crystalline phases) of the composition of the ceramic mass is essential to predict the behavior of the mass and the characteristics of the final product throughout the manufacturing process. It also guides the proportion of each component, in order to optimize the entire processing through economic benefits and to improve the technical and aesthetic qualities necessary for the ceramic body. Generally through mineralogical analysis, chemical composition analysis, differential thermal and thermogravimetric analysis, granulometric analysis,

plasticity index and determination of physical and mechanical properties with temperature changes, they are used to study raw materials and determine their technical uses (SOARES, 2010).

Silicon oxide (SiO2), aluminum oxide (Al2O3), potassium oxide (K2O), sodium oxide (Na2O), calcium oxide (CaO), magnesium oxide (MgO) and iron oxide (Fe2O3), are the main oxides found in the raw materials of a ceramic coating mass and each one has a specific function during the productive processing and will confer the final properties of the ceramic product (SANTOS, 1989).

SiO2 is usually associated with clay, fluxing and quartz minerals. It is the main glazing agent and makes up the main crystalline phases after burning. Free silica reduces plasticity, lowers linear shrinkage, facilitates the drying process and the release of gases during firing. Al2O3 is mostly combined to form clay minerals. It is also a glass-forming agent when combined with fluxing agents, and when present in large quantities it increases the refractoriness and loss to fire of the mass. At the end of the firing, it is part of the crystalline structure, such as mullite for example (SANTOS, 1989).

Alkaline earth oxides (CaO and MgO) are generally derived from calcium and / or magnesium carbonates. They are melting agents and tend to lower the refractoriness of the ceramic mass (SANTOS, 1989).

Fe2O3 comes from iron minerals such as hematite, magnetite, limonite, lepidocrocite, geotite and pyrite, often found in clays. Iron oxide reduces refractoriness and acts on the coloring of the ceramic body, obtaining colors such as beige, yellow, red or brown. The variation in the burning color depends on the concentration of iron in the mass and other constituents such as aluminum and calcium oxides, as well as the burning temperature. At higher temperatures, iron oxide can expand the ceramic piece with the release of gases.

The raw materials that make up the ceramic tiles must always have a low iron oxide content, as this affects the color of the piece produced, because the effectiveness of the pigments added to the composition directly affects the whiteness of the piece (GIBERTONI, 2008).

2. Methodology

The present study is a literature review of the literature review type, which is based on a qualitative and exploratory approach. It seeks to translate the information collected into articles, defining: Availability of raw materials in the State of Piauí for the production of ceramic tiles.

Articles will be collected from the Google Scholar database, from the CAPES and Scielo journals portal, as an inclusion criterion will be used the full articles, published from 2015 to 2020, the following descriptors will be used: White-burning clays; white-burning ceramic coating; ceramic coating; clay. The search will be performed using the words found in the titles and abstracts of the articles. It will also be used for master's and doctoral theses found in universities and colleges, as well as literature related to the theme.

In possession of the articles, criteria for inclusion of those articles will be made that the characteristics were more pertinent to the theme, articles with qualitative approach, exploratory, descriptive, and reflexive-descriptive, which are directly related to the subject of the study, and will be excluded the initial search is for those articles that are outside the theme, that is, abstracts and other forms of publication that are not complete scientific works. The research has an exploratory and descriptive character aiming, respectively, to provide more information on the topic addressed, registering, analyzing, classifying and interpreting the

data obtained through review.

3. Results

3.1 Clays

According to the Brazilian Association of Technical Standards - ABNT (NBR 6502/95), clay is a finely classified soil composed of particles smaller than 0.005 mm in size. The clay has plasticity, texture and consistency under natural conditions and humidity. It is easy to mold it into different shapes when fully wet and has sufficient cohesion when dry, which can form clumps that are difficult to decompose under the pressure of your fingers.

For Rocha, Suarez and Guimarães (2014), clays do not represent a specific type of chemical compound, in fact clay is a set of compounds with very fine granulometry and diameter less than 2μm. Another very important characteristic of these particles is that, when moistened with water, they form a mixture with a certain plasticity. Clay is a very common natural raw material in the preparation of a large amount of ceramic tile masses.

The clay has the function of providing plastic properties in green to guarantee the best performance during the compaction of the ceramic body, as well as the wet, dry mechanical resistance and after firing. In addition to having a simple processing method and available in large quantities (RODRIGUES et al., 2004).

Also according to ABNT NBR6502 / 95, clays can be chemically defined as the purest hydrated aluminum silicate. Plastic clays have a very high alumina content (plastic part) and lean clay has a high silica content (non-plastic part). Greater plasticity is also strongly affected by the size of fine particles and the organic matter of the clays.

In the process of preparing the ceramic tiles mass, mixtures of clays are used, both kaolinitic clays (not very plastic) and clays of the illitic type (plastic), this mixture favors, developing a series of functions such as: the light burning color; act as binders and plasticizers; they facilitate fluidity, due to their melting properties, they provide good burning density and excellent mechanical resistance (BIFFI, 2006).

