PRODUCTION OF TILES WITH NATURAL COLOUR FOR APPLICATIONS IN CIVIL CONSTRUCTION

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ABSTRACT

In Rio Grande do Norte - Brazil, the production of ceramics occupies an important position in the capital goods industry, contributing to the development of local economy, only producing tiles, bricks and blocks of red ceramic. In the most recent geological map of Rio Grande do Norte, there are over 2 thousand points that were analyzed, which produced or produce some kind of mineral. The Rio Grande do Norte shows is characterized by the presence of clay with the natural colour, presenting various oxides that provide the variety of colours (white, yellow, purple, orange, among others), mainly in the coastal region. The variety of shades of clay is due to presence of oxides such as titanium. Depending on firing time and temperature, you can get different colours, without the need for incorporation of other ceramic oxides, ceramic pigments and painting ceramics, in finishing pieces. The purpose of this study is to produce tiles using a ceramic kaolinitic body mixed with clays with a natural colour. Thus, we prepared four groups of samples with

percentages of 20, 30, 40 and 50% natural colour clay. The samples were sintered at 900oC, 1000oC and 1100oC. Tests were performed to determine the colorimetry, porosity, plasticity, in addition to thermal analysis and optical microscopy of the final product. These products will be used for applications in internal environments of Environmental Building.

1. INTRODUCTION

The ceramic industry has in its chemical process, raw materials (clay, kaolin, quartz, feldspar, etc.) that are processed in an operational sequence. For the manufacture of ceramics used to clay, which is generated from decomposition, over millions of years, rocks and other substances feldspathic features of this decomposition is very abundant in the terrestrial crust. Clays are natural materials, earth, which are particles with diameters generally less than 2 μm and formed from chemically hydrated silicates of aluminium, iron and magnesium. They are made up of extremely small crystalline particles of a limited number of minerals known as clay minerals. Any clay can be composed of a single clay or a mixture of several of them. Besides them, the clays may also contain organic matter, soluble salts, particles of quartz, pyrite, calcite, mineral water and other minerals amorphous [1].

Kaolin is formed mainly by kaolinite, which is generally white or nearly white, due to the low iron content. In general, you can make other substances in the form of impurities in trace amounts to the range of 40-50% by volume, having, in general, sand, quartz, flakes of mica, feldspar, iron oxides and titanium. The chemical formula of the mineral kaolinite group is Al_2O_3 $.mSiO_2.nH_2O$, where m ranges 1 to 3 and n from 2 to 4. It is one of the most important and probably one of the six most abundant mineral in the top of the crust (depth up to 10m). World reserves are quite abundant and widely distributed. However, only four countries hold approximately 95.0% of an estimated total of approximately 14.2 billion tons: United States (53.0%), Brazil (28.0%), Ukraine (7.0%) and India (7.0%). Kaolin has many industrial applications and new uses are constantly being researched and developed. It is an industrial mineral of special features because it is chemically inert in a wide pH range, has great power when used as cover or as a pigment extender in applications and cargo cover is soft and not abrasive, have low conductivity of heat and electricity, and cost is low compared to other competing materials. Currently their main application in the ceramic industry is the composition of the ceramic. [2]

The state of Rio Grande do Norte has a diverse range of coloured clays that are used by local artisans in the production of handicrafts and frequently used method for glazing of ceramics [3]. The clays were stained a natural colour without the addition of oxides or dyes, are in white, red, purple and yellow, which are easily located on the beaches and cliffs on the coast of the state. According to Mello, the main factors that control the properties of clays are the mineralogical composition of clay minerals and clay minerals and their particle size distribution of particles, the nature, organic content and textural characteristics of the clay [4].

The purpose of this work is to produce ceramic tiles using ceramic body home kaolinitic clays mixed with natural colour. Thus we have prepared four groups of samples with percentages of 20, 30, 40 and 50% natural clay colour. The samples were sintered at 9000C, 10000C and 1100º C. Tests of colorimetry, porosity, plasticity, thermal analysis and optical microscopy of the final product. These cards will be used for application in the setting of internal environments of Construction.

