USE OF RESIDUE FROM THE EMERALD EXPLOITATION OF SERRA DA CARNAÍBA - BA IN THE PRODUCTION OF GLAZED CERAMIC TILES

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ABSTRACT

Ceramic tiles are generally made up of three layers. The first is the body or biscuit. The second is the engobe, which has a waterproofing function and ensures the adhesion of the third layer. And lastly the glaze, a glass layer that also waterproofs, in addition to decorating the top face of the ceramic coating. The main functions of this coating are to protect and decorate. Protect the base and structure of the building, such as floors and walls. And decorate, finishing the environment, providing visual and aesthetic comfort. The exploitation of emeralds in the Serra da Carnaíba - BA generates large volumes of emerald residues that are constantly abandoned in the environment. The main constituents of this residue are silicon oxide, iron oxide and molybdenite. In the process of firing this residue the mica present oxidizes, resulting in a by-product with golden tones. Another important factor of growing interest in recent years is the use of mineral residues as an additive in the production of ceramic material, trying to improve product quality and increase the variety of applications. The purpose of this work is to study the incorporation of residues from the exploitation of emeralds in the ceramic composition for the production of ceramic tiles, seeking to add economic value and unique aesthetic characteristics to the final product. In this process, ceramic mixtures were prepared from raw materials characterized by X-ray fluorescence and X-ray diffraction (XRF and XRD). Five compositions were prepared using amounts of 10%, 20 and 30% emerald residues for coating the ceramic pieces in the form of a slip. The samples were prepared by pressing in a uniaxial press with a pressure of 3 MPa, being fired at 850, 900 and 1000. Technological tests of water absorption, apparent porosity, apparent specific mass, linear shrinkage and modulus of flexural rupture were then carried out. Preliminary tests suggest that the emerald residue studied can be used as a slip, providing ceramic tiles with interesting aesthetic characteristics; adding value and reducing the environmental impact caused by the disposal of this material directly into the environment.

1. INTRODUCTION

Ceramic tiles generally consist of three layers. The first is the body or biscuit. The second is the engobe, which has a waterproofing function and ensures the adhesion of the third layer. And finally, the glaze, a glassy layer that also waterproofs, besides decorating the upper face of the ceramic coating. The main functions of this coating are to protect and decorate. Protect the base and structure of the building, such as the floors and the wall. And decorate, giving finishing to the environment, providing visual and aesthetic comfort.

The issue of waste recycling and possible reuse, as well as the global environmental issue as a whole has become a decisive factor in decision making. On the other hand, ceramics worldwide have had strong technological development in the last 30 years, where the advancement of special materials, combustion technology, decoration, glazes and, in particular, knowledge of materials science has allowed, through the combination of this different knowledge, the strong development of technology and, consequently, the increase in the production of ceramic materials, offering the market products with better characteristics, produced by a clean technology. [1]

The exploitation of emeralds in Serra da Carnaíba - BA generates large volumes of emerald waste that is constantly abandoned in the environment. The main constituents of this residue are mica, feldspar and molybdenite. Another important factor that has been growing in recent years is the interest in the use of mineral waste as an additive in the production of ceramic material, trying to improve product quality and increase the variety of applications.

There are several social and environmental impacts caused by the extraction and processing of emeralds in the Serra da Carnaíba mines, exploited in a disorderly manner and without previous studies and specialized techniques [2]. One is the accumulation of waste, randomly released into the environment [2, 3,4].

The objective of this work is to study the incorporation of residues from the emerald exploitation into the ceramic composition for the production of glazed ceramic tiles, seeking to add economic value and unique aesthetic characteristics to the final product. In this process, ceramic mixtures were prepared from raw materials characterized by fluorescence and X-ray diffraction (FRX and XRD). Three compositions were prepared using 10%, 20% and 30% amounts of emerald residues coating the ceramic pieces in the form of an engobe. The samples were compacted on a uniaxial press with 3 MPa pressure and fired at 850, 900, 950 and 1000ºC. Subsequently, the engobe was prepared with 10, 20 and 30% mineral residue from the emerald exploitation of Serra da Carnaíba - BA, forming a millimetre layer on these samples. They were then fired at 850, 900 and 1000ºC for 1 h with a heating rate of 10ºC/min. Technological tests of water absorption, apparent porosity, linear shrinkage and flexural modulus were performed. Preliminary tests suggest that the emerald residue studied can be used as a coating, providing ceramic tiles with interesting aesthetic characteristics; adding value and reducing the environmental impact caused by the disposal of this material directly into the environment.