A major concern is the fact that the most frequent contaminating minerals in clays are: iron oxides, pyrite, siderite, titanium minerals, gypsum and dolomite, the shape and type and quantities of these, can modify the properties of clays as mechanical strength, melting point, color and plasticity, as well as influencing the use, process routes and application of clay in the ceramic industry (LUZ and LINS, 2005).

We can differentiate the clays from each other mainly by the association of chemical elements of different nature and by the granulometric distribution. The main categories of clay minerals are kaolinite, illite, halosite, chlorite and smectite. For ceramic tiles, illicit and kaolinite are the most important, and the purest form of clay that we can find in nature is kaolinite (OLIVEIRA et al., 1998).

In his study, Soares (2010), reports that a clay to be considered of good quality used for a certain function it must have an appropriate chemical composition and the quantity of the chemical composition must also be known. The properties of a clay are determined by the presence or absence of oxides of silicon, aluminum, potassium, sodium, iron, magnesium, calcium and others that may be present in lesser quantities.

In the ceramic sector, clays are named according to technical criteria and ceramic jargon, according to their main characteristic evaluated in the firing stage:

- Red or reddish-burning clays: they have a high content of iron oxide (> 4%) and are used mainly in ceramic coating plates with dry prepared pasta;
- White or light-burning clays: they are usually clays kaolinitic with low or no dye oxide content such as iron or titanium and are applied to ceramic coating plates produced by the wet method;
- Fusing clays or gresified: they are composed of a mixture of clay minerals, which include illite, kaolinite and smectite, with varying proportions of quartz and other non-plastic minerals, with the presence of melting oxides (MOTTA et al., 1998). They allow to obtain interesting values of rupture module in green (wet and dry) and also after firing, since they generally give rise to gresified materials. These clays are used in Brazil in the dry production process and have a reddish color;
- Carbonate clays: present a quantity of calcite, dolomite or magnesite in the variable clay matrix, which can reach high values. The mineralogical associations present in these clays can beilíticoclorítica and eventually ilíticocaulinítica. These clays also contribute to give the dough plasticity and, usually after firing, they are beige-orange in color due to the presence of ferrous minerals (OLIVEIRA, 2000).

In the last two decades, the vigorous development of the ceramic tile industry in the world and in the countries has led to a strong increase in the demand for plastic clay. This demand promoted new producers to enter the international market. Many countries have not differentiated plastic clay from ordinary clay (OLIVEIRA and HOTZA, 2015).

The clay has a high concentration of SiOtwo. This oxide is the main vitrifying agent and makes up the main crystalline phases after burning. Free silica improves the dimensional stability of ceramic parts and facilitates the gas release process during the sintering of ceramic bodies. Clay also has a considerable concentration of aluminum oxide, which is a glass-forming agent when combined with fluxing agents, helps to increase the fire loss of the ceramic mass and at the end of the firing is part of the crystalline structure, such as spinel and mullite. The presence of these oxides together is responsible for the refractoriness of the clay (AVELINO, 2019).

3.2 Kaolin

The term kaolin can be used to name kaolinite-containing rocks as the main constituent and can also be used for products produced during processing. Kaolin is a fine-grained rock composed of clayey materials, usually low in iron, white or almost white (GRIM, 1958).

For Luz and Ribeiro (2008), the types of kaolin vary according to their physical properties: brightness, crystallinity, opacity, viscosity and the shape of the particles. Kaolin is related to several impurities, thus not meeting market specifications. Impurities, such as iron and titanium oxides, mica and feldspar, directly affect color and brightness, thus reducing quality. To promote its ideal use, processing operations are necessary, which depended on the intended use. There are two processing processes: dry and wet.

In the production of ceramic tiles, the amount of kaolin varies from 10% to 15%, besides providing whiteness after firing (to make the piece refractory), it is also an important source of aluminum oxide, which during the glazing of the ceramic mass becomes a regulator of the balance of reactions (BIFFI, 2006). In ceramic pieces, kaolin can also be used as an alloy of components in the green state and can also provide plasticity for modeling the body in the presence of water (ALBUQUERQUE et al., 2007).

Kaolin has an important concentration of potassium oxide that is associated with fusing clay minerals. This

oxide is essential for low-porosity (vitrified) ceramics, as it acts as a high level liquid phase builder above 1000 ° C and forms eutectic at lower temperatures (AVELINO, 2019).

3.3 Quartz

Quartz, an allotropic form of silica at room temperature, is one of the purest and most abundant minerals in the earth's crust. Its structure consists of a three-dimensional network of tetrahedrons connected in a compact structure, consistent with its high density. The open spaces in its structure are so small that other atoms cannot enter, which contributes to its high purity. The main sources of quartz for the ceramic industry are sandstones and quartzites made up of connected quartz grains (NORTON, 1973).

