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PRODUCTION OF CERAMIC BLOCK WITH INCORPORATION TO REJECT MINERAL IN TRADITIONAL CERAMICS

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Abstract

The Rio Grande do Norte is the 4th national producer of mineral resources of Brazil. Here are produced the most varied resources, with emphasis on iron, gold, tantalita, kieselguhr, oil, natural gas, limestone, feldspar, salt, quartz, kaolin, ornamental stones, mineral water, gems, scheelita, among others. The mineral extraction activity is considered a highly degrading due to the large volume of material as it moves in the form of ore and waste, where the major concern at present is to manage and provide a final destination for all the waste produced, allowing the minimization of environmental impact and social. Furthermore, the production of ceramics in the state occupies a position of industry, capital goods, contributing to the development of local economy, only producing tiles, bricks and ceramic blocks. The most recent geological map of Rio Grande do Norte, there are over 2 thousand items that were analyzed produced or producing some kind of mineral. This work aims to characterize and evaluate the possibilities of using the tailings of granite and marble, together with the waste of scheelita, the composition of the ceramic blocks. We collected samples of mineral wastes of granite and marble, besides the waste of scheelita companies in the region of the newborn Seridó and then their characterization was performed by determining the size distribution, chemical analysis (EDX), X-ray diffraction, ATD, ATG and SEM. After characterization were prepared four groups of samples with percentages of 10, 20, 30 and 40% to reject the traditional ceramic body. The samples were compressed in a uniaxial press, heated to a temperature around 100° C for 24 hours, removing all the moisture present and the sintered 850°C, 900°C, 1000°C and 1100°C. Were tested for porosity, plasticity, thermal analysis and optical microscopy and SEM of the final product obtained. Based on the results found that these ceramic composites obtained have physical and mechanical characteristics similar to traditional ceramic bodies used in the production of blocks and tiles, in addition to features present within the regulatory specifications for the production of ceramic blocks, demonstrating the technical feasibility and economic production of the same.

Introduction

The ceramic materials are widely employed in materials engineering and in many fields of production and design. In Brazil it is agreed set Ceramic Industry segments that differentiate the products obtained and more precisely the markets that are inserted. However, the continuous demand for higher productivity rates in the world economy has led to the rapid decline of natural resources and at the same time, the generation of large quantities of waste and by-products, most of them not directly recycled. The reuse of waste after observation of its potential is currently considered an alternative that can contribute to the diversification of products, reduce cost of production, provide alternative raw materials for a variety of industries, conservation of nonrenewable resources and energy. In the modern society's increasing value to products that come from recycling of materials.

The intensity of the industrial and demographic growth in recent decades has resulted in generation of significant quantities of waste. Currently, technological efforts have been focused on actions that lead to the use of clean technologies, which enable the total elimination of waste or incorporation within the very process which created them, or even as a feedstock in other processes. The mineral extraction is a highly degrading, due to the large volume of material that it moves in the form of ore and waste. The scheelitífera region of northeastern Brazil is the second largest crustal extension and volume of ore contained. In the northeast scheelite is distributed in order of importance the following states: Rio Grande do Norte, Paraíba, Pernambuco, Ceará and Alagoas. Nationally, the infant holds the largest reserves officially approved by the National Department of Mineral Research - DNPM. The mineralized area as a true full scheelitífera which was about 560 km width and up to 700 km long linear in its central portion. The municipalities hold reserves of scheelite Rio Grande do Norte are: Acari, Bodó, Currais Novos, Lajes and Santana do Seridó. In the global context, the Brazilian participation hovers around 0.3% of world reserves. To these features can be added to the quantities of ore tailings derived from the concentration of mines and prospects. Thus, one can consider these reservations waste as resources that can be enjoyed with innovations in treatment and processing of this mineral. The state of the newborn has large mineral wealth, and one of them is scheelite, where it has become the target of mining companies in the world, mainly as a niche high-value minerals market. The scheelitífera region of northeastern Brazil is the second largest crustal extension and volume of ore contained. Nationally the RN is the holder of the largest reserves officially approved by the National Department of Mineral Research - DNPM. Given this, this work is to encourage the study of the technical, technological and economic use of waste scheelite, with powdered marble and granite for the manufacture of ceramic bricks, assessing the best value for clay / reject in the production of composite proposed.

