ANALYSIS OF THE INCORPORATION OF SCHEELITE RESIDUE IN CERAMICS FORMED WITH KAOLINITE CLAY FROM BOA SAÚDE-RN AND PURPLE CLAY FROM COTOVELO BEACH-RN

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ABSTRACT

Scheelite occurs mainly in north-eastern Brazil, with the highest abundance in the states of Rio Grande do Norte and Paraíba - Scheelite Province of Seridó. Mining is considered an activity that provides a high environmental degradation due to the large amount of minerals and waste involved. Most mining companies have no technologies or processes that allow recycling of the mineral waste generated and deposited in the open. In the Brejuí Mine, located in the city of Currais Novos-RN, the largest Scheelite mine in Brazil, there are a total of approximately 6.5 million tons of Scheelite tailings. The waste has several oxides like CaO, SiO_2, Fe_2O_3, TiO_2, Al_2O_3, MgO and others, which suggests their possible incorporation in ceramic samples, providing improvement in the properties of the material. Besides containing large deposits of red clay and kaolinitic clay, Rio Grande do Norte is one of the few Brazilian states that have coloured clays that arise naturally, mainly in the coastal region. Thus, the study was undertaken to evaluate the influence of different percentages of waste scheelite on the mechanical properties of ceramic

samples with purple kaolinitic clay from Cotovelo Beach. The aesthetic properties offered by coloured clay (colour of the final product after firing) were also to be evaluated. In this work we prepared samples with 4 groups of 5, 10, 20 and 30% clays without waste and a 1 Scheelite tailings group. The raw materials were characterized by XRD, XRF and particle size analysis. The samples were compacted in a uniaxial press, dried at 150ºC for 24 hours and then sintered at 900, 1000 and 1100ºC. The samples were subjected after firing to the three point bend test, and their linear shrinkage, porosity, water absorption and loss on ignition were determined. Preliminary analysis showed that the incorporation of scheelite tailings into the ceramic body was satisfactory and that the presence of purple kaolinitic clay provided with a very interesting variation in colour shades, which could serve a not yet explored niche market.

1. INTRODUCTION

The red ceramics industry is a very important element in the generation of income (wealth) of the Brazilian industrial sector. According to Bustamante and Bressiani (2000), in 2000 the red ceramics sector accounted for approximately 40% of all the income generated in the ceramic sector. The intensity of industrial growth and demographic developments of the last few decades have led to the generation of significant quantities of residue. Currently, technological efforts have been concentrated on actions that lead to the use of clean technologies, which allow the complete elimination of residues or their incorporation within the production process that generated them, or even, for use as raw materials in other production processes. Mineral extraction is a highly degrading activity, due to the large volume of material that it moves in the form of ore and tailings. The ceramic industry, in turn, is the industry that stands out the most in the recycling of municipal and industrial residue, due to its high volume of production, which allows the consumption of large quantities of residue. This, coupled with the physico-chemical characteristics of the ceramic raw materials and the particularities of ceramic processing, makes the ceramics industry one of the major options for the recycling of solid residue. In addition, it is one of the few industrial areas where advantages may be found in its manufacturing process with the incorporation of residue among its raw materials, as an example of an economical use of high-quality raw materials, ever more scarce and expensive, the diversification of supply of raw materials, and the reduction in energy consumption and, therefore, reduction of costs. The ABC (Brazilian Ceramic Association) notes, specifically for red ceramics, the existence of 11,000 small companies distributed throughout Brazil, employing around 300,000 people, and generating a turnover of around R$ 2.8 billion.