2. EXPERIMENTAL AND MATERIALS

Preparing the Samples. For this work we used ceramic body kaolinitic City Parelhas - RN, clays and natural colour, from the cliffs of Praia de Cutuvelo, municipality of Parnamirim-RN. The ceramic paste was comminuted and sieved to obtain a particle size of 65 mesh. The coloured clays have undergone a process of washing and settling, removing the excess salts present that could interfere in the process of sintering. They were then comminuted and sieved, yielding a particle size compatible with the ceramic mass. After the step of screening the colourful clays were calcined in an oven-type furnace at a temperature around 5000C for 1 hour, eliminating all organic material present. In this study worked with clay, yellow, red and purple.

We studied five different percentages to analyze the influence of coloured clay on the kaolinite ceramic body, where Group A had only a ceramic body - composed of 50% Fat Clay + 50% Lean Clay. The other groups that were formed and their composition in terms of the ceramic mass and the coloured clays are shown, in percentages, in table 1.

Group	Percent Ceramic Mass	Percentage of Clay Colour
A	100%	0%
B	80%	20%
C	70%	30%
D	60%	40%
E	50%	50%

Table 1. Composition of the samples.

In the process of sample preparation, the groups consisting of kaolinite ceramic mass and percentages of coloured clays were mixed in planetary mill for a period of 40 minutes to ensure adequate homogenization of the samples.

We made a total of 45 samples, uniaxially in a Marcon hydraulic press up to 15 tonnes, using a 60mm x 20mm rectangular steel die and compaction pressure of 3 tons.

Figure 1 shows the design of the compression die and figure 2 presents a drawing of the sample.

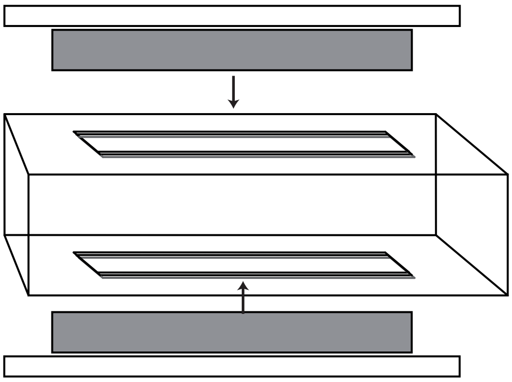


Figure 1. Schematic of the uniaxial matrix used in sample preparation.

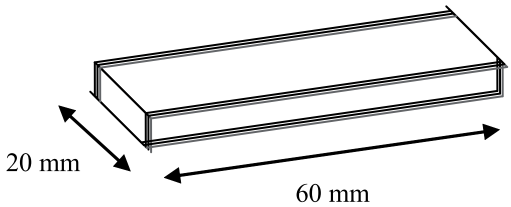


Figure 2. Schematic picture of the samples.

Absorption Test: Establishes the relationship between the mass of liquid absorbed by the test piece and the weight of the dry specimen; the formula used is shown in equation 1:

$$AA = \frac{mu - ms}{ms}$$

Equation 1.

Where:

AA = Water Absorption.

Mu = Weight of the Wet Test Piece;

Ms = Weight of the Dry Test Piece.

Porosity Test: it is the relation between the volume of open pores of the test piece and its apparent volume; the formula used to determine porosity is shown in equation 2:

$$PA = \frac{mu - ms}{mu - mi}$$

Equation 2.

Where:

PA = Apparent Porosity.

Mu = Weight of the Wet Test Piece.

Ms = Weight of the Dry Test Piece.

Mi = Weight of the Immersed Test Piece.

Linear Shrinkage Test: this is the relation between the initial length of the green test piece and its length after firing; the formula used to determine linear shrinkage is shown in equation 3:

$$\% \Delta L_s = \frac{Lo - Li}{Lo} \times 100$$

Equation 3.

Where:

%ΔLs = Linear Shrinkage.

Lo = Length of the Green Test Piece.

Lii = Length after Firing.