2. EXPERIMENTAL AND MATERIALS

In this work, the ceramic body supplied by Empresa Cerâmica Canabrava LTDA, located in the municipality of Jacobina-BA, was used.

The sieving of the body was performed on a 200-mesh sieve, equivalent to ABNT sieve 200. Samples were then sent for X-ray fluorescence and X-ray diffraction analysis.

The ceramic body and the mineral residue after collection were oven-dried at 57ºC for 24 h. Subsequently, they were separately ground in the ball mill (steel balls) for 30 min. After this step they passed the 200-mesh sieve and were sent for X-ray fluorescence and X-ray diffraction analysis.

The formulations used in this work were developed through practical experimental procedure, determining a total of 03 (three) formulations with different percentages of mineral residue for the formation of the engobe, these being 10, 20 and 30%. The choice of this procedure was due to the characteristics of the raw materials used and their application. A preliminary analysis was performed in order to reduce the number of experiments required.

The samples were weighed (12 g each), moistened and mixed with distilled water (close to 10% by weight), acquiring plastic consistency for the forming process. They were then placed in plastic bags, preserving their humidity for a rest period of 24 hours.

After the maturing process the specimens were compacted in a uniaxial press with a capacity for 15 tons. The compaction load used was 3 kgf/cm^2 for 30 seconds. Twenty-seven (27) specimens were made with the ceramic body, distributed in two groups, according to firing temperatures and formed engobes.

The samples obtained, sized 60 x 20 x 6 mm, were identified, weighed and measured. They were then placed in an electric oven at 57°C for 24 h to remove moisture.

The specimens were fired in a MUFLA electric oven at a temperature of 850, 900, 950 and 1000ºC, at a heating rate of 10°C/min for 60 minutes. After the isothermal threshold, the oven was turned off and the samples were cooled inside the oven itself. On these specimens, the technological properties of Linear Shrinkage, Water Absorption, Apparent Porosity and Flexural Strength were determined.

After this stage, the samples were subdivided into three groups, coated by a millimetre layer of engobe with 10, 20 and 30% of emerald exploitation residue.

Figure 1 shows simply the sequence adopted in this work.

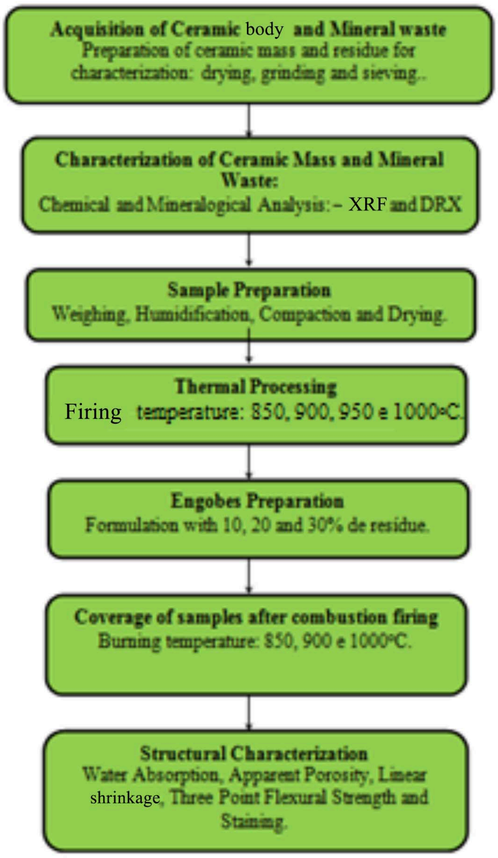

Figure 1 *– Simplified flow chart for the production of ceramic tiles.*

Table 1 shows the nomenclature and composition of the engobe formulations.