The scheelitiferous region in the north-east of Brazil is the second largest of the earth�може crust in extension and volume of ore contained. In the north-east, scheelite is distributed, in order of importance over the following States: Rio Grande do Norte, Paraíba, Pernambuco, Ceará, and Alagoas. At the national level, the RN holds the largest reserves officially approved by the National Department of Mineral Research - DNPM. The mineralized region forms a real scheelitiferous band that would be about 560 km wide and up to 700 km long in its most central portion. The municipalities that hold the scheelite reserves in Rio Grande do Norte are: Acari, Bodo, Currais Novos, Lajes and Santana Serido. This State has large mineral riches, one of them being scheelite, which has become a target of mining companies from all over the world, especially as a niche of ores of great market value. From the 1940s to the present day the quantity of mineral residue from the Brejui Mine fluctuates around 4.5 million tonnes (fine grade reject) and 6.5 million variously-sized reject. The residue has several oxides like CaO, SiO_2, Fe_2O_3, TiO_2, Al_2O_3, MgO and others, which suggests its possible incorporation into ceramic samples, providing improvement in the properties of the material. Besides having large deposits of red clay and kaolinitic clay, Rio Grande do Norte is one of the few Brazilian states that have coloured clays that occur naturally, mainly in the coastal region. Thus, the study was undertaken to evaluate the influence of different percentages of scheelite residue on the mechanical properties of ceramic samples with purple kaolinitic clay from Cotovelo Beach. The aesthetic properties offered by the coloured clay (colour of the final product after firing) were also to be evaluated.

2. EXPERIMENTAL AND MATERIALS

Preparation of the Samples

Preparation of the Samples. In this work kaolinitic clay was used from the municipality of Boa Saúde-RN, Scheelite reject from the Brejui Mine, located in the municipality of Currais Novos-RN and coloured clay (yellow and purple) from Cotovelo Beach, municipality of Parnamirim-RN. Initially the raw materials were comminuted in a ball mill for 24 h, cleaned, and then sieved using a 200 mesh sieve. The formulation of the Composition was prepared by dry mixing, and homogenization in ball mill for 40 minutes with a moisture content of 5%. We prepared three formulations, as shown in table 1.

SAMPLES	KAOLINITIC CLAY %	SCHEELITE RESIDUE%	CLAY PURPLE %	CLAY YELLOW %
M - M_{11}, M_{12}	80	10	10	-
M – M_{21}, M_{22}	80	10	-	10
N - N_{11}, N_{12}	85	20	05	-
N – N_{21}, N_{22}	85	20	-	05
P - P_{11}, P_{12}	65	30	05	-
P – P_{21}, P_{22}	65	30	05	-

Table 1. *Sample compositions.*

Uniaxial compaction was subsequently performed in metal die with compaction pressure of 2.5 ton, forming samples of 60 x 20 x 5 mm. Figure 1 shows the design of the compaction die and in figure 2 presents an illustrative photo of the samples.

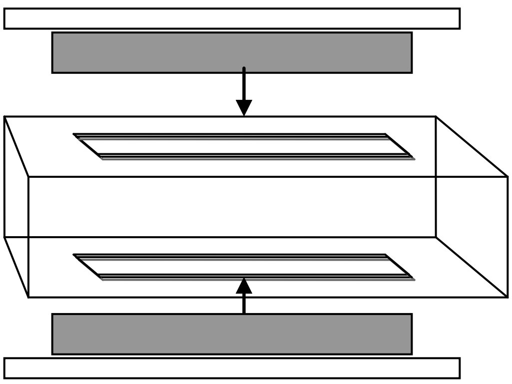


Figure 1. *Outline of the uniaxial die used in forming the samples.*

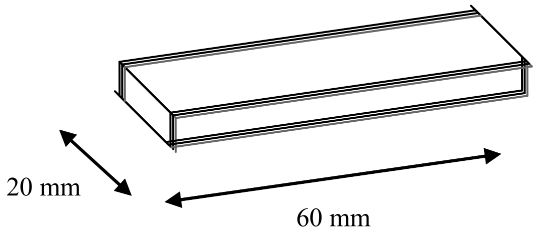


Figure 2. *Diagram illustrating the test piece.*

Sintering: After compaction, the test bodies were placed in an oven for 24 hours, at a temperature of about 100 °C, to eliminate the moisture present. The pieces were then sintered, according to the samples of 3 groups. The sintering temperatures used were 850 °C, 900 °C and 1000 °C, with a heating rate of 10 °C/min, for 60 minutes. The furnace used was a JUNG, model 0713 muffle furnace.