Three Point Bending Test: Consists of applying an increasing load in the centre of the specimen, supported at two points. The load applied part of an initial value of zero and increases slowly until the break of the specimen. In this test we used a bar supported at each end, with the application of pressure in the centre of the distance between the supports, i.e., there were three load points, which is why it is called three point bending. The samples were tested in a universal mechanical testing press with a loading speed of 0.5 mm/min. The bending strain is expressed in MPa and defined by equation 4:

$$MRF = \frac{3PL}{2bh^2}$$

Equation 4.

Where:

MRF = Bending Strength.

P = Maximum Breaking Load.

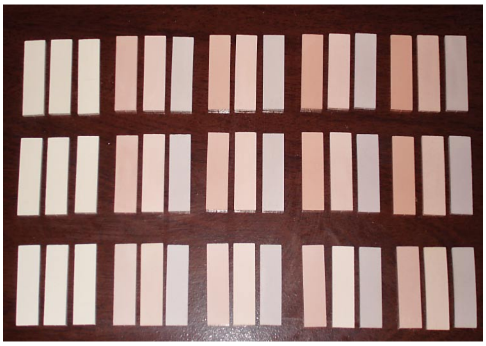
L = Distance between Supports.

b = Width of the Sample.

h = Height of the Sample.

Sintering: After compaction the samples were placed in an oven for a period of 24 hours at a temperature of around 1000C, to remove any moisture. For sintering, the samples are subdivided into 05 (five) groups, consisting of 09 (nine) samples of each group. The sintering temperatures used were 900°C, 10000C and 1100º C, with a heating rate of 5ºC/min for 60 minutes. The kiln used was the JUNG model 0713 type furnace. Figure 3 shows the compacted and sintered samples.

A B C D E



a) Sintering at 900ºC, b) Sintering at 1000ºC, c) Sintering at 1100ºC.
Figure 3. Samples sintered at 900º, 1000º and 1000ºC, at a heating rate of 5ºC/min.

Dispersive X-ray Fluorescence Spectra - EDX. Chemical analysis by EDX can identify the chemical elements that make up the sample to be analyzed. Thus, it became necessary to use such analysis is to determine the percentage of each element used in the waste and, thus, predict their possible influences on the mechanical properties of samples.

3. RESULTS AND DISCUSSION

In table 2 we have the chemical analysis of coloured clays, made by Fluorescence X-ray - EDX.

Oxides	In Red Clay %	In yellow Clay %	In Purple Clay %
SiO_2	38.515	36.384	42.754
Al_2O_3	40.602	35.890	40.697
Fe_2O_3	16.023	26.893	11.798
MgO	0.214	-	0.375
K_2O	0.341	0.315	0.313
SO_3	0.078	0.117	0.063
Other constituents	4.227	0.401	4

Table 2. Result of Chemical Analysis in coloured clay.

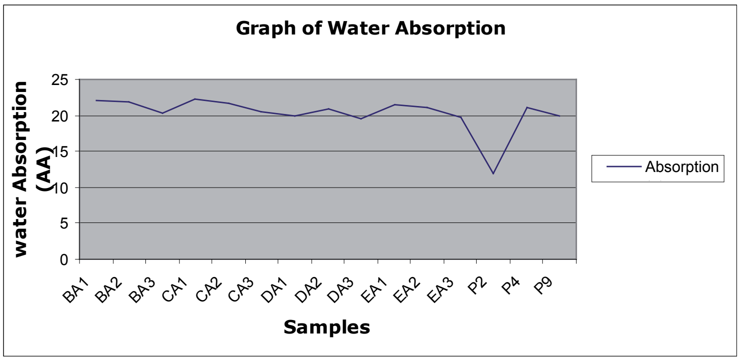
All coloured clays showed high levels of oxides of silicon and aluminium (SiO_3 and Al_2O_3). Analysis of the SiO_3/Al_2O_3 ratio shows that these clays are of the kaolinitic type. [5]

The MgO content in the red and purple clays can be an indication of the presence of clay minerals of mica and / or smectite clay.

