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PRODUCTION TILES WITH NATURAL COLOR FOR APPLICATIONS IN CIVIL CONSTRUCTION

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Abstract

In Rio Grande do Norte - Brazil, the production of ceramics occupies a position of the capital goods industry, contributing to the development of local economy, only producing tiles, bricks and blocks of red ceramic. The most recent geological map of Rio Grande do Norte, there are over 2 thousand points that were analyzed produced or produces some kind of mineral. The Rio Grande do Norte shows a characteristic that is the presence of clay with the natural color, presenting various oxides that provide the variety of colors (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. Ranging is the time and temperature of burning, you can get different colors, without the need for incorporation of other ceramic oxides, ceramic pigments and painting ceramics, when the finishing of parts. The purpose of this study is to produce tiles using ceramic body of origin kaolinitic clays mixed with natural color. Thus, we prepared four groups of samples with percentages of 20, 30, 40 and 50% natural color of clay. The samples were sintered to 900°C, 1000°C and 1100°C. Tests were performed colorimetry, porosity, plasticity, thermal analysis and optical microscopy of the final product obtained. These cards will be used for application in internal environments of Environmental Building.

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 chemically hydrated silicates of aluminum, iron and magnesium. Is comprised 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, with 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 from 1 to 3 in 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 colored 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 color 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, content of organic 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 color. Thus we have prepared four groups of samples with percentages of 20, 30, 40 and 50% natural clay color. The samples were sintered at 900^0C, 1000^0C and 1100^0 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.

Experimental and Materials

Preparing the Samples. For this work we used ceramic body kaolinitic City Parelhas - RN, clays and natural color, 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 colored 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 colorful clays were calcined in an oven-type furnace at a temperature around 500^0C 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 clay colored ceramic body in kaolinite, where Group A had only ceramic mass - composed of 50% Fat Clay + 50% Lean Clay - and other groups formed and its composition by mass ceramics and the colored clays, and the percentages shown in Table 1.

Table 1. Composition of the samples.

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

In the process of sample preparation, the groups consisting of kaolinite ceramic mass and percentages of colored 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 hydraulic press Marcon up to 15 tonnes, using an array of steel rectangular 60mm x 20mm and compaction pressure of 3 tons. In Figure 1 we have the design of the array of compression and figure 2 we have a drawing showing the sample.

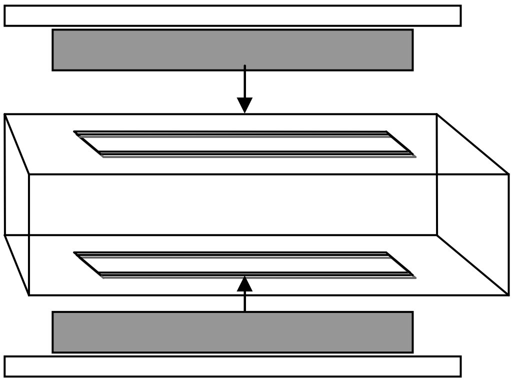


Figure 1. Schematic of uniaxial matrix used in the preparation of samples.

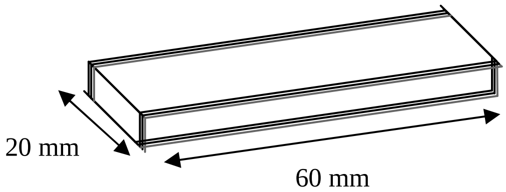


Figure 2. Schematic picture of the samples.

Assay of Absorption: Establishes the relationship between the mass of liquid absorbed by the body-of-proof saturated liquid and the weight of dry specimen, the formula used is shown in Equation 1:

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

Where:
AA = Water Absorption
Mu = Weight of the Sample of Humid Test;
Ms = Weight of the Dry Sample of test.