Experimental and Materials

Preparing the Samples

Preparing the Samples. In this study we used ceramic sample Cerâmica Ouro Branco (50% lean clay + 50% clay content), located in the city of Ielmo Marinho-RN, reject granite and marble from the step of polishing the water being collected in a processing industry located in Natal, Brazil, and tailings from Scheelite Mine Brejuí, located in the city of Curais Novos-RN. The formulation of the composites was prepared by mixing the dried and made the comminution and mixing in ball mill for 40 minutes. Five formulations were prepared, where the waste of granite and marble and scheelite in the samples with the same mass percent. Table 1 we used the compositions. Overall it was made a total of 60 samples with a particle size <200 mesh.

Table 1. Composition of the Samples.

Group	Percent Mass Ceramic	Mineral reject rate (50% of scheelite + 50% granite and marble)
A	100%	0%
B	90%	10%
C	80%	20%
D	70%	30%
E	60%	40%

Were later uniaxial compression in the metal matrix at a pressure of 3 tons of compression, in the form of specimens whose dimensions are 60 x 20 x 5 mm3. In Figure 1 we have the design of the array of compression and figure 2 we have a drawing showing the samples.

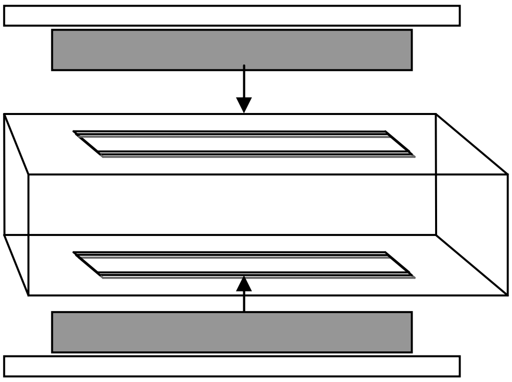


Figure 1. Schematic of uniaxial matrix used in the preparation of samples.

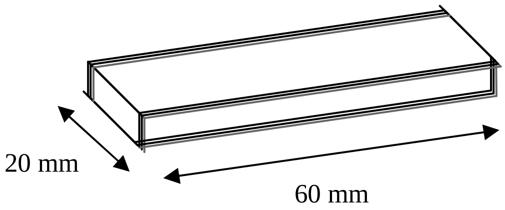


Figure 2. Schematic picture of the samples.

Sintering: After compaction the samples were placed in an oven for a period of 24 hours at a temperature of around 100^{0}C, for elimination of moisture present. Were later sintering, the samples are subdivided into 05 (five) groups, consisting of twelve (12) samples of each group. The sintering temperatures used were 850^{0}C, 900°C, 1000^{0}C and 1100ºC, with a heating rate 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.

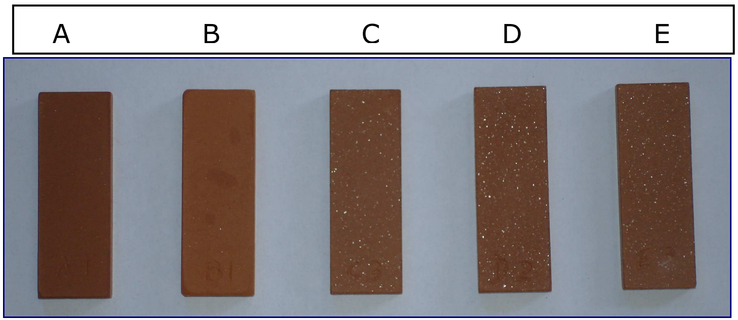


Figure 3: Samples sintered at 850^0, 900°, 1000° e 1000°C, with rate heating 5°C/min..