ENGOBE NOMENCLATURE	MINERAL RESIDUE(%)
T1	10
T2	20
T3	30

Table 1 *- Composition and nomenclature of the engobe formulations.*

Sample Preparation

In this work a total of 27 (twenty-seven) samples were made, three for each formulation and firing temperature.

The samples were weighed (12 g each), moistened and mixed with distilled water (close to 10% by weight), acquiring plastic consistency for the forming process. They were then placed in plastic bags, preserving their humidity for a rest period of 24 hours.
After the maturing process the specimens were compacted on a 15-ton uniaxial press using a 60 mm x 20 mm x 2 mm metal die. The compaction load used was 3 kgf/cm2 for 30 seconds.

After compaction the specimens were identified and placed for drying in an electric oven for a period of 24 hours at a temperature of 57oC.

Subsequently, the engobes (10, 20 and 30% of mineral residue) were prepared and a millimetre layer was placed on the samples.

Thermal Processing

The samples were fired at a temperature of 850, 900, 950 and 1000oC. After cooling, they were subdivided into three groups and coated, respectively, by engobes with 10, 20 and 30% mineral residue. After drying in the oven, they were fired at 850, 900 and 1000oC, with 1-hour isotherm and heating rate of 10oC/min.

Structural Characterization

The technological properties of the specimens were determined by analysing the results of the Water Absorption, Apparent Porosity, Linear Firing Shrinkage and Three Point Rupture Stress tests; besides the visual analysis of the obtained coloration.

In the analysis of the colour of the specimens, they were grouped according to the firing temperature, making up three groups and then being photographed; the variation of the tone of the pieces with the increase in the firing temperature and mineral residue content used was noted.

3. RESULTS AND DISCUSSION

Characterization of raw materials

The ceramic body used in this work went through the mechanical grinding process, followed by the sieving step; using particulate matter with passing grain size on the 200-mesh sieve.

Table 2 shows the result of the X-ray fluorescence analysis performed on the ceramic body and Table 3 the mineral residue from the emerald exploitation of Serra da Carnaíba - Ba.

OXIDES	SiO_2	Al_2O_3	Fe_2O_3	CaO	BaO	MgO	SO_3	Cl	K_2O	TiO_2	Others
%	49,64	29,99	7,87	4,60	2,45	1,70	1,11	0,13	0,95	0,97	0,59%

Table 2 *– Semi-quantitative analysis ceramic body - XRF.*

OXIDES	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	TiO_2	SO_3	Cl	P_2O_5	CuO	ZrO_2	Rb_2O	Others
%	58,62	25,16	7,26	4,30	2,40	1,01	0,34	0,20	0,37	0,06	0,06	0,05	0,17

Table 3 *- Semi-quantitative analysis of the mineral residue from emerald mining of Serra da Carnaíba - Ba.*

In the ceramic body, it is observed that the main oxide present is SiO_2 (silica), with a content of 49.64 %%, indicating the presence of silicates (clay minerals, micas and feldspar) and free silica, in the form of quartz, providing reduction in clay plasticity. The other oxide in greater proportion is Al_2O_3 with 29.99%, usually combined to form the clay minerals. Iron oxide – Fe_2O_3 has a content of 7.87%, providing a dark shade in the ceramic mass after firing (orange). Calcium oxide - CaO, with 4.60% and magnesium oxide - MgO, with 1.70%, are fluxing agents and provide a decrease in refractory ceramic samples.

In the mineral residue of the emerald exploitation the most present oxide is silicon oxide - SiO_2, with 58.62%, indicating the presence of silicates (mica, feldspar), reducing the plasticity of the ceramic mass, followed by aluminium oxide, Al_2O_3 with 25.16%, indicating the presence of clay minerals. It has iron oxide with 7.26%, giving the residue a dark shade, potassium oxide - K_2O with 4.30% and manganese oxide - MgO with 2.04%. Other oxides with contents below 1% are considered impurities.

Figure 2 shows the diffractogram of the ceramic mass used in this work.