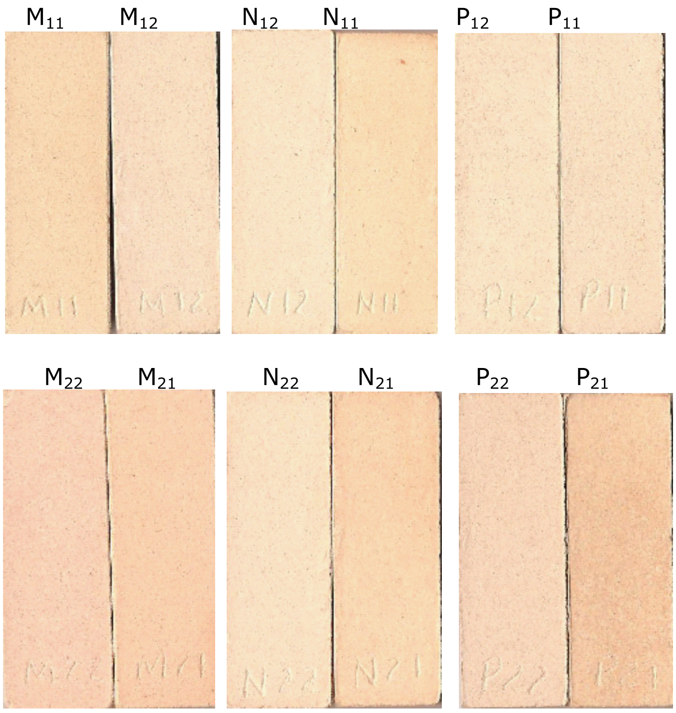


Figure 3: *Samples sintered at 900 and 1000 °C, with a heating rate of 10 °C/min.*

Water absorption: To determine the influence of the quantity of waste of ornamental stones on the water absorption it was necessary to weigh the test pieces after sintering and subsequent immersion in water for a period of 24 hours. The percentage of water absorption was determined in accordance with the following formula:

$$AA = \frac{mu - ms}{ms} \qquad (1)$$

Where:

AA = *AA (%)* – is the percentage of water absorption

Mu – wet mass of the samples

Ms – dry mass of the samples

Porosity test: This determines the relationship between the volume of open pores of the test piece and its apparent volume; the porosity formula is presented in Eq. 2:

$$PA = \frac{mu - ms}{mu - mi} \qquad (2)$$

Where:

PA = Apparent Porosity;

Mu = Weight of Saturated Sample;

Ms = Weight of Dry Sample;

Mi = Weight of Immersed Sample.

Linear Shrinkage test: This determines the relationship between the initial length of the piece and the length after the firing, the shrinkage linear formula is presented in Eq. 3:

$$\% \Delta L_s = \frac{Lo - Li}{Lo} \times 100 \qquad (3)$$

Where:

%ΔLs = Linear Shrinkage

Lo = Length of the Green Sample,

Li = Length After firing.

Resistance to three point bending: For this test, all samples had their length, width and height measured with a Mitutoyo digital calliper with a resolution of 0.05 mm. The samples were tested at a speed of 0.5 mm/min. The modulus of rupture was calculated using the following formula:

$$RF = \frac{3PL}{2bh^2} \qquad (4)$$

Where:

TRF = Fracture Strength;

F = Load at the moment of fracture;

L = Distance between the points of support;

b = Sample width;

h = Sample height.

X-ray fluorescence – XRF: Chemical analysis by EDX enables us to identify the chemical elements that make up the sample to be analysed. It was necessary to use this analysis to determine the percentage of the oxides present in the raw materials used, and thus to predict possible influences on the mechanical properties of the samples.