Assay of Porosity: it is the relation enters the volume of open pores of the body-of-test and the apparent volume of the same formulates, it of the porosity is shown in the Eq. 2:

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

Where:
PA = Apparent Porosity
Mu = Weight of the Humid Body of Test
Ms = Weight of the Body of Dry Test
Mi = Weight of the Immersed Body of Test

Assay of Linear Retraction: it is the relation enters the initial length of the green body-of-test and the length after the burning formulates, it of the linear retraction is shown in the Eq. 3:

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

Where:
%ΔLs = Linear Retraction
Lo = Length of the Body of Test the Green
Lii = Length After Burns

Assay of Flexão in Three Points: Consists of applying an increasing load in the center 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 bisupported with application of pressure in the center of the distance between the supports, ie, there were three points of load, hence calling it an experiment with three point bending. The samples were tested in a press universal mechanical test with loading speed of 0.5 mm/min.. The bending strain is expressed in MPa and defined by Equation 4:

$$MRF = \frac{3PL}{2bh^2} \quad (4)$$

Where:
MRF = Resistance the flexão
P = Maximum load of Rupture
L = In the distance between the Supports
b = Width of the Sample
h = Height of the Samples

Sintering: After compaction the samples were placed in an oven for a period of 24 hours at a temperature of around 100^0C, for elimination of moisture present. Were later sintering, the samples are subdivided into 05 (five) groups, consisting of 09 (nine) samples of each group. The sintering temperatures used were 900°C, 1000^0C and 1100º C, with a rate of warming of 5ºC/min. for 60 minutes. The oven used was the type furnace, brand JUNG - model 0713. In Figure 3 we have the samples compacted and sintered.

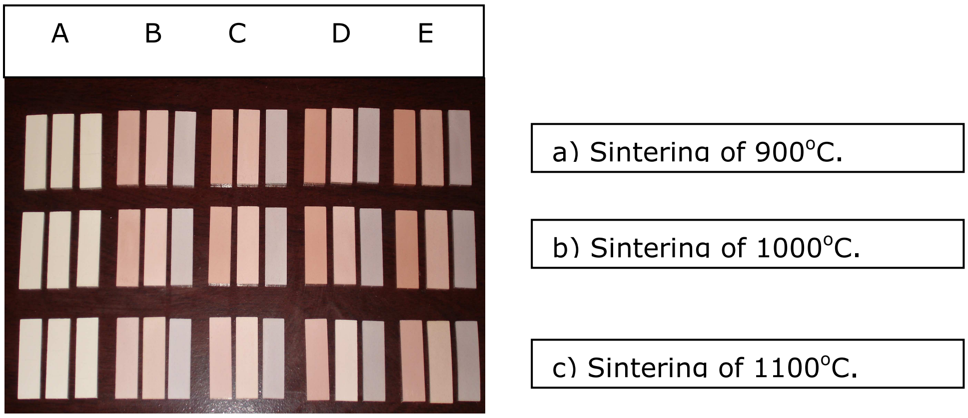


Figure 3: Samples sintered at 900^o, 1000^o e 1000^oC, with rate heating 5^oC/min..

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.

Results and Discussion

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

Table 2. Result of Chemical Analysis in colored clay.

Oxides	In Red Clay%	In yellow Clay%	In Purple Clay%
SiO_2	38,515	36,384	42,754

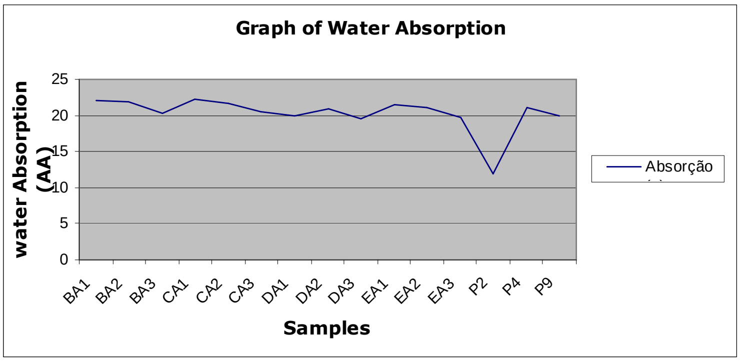
Al_2O_3	40,602	35,890	40,697
Fe_2O_3	16,023	26,893	11,798
MgO	0,214	-	0,375
K_2O	0,341	0,315	0,313
SO_3	0,078	0,117	0,063
Other constituents	4,227	0,401	4