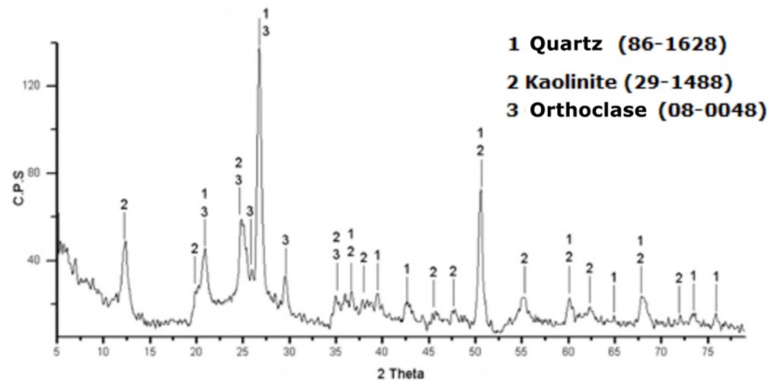

Figure 2 *–Diffractogram of the ceramic body.*

The diffractogram shows quartz (SiO_2), kaolinite [$Al_2Si_2O_5$ $(OH)_4$, which is in accordance with the results obtained by X-ray fluorescence analysis. The orthoclase present indicates the presence of feldspar.

Figure 3 shows the diffractogram of the mineral residue from the emerald exploitation of Serra da Carnaíba - Ba, presenting the mineralogical analysis of this raw material.

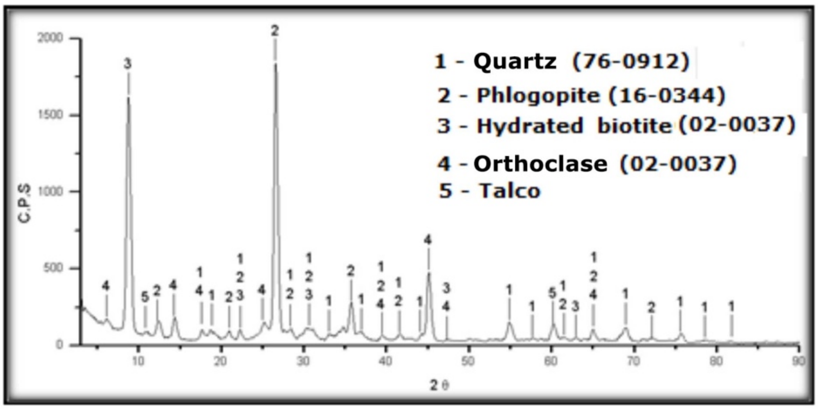

Figure 3 *- Diffractogram of the mineral residue.*

The diffractogram performed in the residue shows the presence of silica - SiO_2, biotite and phlogopite, matching the X-ray fluorescence analysis.

Technological Tests

Figure 4 shows the result of the Linear Shrinkage test, with a standard deviation of maximum 0.5%, performed on Canabrava's ceramic body samples.

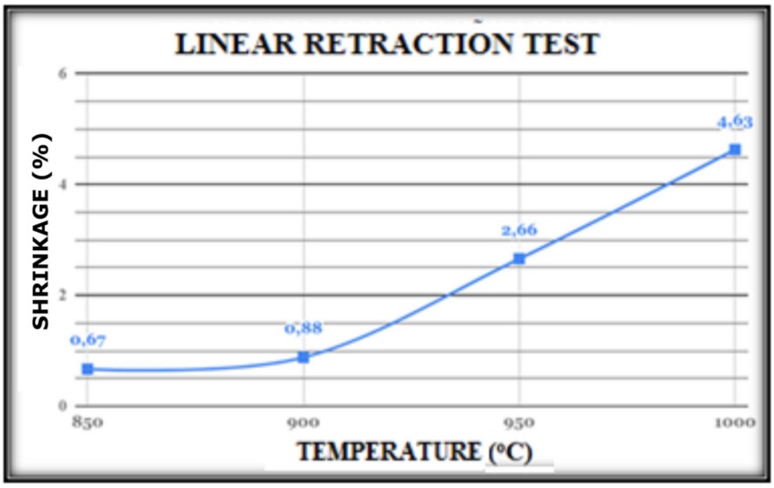

Figure 4 *– Linear shrinkage graph of samples at different firing temperatures.*

It is noticeable that the samples in the ceramic body studied showed an increase in linear shrinkage with the rise in firing temperature, with the lowest values at 850ºC and the highest at 1000ºC.