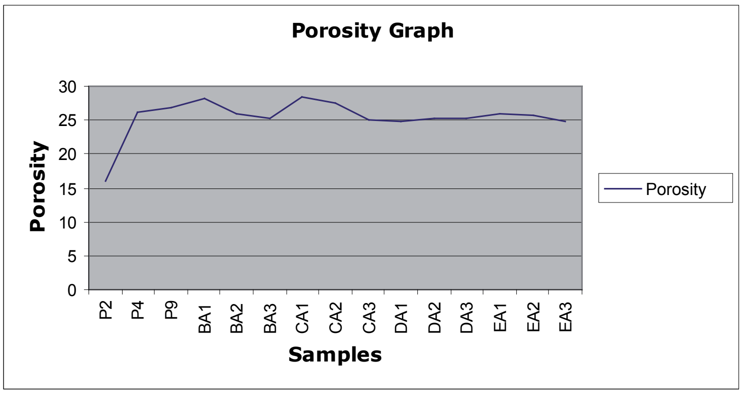
The iron oxide present in most clays reduces the plasticity, but also reduces shrinkage and facilitates drying. It also decreases the mechanical strength, but the little that melts in sintering provides the glaze with hardness. This element is present in three clay colours and the percentage content of iron is found with higher rate in yellow clay, which indicates the trend of fresh clay to become orange after burning. [6]

Graphs 1 and 2 show, respectively, the Water Absorption and Apparent Porosity of the standard samples and samples with 20, 30, 40 and 50% clay colour after sintering.

It may be observed that higher firing temperatures provide a reduction of these pores, which reduces the absorption of water. In the test, the samples with clay colour - yellow, had a percentage of absorption around 20, showing it is satisfactory for this application.



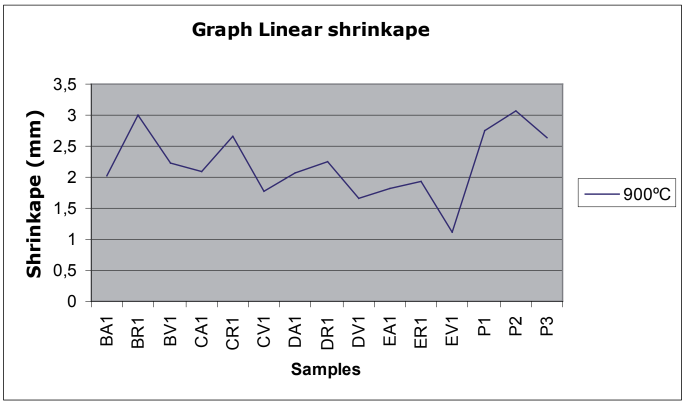
Graph 1. Water absorption in standard samples and yellow-coloured clay, after sintering at 900, 1000 and 1100ºC.



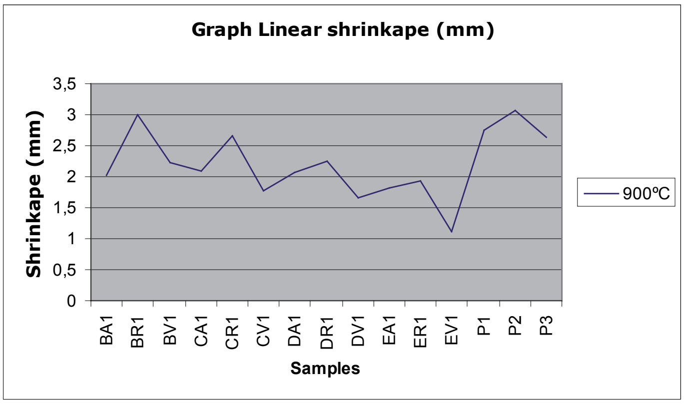
Graph 2. Apparent porosity of the standard samples and yellow-coloured clay after sintering at 900, 1000 and 1100ºC.

In graph 2 we can see that there was an increase in porosity when the coloured clay increased in kaolinitic ceramic sample. Moreover, this was reduced with increasing temperature. The average porosity was around 25, with the compositions B, C and D showing the best results.