X-ray diffraction - XRD: X-ray diffraction allows us to determine the crystalline phases present and the relationship of their elements with their proportion in the form of oxides. The chemical-mineralogical characterization of clays and tailings and the determination of the properties that their components contribute to the ceramic mass allow it to be established what must be done to alter one or more of the properties of the ceramic body, and to improve the properties of the final product.

Particle size analysis: Particle size analysis of the raw materials used was performed by the CILAS 920 laser instrument.

3. RESULTS AND DISCUSSION

Table 2 details XRF chemical analysis of scheelite residue and table 3, chemical analysis of coloured clays.

Composition	% by weight
CaO	58.898
SiO_2	20.919
Fe_2O_3	9.774
Al_2O_3	5.579
MgO	2.024
K_2O	0.870
MnO	0.855
TiO_2	0.356
SrO	0.338
SO_3	0.147
ZnO	0.037
ZrO_2	0.025
Rb_2O	0.016

Table 2: *XRF of Scheelite residue.*

The composition of the scheelite tailings presents a high content of calcium oxide (CaO), in addition to magnesium oxide (MgO), which are fluxing agents and tend to diminish the refractoriness of the pieces, indicating the presence of calcite, dolomite and tuff masses that require grinding and sintering temperatures of approximately 1100 ^{o}C. The silica or silicon oxide (SiO2) indicates the presence of silicates and free silica. The clay minerals are silicates that come from feldspars. The free silica corresponds to quartz; alumina or aluminium oxide (Al2O3): this for the most part combined, forming the clay minerals; the iron oxide (Fe_2O_3), which is responsible for the red or yellowish colour, reduces plasticity, but also reduces shrinkage and facilitates abrasion. It reduces mechanical resistance and provides the glaze with hardness, since it fuses little during sintering.

Chemical Elements	% Yellow Coloured Clay	% Purple Coloured Clay
SiO_2	36.384	42.754
Al_2O_3	35.890	40.697
Fe_2O_3	26.893	11.798
MgO	-	0.375
K_2O	0.315	0.313
SO_2	-	-
SO_3	0.117	0.063
Other elements	0.401	4.00

Table 3: XRF *Coloured Clays.*

Analysis of the chemical test results indicates that there are high levels of silicon oxide (SiO_2) and aluminium oxide (Al_2O_3) in the coloured clays, demonstrating that these clays are of a kaolinitic type. Their composition also contains clay minerals of the mica or smectite group, which display a high rate of plasticity. Iron oxide (Fe_2O_3) is found in higher concentration in the yellow clays. This fact shows its natural tendency to transform into orange after sintering.

Figure 4 shows the X-ray powder diffractogram of scheelite tailings.