Figure 5 shows the result of the water absorption (WA) test in the formulations studied, with a maximum deviation of 0.5%.

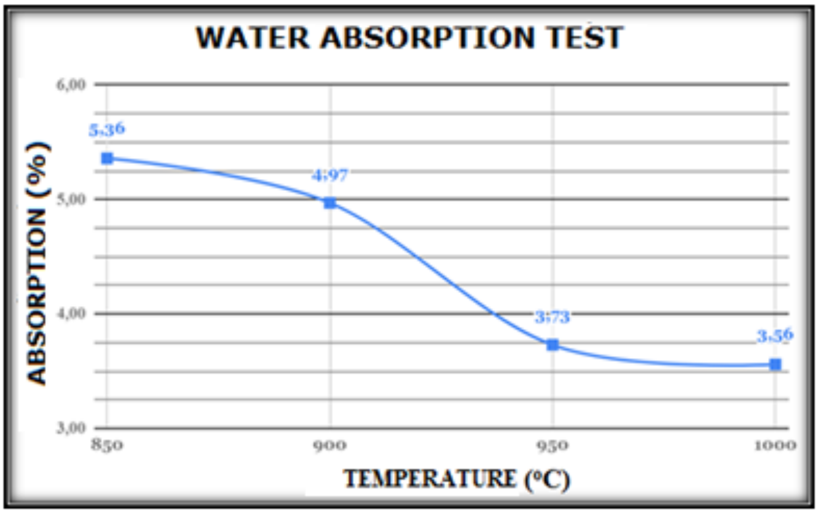

Figure 5 *– Water absorption graph of samples at different firing temperatures.*

The water absorption result of the samples is consistent with the results obtained in the linear shrinkage test shown in Figure 4. There is a reduction in water absorption with the increase in firing temperature of the ceramic bodies. The highest water absorption was found at 850°C, around 5.36%, while the lowest absorption, around 3.56%, was at 1000°C. Notably, the higher the firing temperature the lower the water absorption content.

Figure 6 shows the apparent porosity (AP) test result in the formulations studied, with a standard deviation of not more than 1.4%.

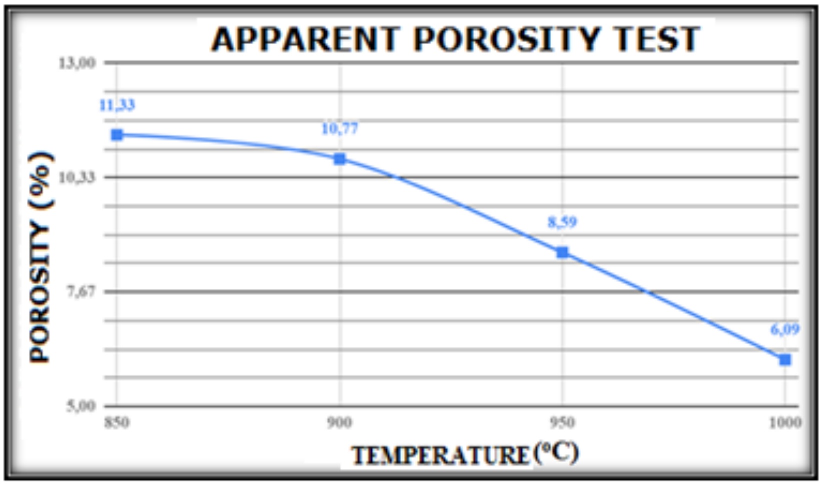

Figure 6 – *Apparent porosity graph in the formulations.*

The apparent porosity test results of the specimens at the different firing temperatures studied are consistent with the results of water absorption and linear firing shrinkage. Generally, a decrease in apparent porosity is noted as the firing temperature increases. In the firing temperature range between 850°C and 900°C there is a variation around 1 to 2%. The lowest apparent porosity occurs at a temperature of 1000°C, in the range of 6.09%. This is because in this temperature range the formation of liquid phase occurs.