All colored clays showed high levels of oxides of silicon and aluminum (SiO_3 e Al_2O_3). Analyzing the relationship SiO_3/Al_2O_3, realizes that these clays are kaolinitic type. [5]

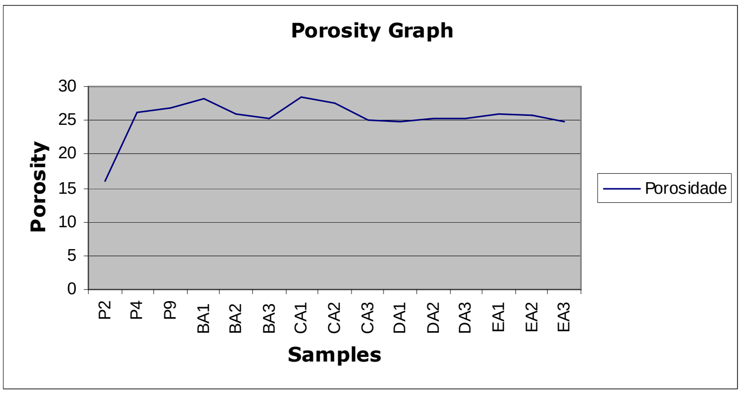
MgO content in red and purple clays can be an indication of the presence of clay minerals of mica and / or smectite clay.

The iron oxide present in most clays reduces the plasticity, but also reduces shrinkage and facilitate drying. It also decreases the mechanical strength, but the little that melts in sintering provides hardness to glaze. This element is present in three clay color 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 color after sintering. We notice that firing temperatures higher provide the reduction of these pores, which reduces the absorption of water. In the assay, the samples with clay color - yellow, had a percentage of absorption around 20, showing satisfactory for this application.



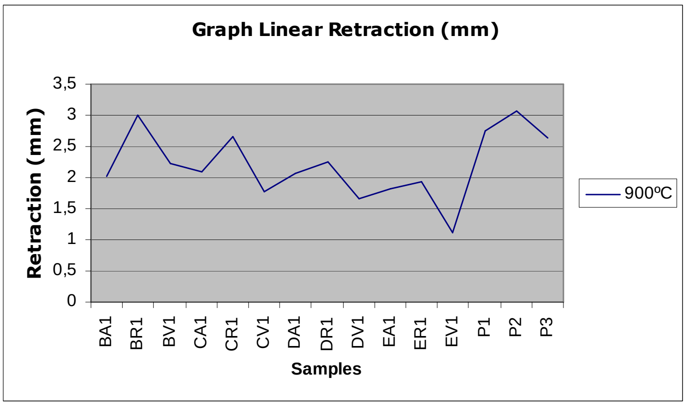
Graph1: Water absorption in standard samples and clay-colored - yellow, after sintering at 900, 1000 e 1100^oC.



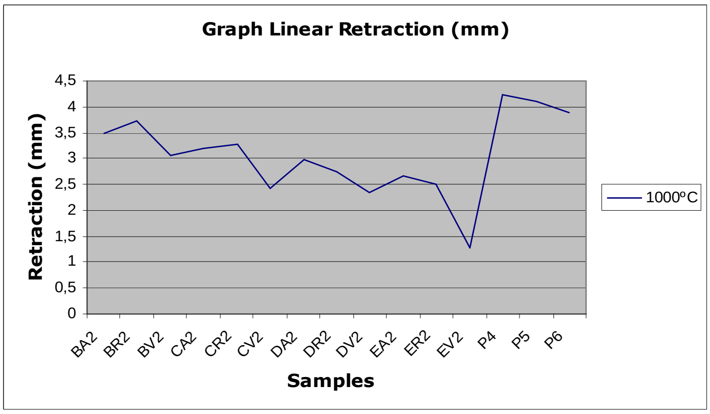
Graph 2: Apparent porosity of the standard samples and clay-colored yellow after sintering at 900, 1000 e 1100^oC.