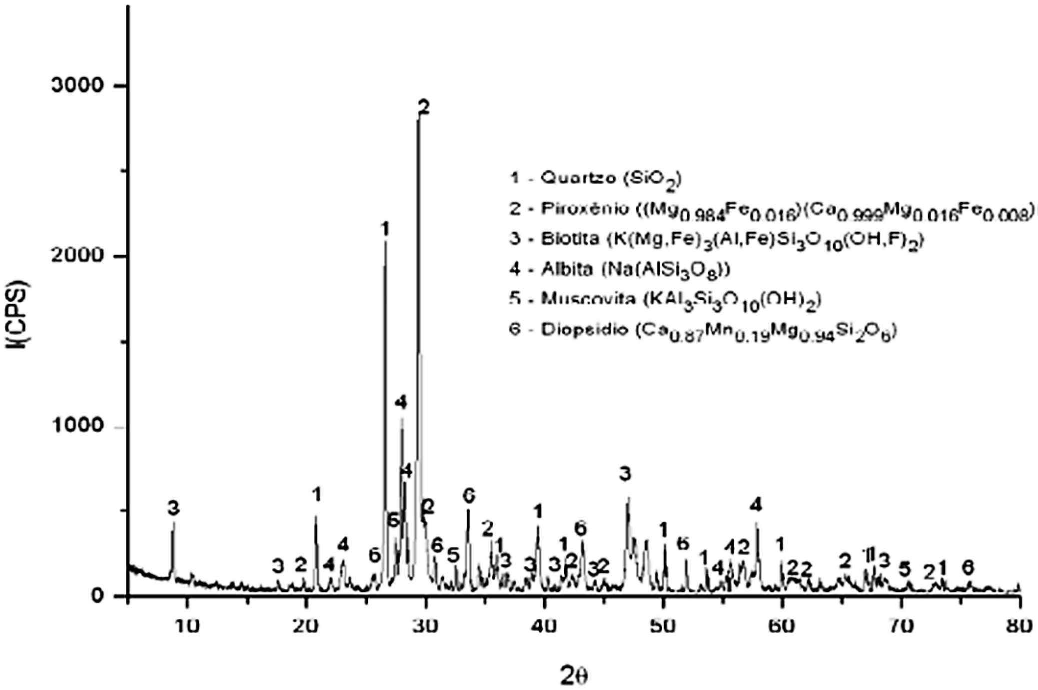


Figure 4: *X-ray diffraction patterns of the raw materials.*

Analysis of the XRD results indicates that the main peaks found correspond to the oxides found by XRF - Table 2.

Table 4 details the chemical analysis of kaolinitic clay in Boa Saúde-RN.

Oxides	(%)
SiO_2	76,22
Al_2O_3	21,27
Fe_2O_3	1,04
K_2O	0,81
TiO_2	0,37
SO_3	0,16
CaO	0,10

Table 4*: Chemical Analysis of the clay from the municipality of Boa Saúde (RN).*

The chemical composition presented in table 1, shows a high content of silicon oxide (SiO_2 = 76.22%) and of alumina (Al_2O_3 = 21.27%). It was observed that the relation alumina/silica always remains below 1, and is thus a raw material for mullite at high temperatures, which allows the improvement of the mechanical properties of the sintered piece. We observed a low content of iron oxide (Fe_2O_3 =1.04%), which makes the colour after sintering acquire a strong tone of cream, of course suggesting the possibility of use in white ceramics. The chemical analysis revealed a very low content of K_2O (0.81%), indicating the rare presence of illite.

Figure 5 shows the porosity test performed on the samples. Note that there was a variation, albeit not a significant one, in apparent porosity with the addition of the mineral tailings.