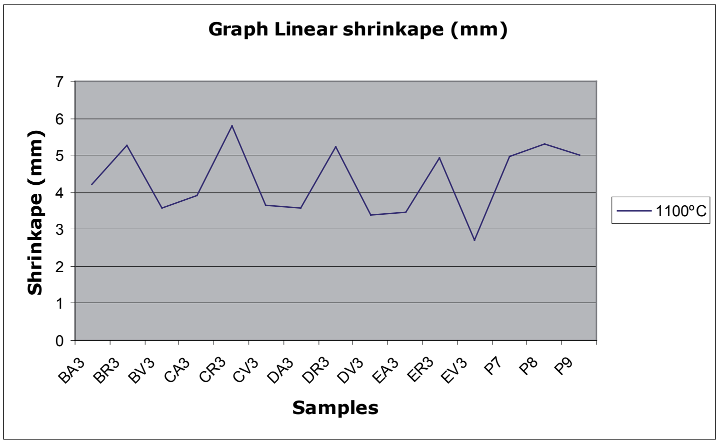
Graphs 3, 4 and 5 show the linear shrinkage of the reference samples and the samples with percentages of coloured clay at sintering temperatures of 900, 1000 and 1100ºC.



Graph 3. Linear shrinkage of samples sintered at 900ºC, for 1 hour.



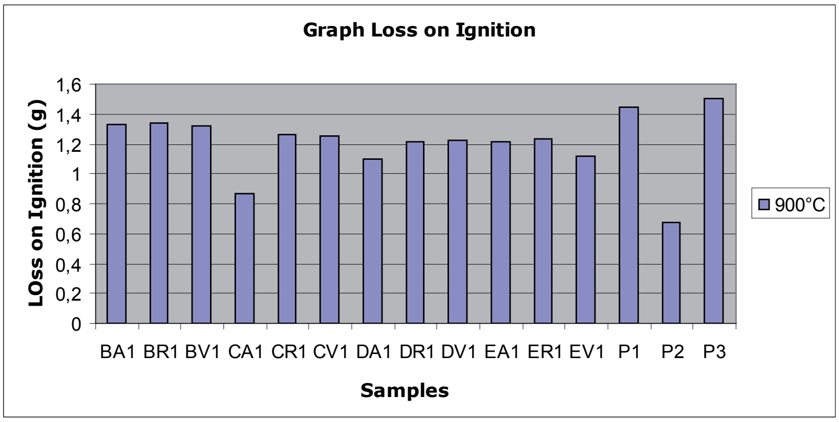
Graph 4. Linear shrinkage of samples sintered at 1000ºC, for 1 hour.



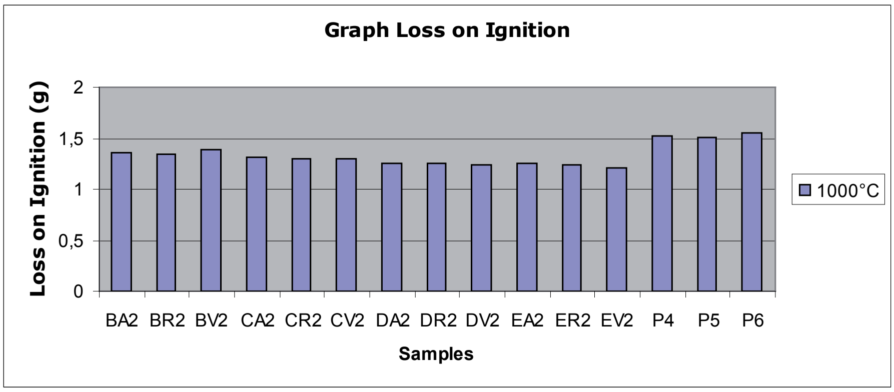
Graph 5. Linear shrinkage of samples sintered at 1100ºC, for 1 hour.

It is observed that the samples consist only of ceramic sample kaolinite showed higher linear shrinkage and higher temperatures cause a greater shrinkage in the ceramic samples. The addition of coloured clay to ceramic sample kaolinite brought about a marked reduction in linear shrinkage of all samples, and the yellow clay and red ones that showed the lowest rate of linear shrinkage.