In Graph 2 we can see that there was an increase of porosity with increasing the clay colored ceramic sample kaolinitic, for ceramic sample pattern. Moreover, reduction of the same with the increasing temperature. The average porosity was around 25, with the compositions B, C and D the best results.

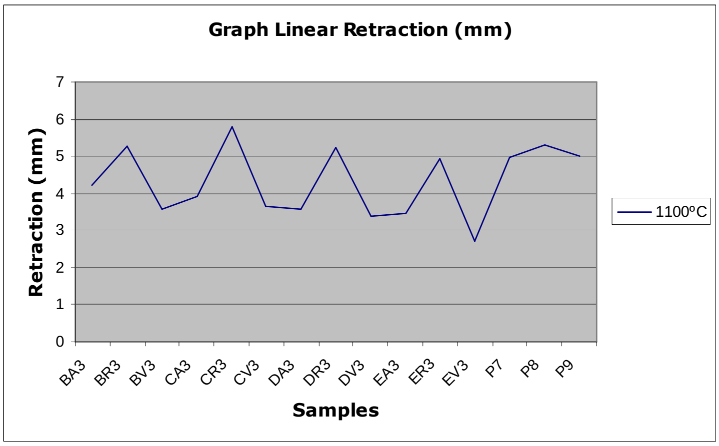
Graphs 3, 4 and 5 show the linear shrinkage of the standar samples and samples with percentages of colored clay in the sintering temperatures of 900, 1000 and 1100^{0}C.



Graph 3: Linear retraction of samples sintered at 900ºC, during 1 hour.



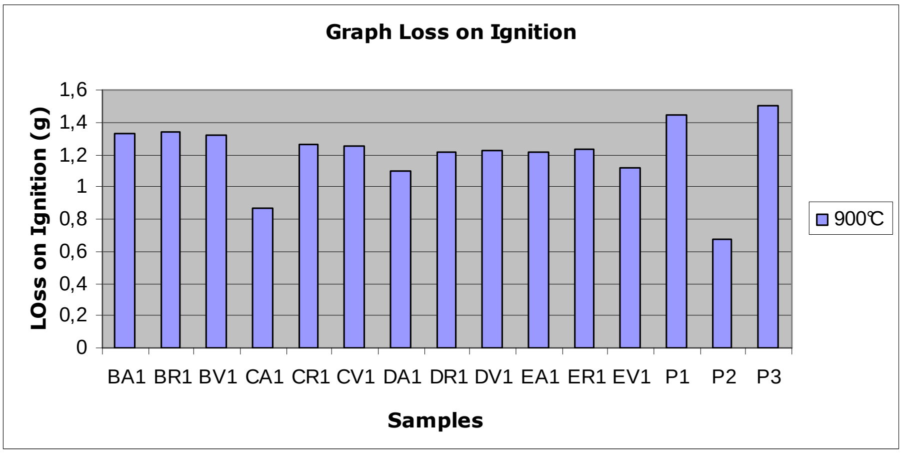
Graph 4: Linear retraction of samples sintered at 1000ºC, during 1 hour.



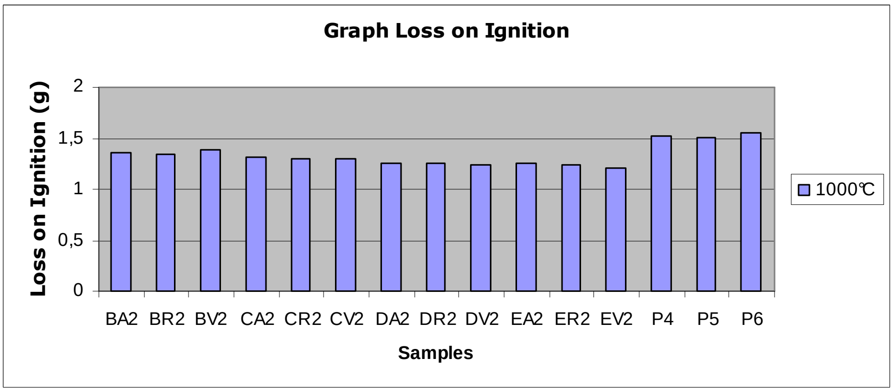
Graph 4: Linear retraction of samples sintered at 1100ºC, during 1 hour.