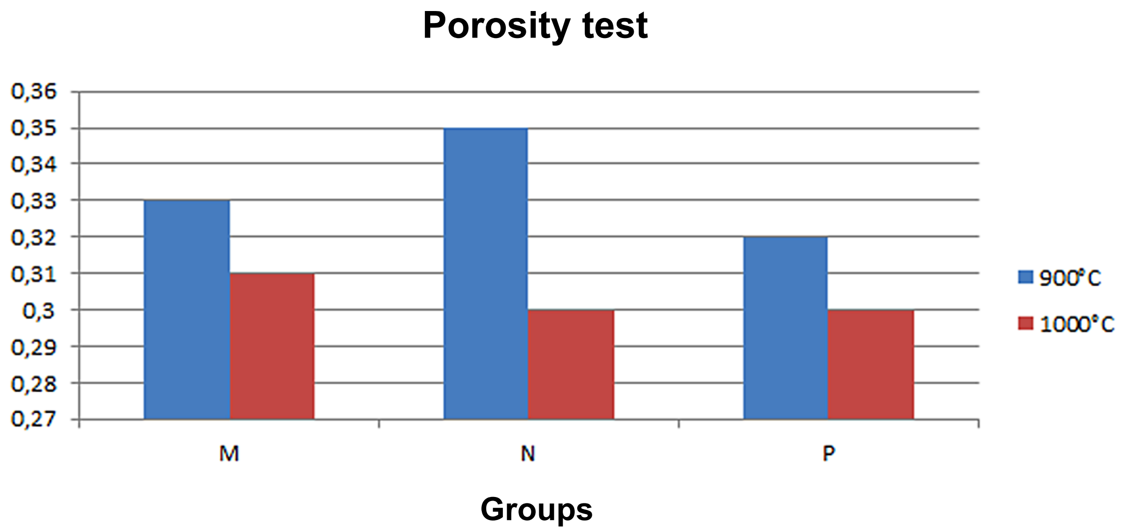


Figure 5: *Porosity test.*

It is possible to note that the higher the firing temperature, the lower the quantity of pores. The samples had NO lower number of pores at a temperature around 1000°C, while the other compositions obtained values close to this. Figure 6 shows the Water Absorption percentage as a function of the mineral and reject content with the firing temperature.

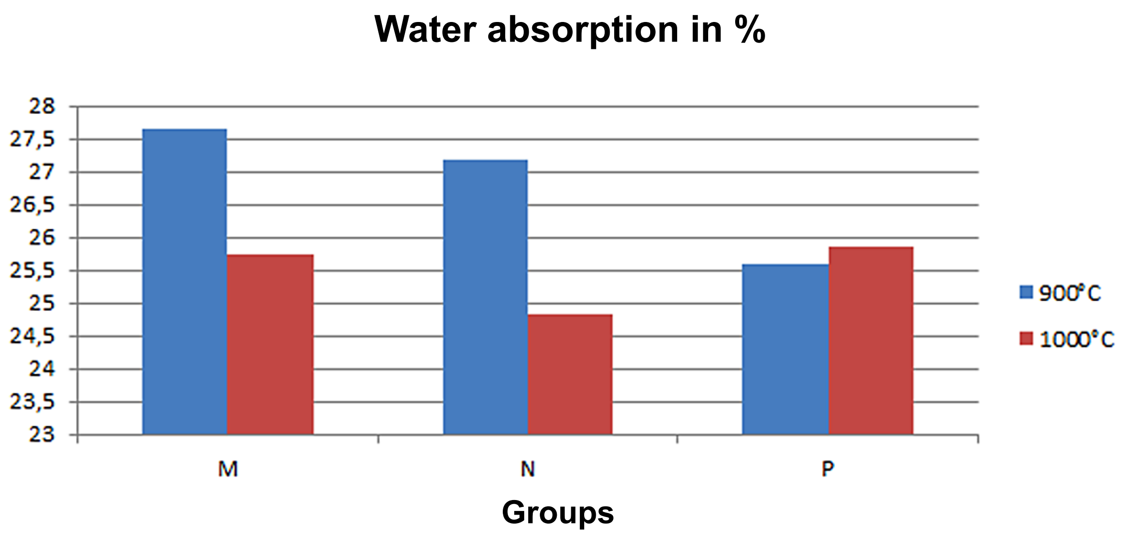


Figure 6: *Water Absorption in the samples sintered at 900 °C and 1000 °C for 1 hour.*

It is clear that the higher the temperature, in general, the greater the decrease in water absorption, since there is a reduction in the porosity of the samples. The lowest water absorption has occurred in the group N samples.

Figure 7 shows the results of the test Linear Shrinkage performed in standard samples and samples with the mineral tailings.