In nature, quartz exists in polymorphic forms: tridymite and cristobalite. As the temperature changes, phase changes occur and each phase change has its own specific name. Alpha quartz, the most common of the polymorphs, is stable at room temperature, becoming beta at 573 ° C with an increase in volume of around 3%, and tridimite at 870 ° C. At a temperature of 1470 ° C, the transformation to cristobalite occurs, up to the melting point at 1713 ° C (KLEIN and DUTROW, 2012).

Quartz plays a very important role in coating ceramics, because it adjusts the plasticity of the dough, promotes the drying step and the escape of gases during the firing process, guarantees the stability of the pieces, regulates the viscosity of the liquid phase formed during the burning and the thermal expansion coefficient (FERRARI et al., 2000). Despite having a very important function, quartz is a low-cost raw material.

For Albuquerque et al., (2007), quartz acts as a filler, with the sintering temperature being the stable phase, reducing shrinkage, that is, it plays a role in controlling the expansion and distortion of the ceramic piece. It is also used to reduce the plasticity of the raw material mixture and increase the permeability of the raw material.

Quartz sand is used to maintain the structure in the mass when, due to the increase in temperature, the other components melt. In addition, it is an important regulator of the relationship between silica and alumina for the formation of mullite, a phase that increases the resistance of the pieces. It presents a considerable amount of silicon oxide (SiO2), thus proving the purity of this material, on the other hand it presents a low amount of aluminum oxide. Quartz will help reduce the shrinkage of the mass, since during the formation of the liquid phase it will behave as if it were the “skeleton” of the material. (AVELINO, 2019).

The author above also mentions that, in general, the thermal behavior of sand is very similar to that of clay. This is due to the similarity in the chemical and mineralogical composition of these raw materials.

3.4 Limestone

Limestone is a rock composed mainly of calcium carbonate and can appear in the form of calcite or aragonite, the latter being an auxiliary substance for minerals. In the earth's crust, there is almost no limestone composed only of calcium carbonate (Holanda et al., 1987).

Limestone is a natural substance of the highest importance for industries and occurs in sedimentary deposits forming white or more or less regular layers. It is a calcium carbonate, sometimes pure, sometimes containing proportions of iron, manganese, alkaline salts, magnesium, silica, alumina, clay, etc. It is introduced into the masses in the form of fine powder and sometimes by the clays themselves as a calcium

compound. It is important to emphasize that the limestone concretions should be finely ground or removed, if possible, because if the limestone, even if ground, is abundant, it may deform the ceramic bodies when burned at high temperature (SENAI, 2006).

The addition of 1% lime to a mass has the same melting power as 10% feldspar, at temperatures above 1100ºC. The use of limestone in the masses makes them lighter and improves thermal expansion, in addition to increasing mechanical strength. In the ceramic tile industry, limestones are used for the manufacture of tiles and some types of floors (SENAI, 2006).

3.5 Talc

Talc is a hydrated magnesium silicate with theoretical mineralogical composition. Its application in the mass of ceramic materials has the following objectives: to change the melt to react with feldspar at lower temperature to form a eutectic reaction; reduce the glazing temperature of the pasta; accelerate the densification of the material; form a crystalline phase with high mechanical resistance and improve resistance to thermal shock during rapid firing cycles (VIEIRA et al, 2007);

In Brazil, numerous studies have already been carried out involving directly or indirectly light-burning clays, so we can highlight:

- CARDOSO et al 1998 describes a study carried out on raw materials used by some traditional white ceramic industries in the state of São Paulo. In this work, the author evaluates five kaolins, a ceramic filite and four ball clay, raw materials from different Brazilian states;
- CARVALHO, 2000 carried out a mineral research in an occurrence of clays in the valley of the Baldun River (RN), evaluating the technical and economic viability of the exploration of this deposit. The author verified a reserve of 51,702 tons that can be used in the white ceramic industry;
- MELO et al, 2002 developed a study of four clays from some regions of Rio Grande do Norte. The author found that clays can be used in the white ceramic industry.
- MOTTA et al, 2004 presents the geological and technological characteristics of plastic raw materials used by the traditional ceramic industry, including light-burning kaolinitic clays;

4. Conclusion

The main basic white-burning raw materials used in the production of ceramic tiles were studied: quartz, kaolin, talc, limestone, and how these raw materials positively influence the ceramic coating mass. Piauí's raw materials are viable and of good quality for mass applications of ceramic tiles. All of these raw materials are fundamental for the composition of the various masses of the clay-based ceramic industry, also called traditional ceramics, and their good supply constitutes a competitive factor for the Brazilian ceramic sector, in the domestic and foreign markets. However, despite an apparent balance between production and consumption, the supply that meets the different market specificities is not yet complete.

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