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

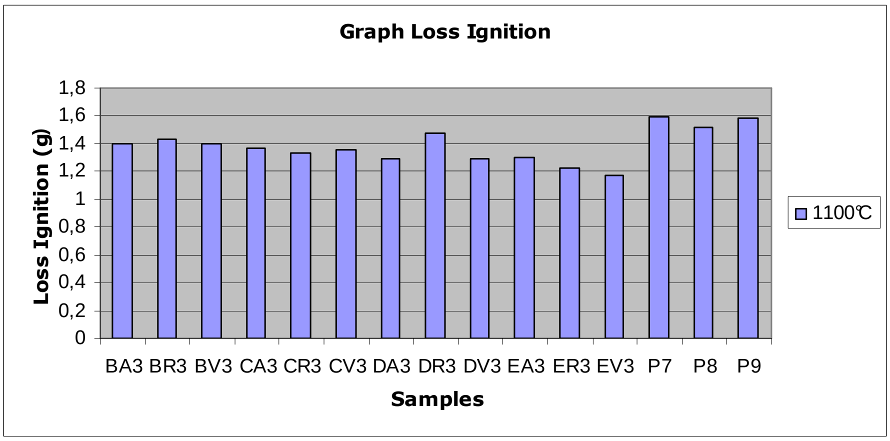
In Graphs 6, 7 and 8 have the Loss on Ignition of the standard samples and clay-colored, at 900, 1000 and 1100^{0}C.



Graph 6: Loss on ignition of samples sintered at 900^{o}C, during 1 hour.



Graph 7: Loss on ignition of samples sintered at 1000^{o}C, during 1 hour.



Graph 8: Loss on ignition of samples sintered at 1100^{o}C, during 1 hour.

Note that the largest loss on ignition occurs in the standard samples, in 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 colored).

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

	Fmax.	FBreak
Nr	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

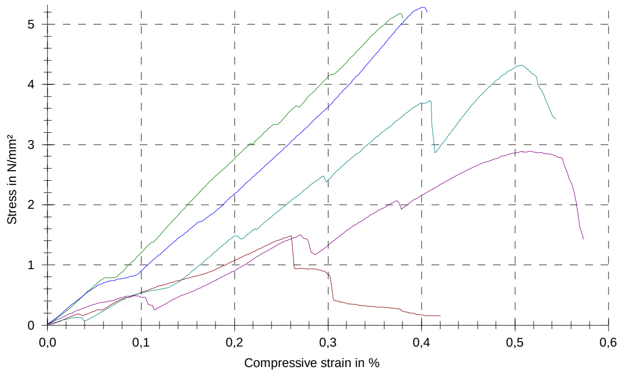


Figure 4: Flexural assay performed in the samples sintered at 900°C, during 1 hour.

	Fmax.	FBreak
Nr	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

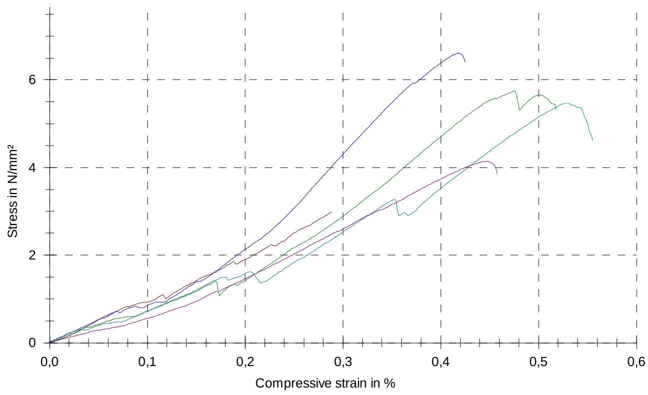


Figure 5: Flexural assay performed in the samples sintered at 1000°C, during 1 hour.