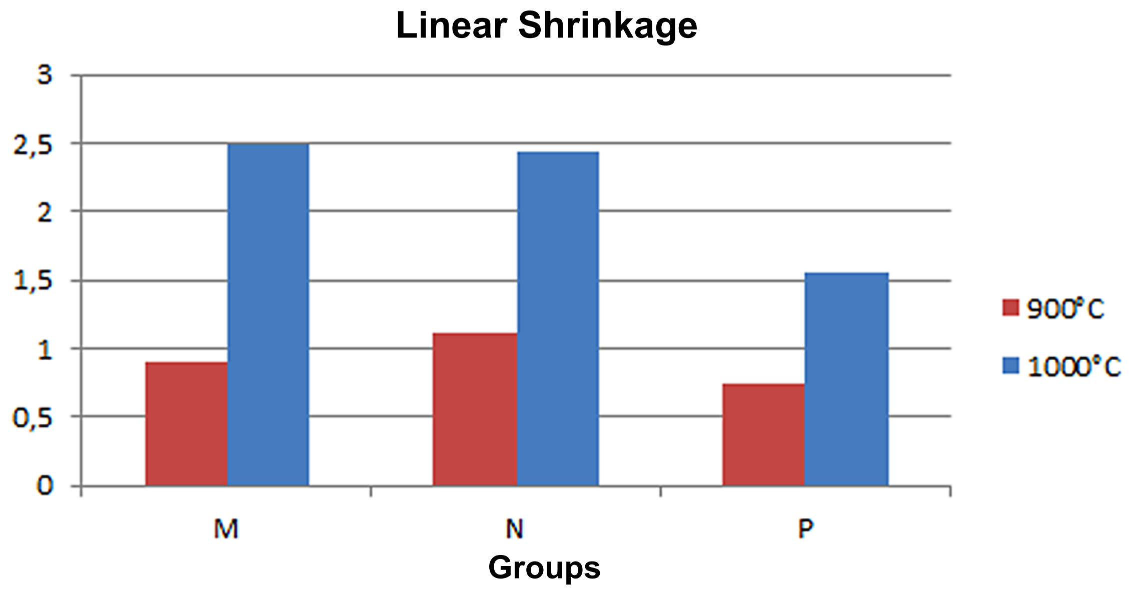
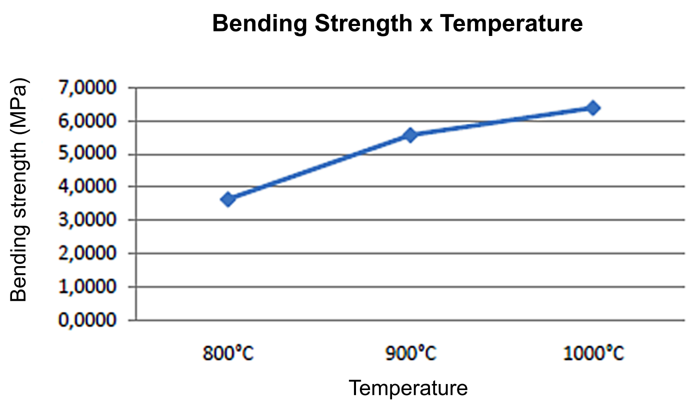


Figure 7: *Linear Shrinkage in samples sintered at 900°C and 1000°C for 1 h.*

It may be observed that the lowest linear shrinkage values were obtained for the temperature around 900 ºC. Higher temperatures caused a greater drop, of about 20 and 30% for this reject. The increase in mineral reject in the ceramic mass led to a sharp reduction in linear shrinkage of all samples, and samples P had the lowest rates of linear shrinkage.

Figure 8 shows the change in fracture strength of standard samples of kaolinitic clay from Boa Saúde at temperatures of 800, 900 and 1000 ºC.

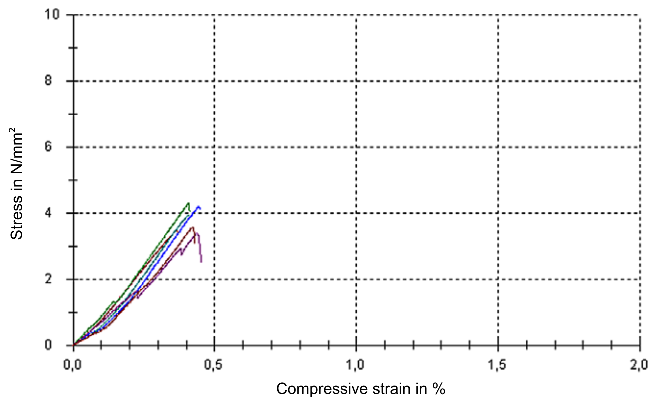


TEMPERATURE ºC	Fbreak MPa
800	3,6349
900	5,5630
1000	6,3783

Figure 8: *Bending strength of the sintered bodies at 800, 900 and 1000 ºC.*

In the measurements of the fracture strength (TRF) of the samples of kaolinitic clay, it may be observed that at higher temperature the ceramic material is more uniform so that the bending strength of the test specimens also rises. These figures show a substantial increase in the closing of the pores. The test pieces provide values well above the recommended minimum; whose limit values for use in structural applications are higher than 2.0 MPa.