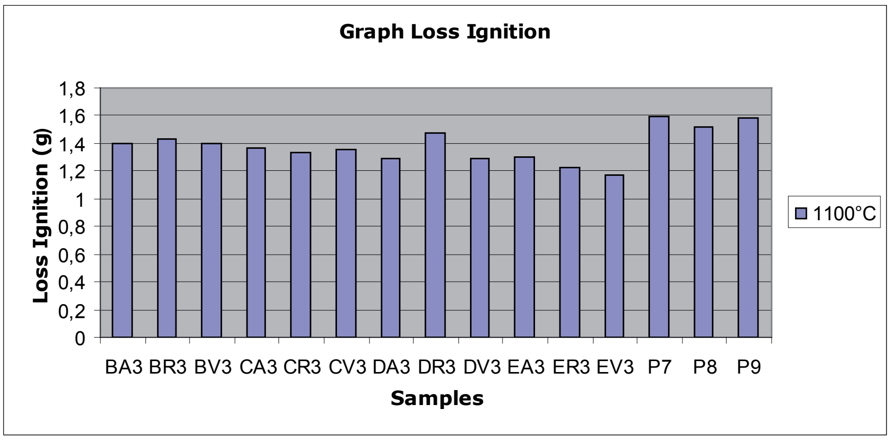
In graphs 6, 7 and 8 have the Loss on Ignition of the standard samples and clay-coloured, at 900, 1000 and 1100ºC.



Graph 6. Loss on ignition of samples sintered at 900ºC, for 1 hour.



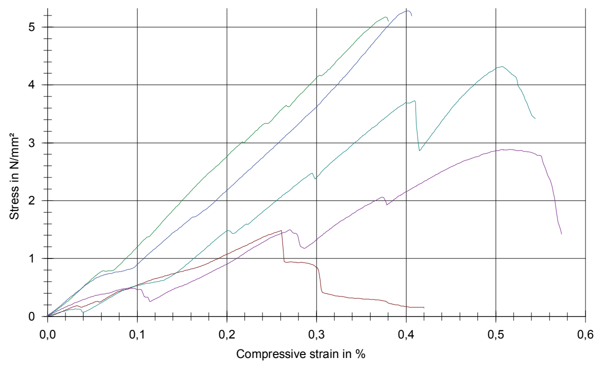
Graph 7. Loss on ignition of samples sintered at 1000ºC, for 1 hour.



Graph 8. Loss on ignition of samples sintered at 1100ºC, for 1 hour.

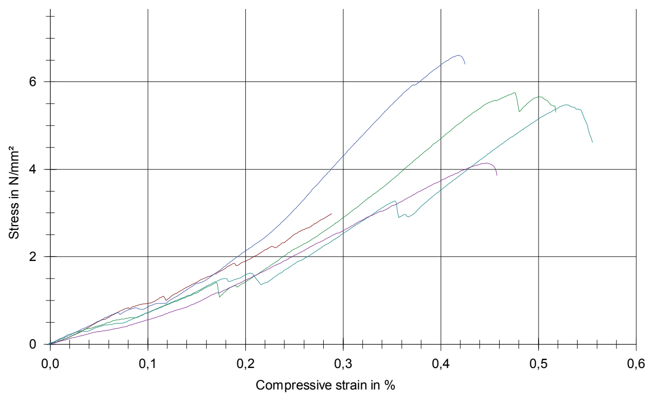
Note that the largest loss on ignition occurs in the standard samples, at all firing temperatures. Fire Loss in grams remained stable with a loss of between 1.2 and 1.4 g for the compositions B, C, D and E. The greatest losses were found for samples with composition B (around 20% clay coloured).

Figures 4, 5 and 6 illustrate the variation of the tensile strength of the standard samples with concentrations of 20% to 50% clay colour - red.



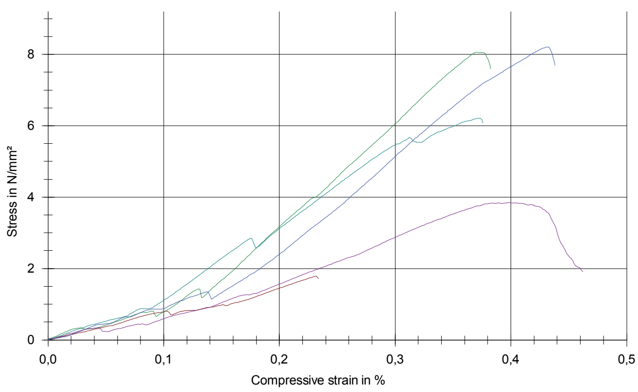
	Fmax.	FBreak
Ref	MPa	MPa
P1	1.48	-
Cv1	5.17	5.10
Bv1	5.28	5.19
Dv1	4.32	3.42
Ev1	2.88	1.42

Figure 4. Flexural test performed in the samples sintered at 900ºC, for 1 hour.