	Fmax.	FBreak
Nr	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

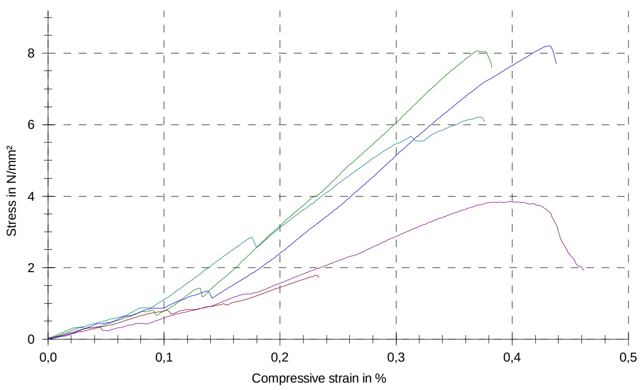
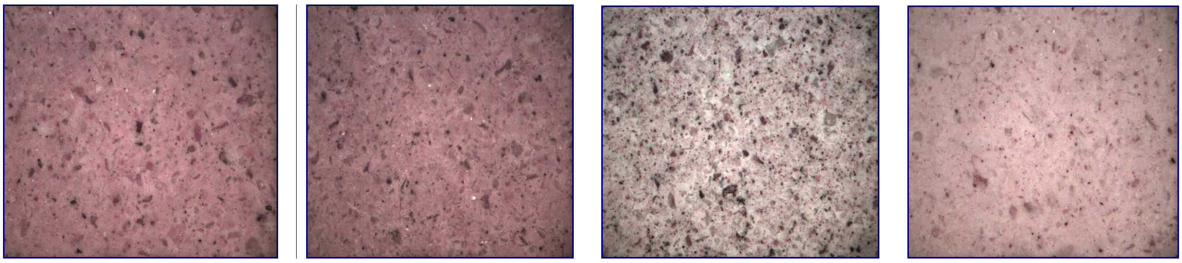


Figure 6: Flexural assay performed in the samples sintered at 1100°C, during 1 hour.

It is perceived that the higher the firing temperature, thus reducing the amount of pores present, the greater the resistance to bending. Compositions B and C showed the best results in all tests of strength, emphasizing on the sintering temperatures higher.

In figure 7 we have the representative micrographs of samples ceramic clays with various percentages of clay natural color - yellow, red and purple.



a) b) c) d)

Fig. 7: Photomicrographs of samples sintered at 1000 e 1100°C, during 1 h, with increase of 100x:

a) Sample CA2 – Composition C, yellow colored clay, sintered at 1000°C;
b) Sample DA3 – Composition D, yellow colored clay, sintered at 1100°C;
c) Sample CR2 – Composition C, purple colored clay, sintered at 1000°C;
d) Sample BV3 – Composition B, red colored clay, sintered at 1100°C.

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

Conclusions

The standard samples, consisting mainly of ceramic sample kaolinite, showed the characteristic color of kaolin, or white, tending to the cream at temperatures above 1000°C. Clays collected from the beach Cutuvelo/RN have natural pigments with different compositions. Such compositions directly influence the natural color of clay. Iron is the main agent and pigments, during firing, it becomes changing the color of clay. [7]

Color stability is maintained the temperature of 900°C to 1100°C, intensifying the higher temperatures.

The combination of clay with colored 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 colored ceramic sample kaolinitic significantly improved the mechanical properties of the samples, where the addition of 20 to 30% of colored clay (composition B and C) showed the best results and thus the percentage would be advisable for future application to obtain ceramics with different colors and unique. The use of these clays in combination with ceramic samples clays 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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