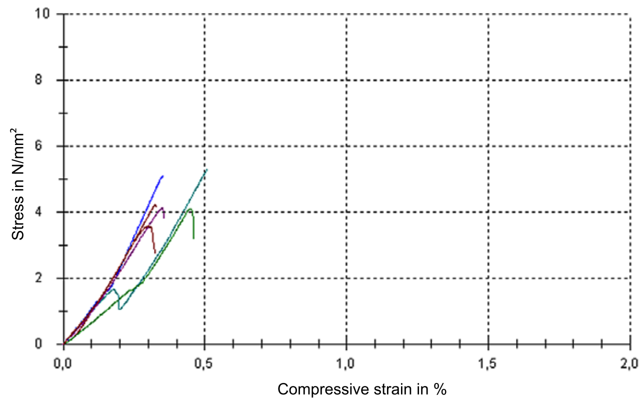
Figure 9 illustrates the variation of the fracture strength of the samples sintered at 900 °C.



SAMPLES	Fbreak MPa
M_{12}	3,37
M_{22}	4,02
N_{12}	4,11
N_{22}	3,90
P_{12}	2,50
P_{22}	3,05

Figure 9: *Bending test performed on the samples sintered at 900 °C for 1 hour.*

Figure 10 illustrates the variation of the fracture strength of the samples sintered at 1000°C.



SAMPLES	Fbreak MPa
M_{12}	4,22
M_{22}	4,11
N_{12}	5,09
N_{22}	5,29
P_{12}	4,12
P_{22}	3,58

Figure 10: *Bending test performed on the samples sintered at 1000 °C for 1 hour.*

It is clear that the higher the firing temperature, therefore reducing the amount of pores, the greater the bending strength. The type N samples, with 10% tailings, showed the best results, although these were close to the values achieved by other compositions. In general, high levels of tailings provide a reduction in bending strength. Owing to the chemical composition of the tailings, they a present a high content of oxides that act fluxes, in addition to other oxides such as Al_2O_3 and Fe_2O_3 which probably contributed to the increase in the resistance of the final product. The values achieved were, in general, higher than in the samples without rejects, and higher than those recommended by the standards for application in structural ceramics.

4. CONCLUSIONS

High levels of mineral tailings would affect conventional ceramic processing, because, in general, these products are produced by extrusion (tiles, blocks, ...). The difficulty is due to the differences in plastic behaviour between the clay and the tailings (which reduce plasticity), making the manufacturing process more difficult. In addition, high levels of tailings would favour a reduction in mechanical strength of the final product. It was observed that, at the firing temperatures used, the results obtained were higher than those of the standard ceramic mass used, suggesting that the use of reject mineral with percentages around 20-30% could be technically feasible and economically interesting. Another important factor is to redirect and better use natural resources, providing an alternative to the usual disposal route of mineral residues, in addition to adding value to the material produced through the improvement of their physical and mechanical properties.

It was evident that the research into the use of reject minerals, by their incorporation into the clay body, could possibly be of great importance; in addition to reusing the waste discarded by the mining industry, they would contributing positively to the environmental issue.

In relation to the incorporation of the coloured (yellow and purple) clay, it is clear that it was possible to obtain several tones for the final product, ranging from light-coloured beige to a more intense yellow in the case of the yellow clay, and a darker or lighter pink, depending on the purple clay content. The levels used were satisfactory and the coloration was quite interesting on a commercial level, a being a differentiating factor.

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