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Ceramic colorant from untreated iron ore residue

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HIGHLIGHTS

- ► Iron ore residue used as a colorant for glazed ceramics.
- ► Residue used without any kind of pretreatment.
- ► The color of the glaze changes due to the type of glaze and firing temperature.
- ► Color variation is a function of crystal phase modification during firing.
- ► The untreated iron ore residue can be used as a ceramic colorant for roof tiles.
- ► Stable color was achieved at intermediate temperatures (1100 °C).

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ABSTRACT

This work deals with the development of a ceramic colorant for glazes from an untreated iron ore residue. 6 mass% of the residue was added in suspensions (1.80 g/cm^3 density and 30 s viscosity) of white, transparent and matte glazes, which were applied as thin layers (0.5 mm) on engobeb and not fired ceramic tiles. The tiles were fired in laboratory roller kiln in a cycle of 35 min and maximum temperatures between 1050 and 1180 °C. The residue and glazes were characterized by chemical (XRF) and thermal (DTA and optical dilatometry) analyses, and the glazed tiles by colorimetric and XRD analyses. The results showed that the colorant embedded in the transparent glaze results in a reddish glaze (like pine nut) suitable for the ceramic roof tile industry. For the matte and white glazes, the residue has changed the color of the tiles with temperature.

1. Introduction

Nowadays the industrial activities produce a certain amount of waste that is not inherent to the production process. Since the reduction of waste generation although a priority is technically limited, the best solution is recycling. One of the greatest difficulties in order to take concrete actions for processing and disposal of industrial wastes, besides the economical, political and administrative problems, is the lack of processing techniques that can deal with the size and characteristics of the localities interested in solving these problems [1–3].

The search for improved environmental quality is closely related to the reduction of waste generated by industrial activity, thus setting the global movement for recycling. The generation of waste tends to decrease both in Brazil and worldwide. Companies are realizing that the generation of waste is associated with costs, requiring treatment and/or proper disposal. The tendency is to act preventively, changing the production process and using cleaner technologies. Due to lack of adequate infrastructure or high costs for final disposal in places previously prepared, the sludge is usually deposited in inappropriate places. This causes an increase in losses and production costs, as well as generating significant environmental impacts [1–5].

With increasing restrictions imposed by environmental legislation, as well as market demand for environmentally friendly products and processes, many studies have been developed to promote the reduction of generation, treatment, reuse and proper disposal of waste. Some of these studies have demonstrated successfully that the ceramic industry can act as a great ally to consume certain types of waste, incorporating them into the ceramic paste [2,3].

The technologies used to manufacture ceramic tiles have been subject to important processes of innovation, and there is no doubt that the need to reduce environmental impacts makes the ceramic tile industry a strong ally in the use of various types of industrial waste as raw materials. Recycling of waste that have economic value is the most attractive way to solve the problems of waste treatment and final disposal, mainly because recycling is

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considered an important factor in reducing consumption of natural resources and a way to reduce the amount of pollutants released into the environment [6–9]. That is the opinion of the industrial segment and the point of view of state organisms for environmental protection.

Ceramic frits are glassy materials in nature that are prepared by melting at high temperatures (around 1500 °C) of a combination of mineral raw materials (quartz, feldspar, kaolin, etc.) and chemicals (borates, carbonates, among others). Frits allow flexibility in the application of raw materials used in ceramics and increase the glaze firing range, allowing a greater uniformity in the glaze layer, reduce the appearance of surface defects originated from the ceramic body and give the finished product a smooth, shiny and waterproof surface texture. The fritting process also brings benefits such as transforming soluble components into a glass insoluble in water, plus inerting some toxic oxides [6–9].

Glazed ceramics are always selected by their esthetics and, in particular, their color, and both factors represent the conditional parameter to obtain a colored glazed material whose characteristics are rarely determined by unique functional properties like hardness or strength. Among the possible coloring methods, due to technical or economic reasons, the most effective way to achieve a stable color is the use of pigments. In turn, pigments are defined as a compound, usually calcined, formed by colored metal oxides that mixed with a glaze or pasta form a uniform and colored ceramic tile [10,11]. The pigments stability does not depend on its chemical composition, but depends on its crystal structure, i.e., its mineral composition. The raw materials composition does also affect the reaction. Often chemicals such as salts and hydrated oxides are used as raw materials, which during the heating process decompose, and the use of oxides that interfere with the crystal structure must be avoided. This procedure enhances the reactivity of the decomposition products, such as free radicals that form the crystal structure that will provide the desired coloring material to be calcined [12–19].