Figure 7 shows the result of the three-point flexural strength test performed on the specimens.

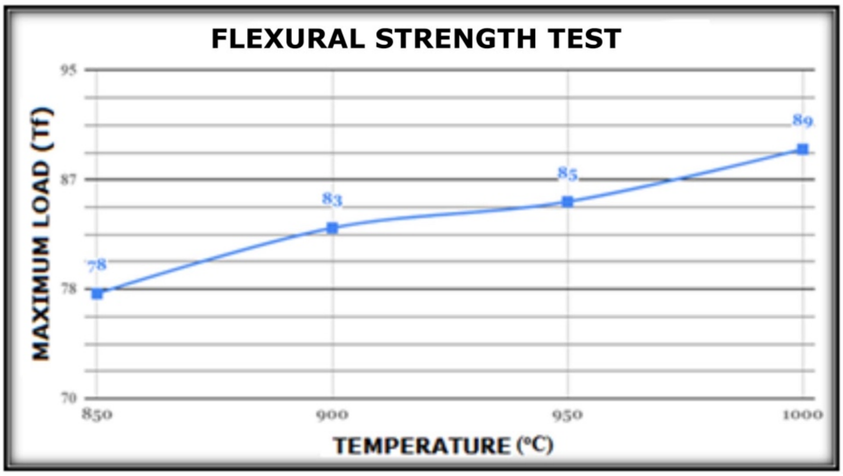

Figure 7 *– Flexural strength test in the formulations.*

The highest flexural strength values are observed at 1000°C, where the maximum rupture load was around 89 Tf, and the lowest at 78Tf, at 850°C. Notably, the higher the firing temperature, the higher the resistance due to the lower apparent porosity and to the formation of liquid phase, starting the vitrification process.

<u>Staining samples with and without engobe</u>

Figure 8 shows the photo of the samples after firing at temperatures of 850°C, 900°C and 1000°C, respectively.

Figure 8 *– Samples fired at 850, 900 and 1000°C.*

The Figure 9 shows the photo of the engobe layer samples with 20% mineral residue after firing at temperatures of 850, 900 and 1000°C.

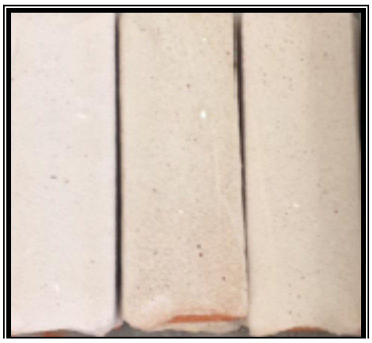

***Figure 9** – Samples fired at 850, 900 and 1000°C.*

Figure 10 shows an engobed sample with 100% mineral waste from the Serra da Carnaíba-Ba emerald farm.

***Figure 10** – Engobed sample with 100% mineral residue fired at 1000°C.*

It is noticed that in the studied firing temperatures, the higher the firing temperature the more intense the tone of the samples.

Using the engobe with 100% mineral residue, the surface of the sample denotes an intense golden shine, resulting from the oxidation of the mica present. Incorporating the mineral residue into the engobe with other ceramic constituents, this golden hue is more discreet.

4. CONCLUSIONS

The results indicate that the use of emeralds mineral residue in the formation of engobe for ceramic tile coatings is interesting. Comparatively, formulations with 20 and 30% residue showed the best results with a more intense golden lustre. Also, there is no change in the technical properties of the samples. These pieces have a golden lustre due to the oxidation of the mica present in the residue, and this aesthetic factor is an interesting point for the production of decoration and/or coating pieces, adding value to the final product.

In addition, the disposal of these residues in the environment is reduced and, consequently, the environmental impact caused by the exploitation of ornamental rocks in the plateau diamantine region.

5. REFERENCES

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