	Fmax.	FBreak
Ref	MPa	MPa
P5	2.99	2.99
Bv2	5.75	5.31
Cv2	6.61	6.41
Dv2	5.48	4.61
Ev2	4.14	3.86

Figure 5. Flexural test performed in the samples sintered at 1000ºC, for 1 hour.

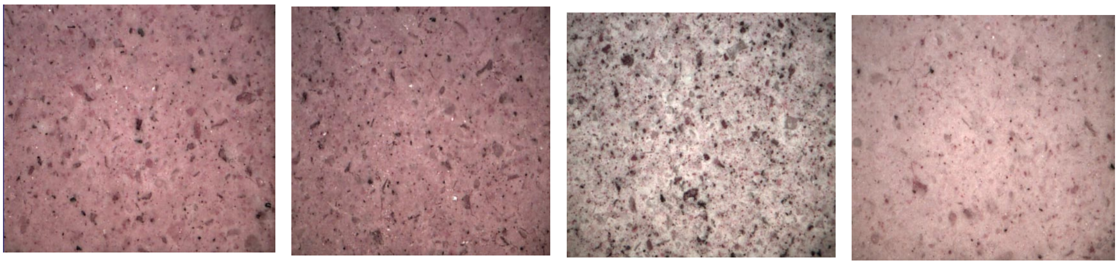


	Fmax.	FBreak
Ref	MPa	MPa
P7	1.79	1.72
Bv3	8.07	7.60
Cv3	8.21	7.71
Dv3	6.21	6.08
Ev3	3.85	1.92

Figure 6. Flexural test performed in the samples sintered at 1100ºC, for 1 hour.

It is observed that the higher the firing temperature, thus reducing the amount of pores present, the greater the bending strength. Compositions B and C showed the best results in all the strength tests, particularly at higher sintering temperatures.

Figure 7 shows the representative micrographs of samples of ceramic clays with various percentages of clay natural colour - yellow, red and purple.



a) b) c) d)

Fig. 7. Micrographs of samples sintered at 1000 and 1100ºC, for 1 h, with a magnification of 100x: a) Sample CA2 – Composition C, yellow coloured clay, sintered at 1000ºC; b) Sample DA3 – Composition D, yellow coloured clay, sintered at 1100ºC; c) Sample CR2 – Composition C, purple coloured clay, sintered at 1000ºC; d) Sample BV3 – Composition B, red coloured clay, sintered at 1100ºC.

The structure common to all samples can be seen in micrographs, with good homogenization of those held in the planetary mill and the characteristic colour of each one after firing, nitrogen oxides present and firing temperature. The black dots denote the presence of pores.

4. CONCLUSIONS

Standard samples, consisting mainly of a ceramic sample of kaolinite, showed the characteristic colour of kaolin, or white, tending to the cream at temperatures above 10000C. Clays collected from the beach Cutuvelo/RN have natural pigments with different compositions. Such compositions directly influence the natural colour of clay. Iron is the main agent and pigments, during firing, making the colour of the clay change. [7]

Colour stability is maintained the temperature of 900ºC to 1100ºC, intensifying at higher temperatures.

The combination of clay with coloured ceramic sample provided a kaolinitic emergence of a range of tones, ranging from light to the most intense, which enriches and provides a wide variety of applications in the decorative piece.

The incorporation of the clay coloured ceramic sample kaolinitic significantly improved the mechanical properties of the samples, where the addition of 20 to 30% of coloured clay (composition B and C) showed the best results and thus the percentage would be advisable for future application to obtain ceramics with different and unique colours. The use of these clays in combination with ceramic clay samples proved to be very interesting and technically feasible, and serve a niche market not yet explored. Economically this venture proves to be interesting and will facilitate the rational use of this feature still little explored.

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