The value of a pigment depends on its optical and physical properties. These, in turn, depend directly on the crystal structure of the pigment and its physical characteristics such as particle size distribution, particle shape and degree of agglomeration, and chemical characteristics like composition, purity and stability. In fact, the most important properties to consider are the pigment ability to develop color (pigmenting capability) and opacity inside the matrix in which it is dispersed. Numerous other factors must be taken into account when selecting a pigment for a specific application. Among these the most stringent is the chemical stability requirements imposed by the industrial processing. A pigment used for coloring the ceramic paste or the engobe must be stable to firing temperatures generally between 1200 and 1300 °C. A pigment for glazes should be stable in the firing temperature of the specific glaze, between 1000 and 1200 °C, and must present corrosion resistance against the flux present in the composition. Finally, a third-firing pigment should be stable in the firing temperature of the decoration, between 625 and 775 °C and must be resistant to the strong effect of the flux present in the composition of the frits (usually based on lead oxides) [7,8,20].

In order to be industrially used, a pigment should be compatible with the other components of the glaze or the ceramic body to be colored without chemically reacting with them. The most significant consideration in selecting a pigment for a particular industrial application is the presence or absence of ZnO in the enamel. The $(Al,Mn)_2O_3$, $(Fe,Cr)_2O_3$, chromium/tin and pink chromium/tin solid solutions are not stable in the presence of ZnO because of the preferential formation of spinels with transition metals. On the other hand, other pigments, as the $(Al,Cr)_2O_3$ solid solution, require high concentrations of ZnO. In addition, the presence or absence of PbO on the glaze is very important for the stability of pigments. A glaze containing a lead based frit (e.g., a third-firing glaze) cannot be used with pigments with crystal structure similar to that of zirconium silicate, because the zirconium silicate crystal dissolves in the matrix [7,8,20].

Therefore, the ceramic tile industry has needed more and more chemically and thermally stable pigments at high temperatures (1100–1300 °C) due to new developments. The continued and growing use of iron oxide pigments is based on its relatively low cost, coupled with high stability under normal environmental conditions. The element iron usually exists in nature in the form of oxides, although it can also be found as hydroxides, silicates, carbonates and sulfides in small events, and even in native form, in small proportions. It is the most abundant metal in Earth's crust after aluminum and silicon. Although these minerals are highly distributed, only few deposits are sufficiently pure for the required properties and justify its processing in the form of pigments. Iron oxide pigments are those derived from selected natural minerals and should not be confused with the iron ore mined for the production of steel. These are selected based on iron content and process economics. Natural sources of iron ore for use as pigments are selected for their special physical and chemical properties [14,16,18,19].

The use of processed iron ore containing metal oxides as a pigment tends to lower the cost of a colored glaze because of its low commercial value compared to a glaze colored with an imported red dye, but there is also another reason for its use, to give a correct destination to a residue that is very common in areas of extraction of iron ore [21–27]. However, in this work the reactions detected by XRD with the glazes upon firing (and responsible for changes in color) have shown that the residue was acting as a dye or colorant and not properly as a stable pigment. This result was expected since the iron ore residue was used directly, whit no treatment, and the waste is basically composed by iron oxide.

Therefore, the objective of this work was the development of a colorant for ceramic glazes derived from industrial waste from the beneficiation of iron ore, and the study of the colorant color variation as a function of temperature and type of glaze. The main feature of the work is that, unlike many studies carried out with pigments made from waste, in here the iron residue was not treated or processed before being used as a ceramic colorant.

2. Experimental

2.1. Pigment preparation

The iron ore waste was provided by a mining company from Minas Gerais State, Brazil, to be used as a colorant for three distinct types of glazes, developed from a white, a transparent and a matte frit. The glazes containing the iron ore residue were applied as ceramic suspensions onto not fired and not engobed ceramic substrates (semi grés tiles).

The residue is basically the mud coming from the processing of iron ore and classified according to the NBR 10004 Brazilian Standard (based on ISO 11932:1996 Standard) as a class IIa non-inert material (data supplied by the mining company) due to the iron content obtained after the solubilization test (0.5 μg/mL for a standard limit of 0.3 μg/mL). The dry residue presents as minor components Cr (0.003 μg/mL for a limit of 0.5 μg/mL), Cd (0.009 μg/mL for a limit of 0.5 μg/mL) and Pb (0.09 μg/mL for a limit of 5 μg/mL) after the leaching test. The sludge presents 30% wt. moisture and a pH of 10. According to the company that supplied the mining waste, 12 000 tons of waste are produced on daily basis, giving rise to the need for its reuse.