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:

$$AA = \frac{mu - ms}{ms} \tag{1}$$

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
Li = Length After Burns

Assay of strength 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

Fluorescence X-ray-EDX. Chemical analysis via EDX to identify the chemical elements that make up the sample to be analyzed. Thus, it became necessary to use this analysis to determine the percentage of oxides present in the tailings of granite and marble and scheelite and, thus, predict its possible influence on the mechanical properties of the samples.

Diffraction of X-rays– DRX. The diffraction of x-ray allows us to determine the crystalline phases present and the relationship of its elements with their proportion in the form of oxides. The chemical and mineralogical characterization of the clays and rejects and the determination of the components that attach to the ceramic sample allow us to understand that the beneficiaries should be made to change one or more properties of the ceramic sample, and improve the properties of the final product.

Results and Discussion

In table 2 we have the chemical analysis of scheelite reject in the Table 3 the chemical analysis of reject of the granite and marble by EDX.

Table 2: Chemical Analysis of the scheelite reject.

Composition	% in weight
$CaWO_4$	45.141
SiO_2	29.985

Al_2O_3	8.689
Fe_2O_3	7.891
MgO	3.573
SO_3	2.879
K_2O	0.949
MnO	0.426
TiO_2	0.348
ReO_2	0.045
Yb_2O_3	0.043
V_2O_5	0.031

The reject is considered as constituted a variation of tungsten oxide, which is derived from the scheelite concentrate, and a percentage of silica or silicon oxide. However, it has much lower levels of oxides of K, Mn, Ti, Re, Yb and V.

Tabela 3: Chemical Composition of marble and granite reject.

Constituients	Al_2O_3	SiO_2	SO_3	K_2O	Fe_2O_3	P_2O_5	TiO_2	V_2O_5	MnO	Ir_2O_3	ZnO	CuO	PtO_2
Reject (%)	48,169	47,954	1,829	1,112	0,484	0,256	0,089	0,053	0,016	0,014	0,010	0,008	0,006

The marble and granite reject used is composed predominantly of alumina (Al_2O_3) and silica (SiO_2), and oxides flux. These oxides will influence the burning process, promoting the formation of the liquid phase and promoting densification and sintering process.

In Figures 4 and 5 has the diffractogram of X-rays of scheelite reject and the marble and granite, respectively.

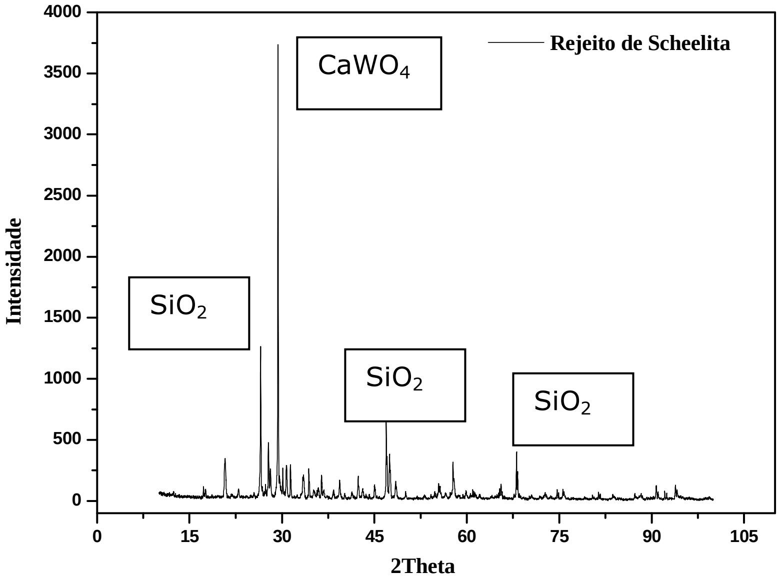


Figure 4: X-ray diffraction patterns of the raw materials.

It appears that the reject is composed primarily of $CaWO_4$ and silicon oxide. The other peaks of lower intensity are, in general, of SiO_2. Thus, the crystalline phases identified confirm the chemical compositions presented in Table 2.

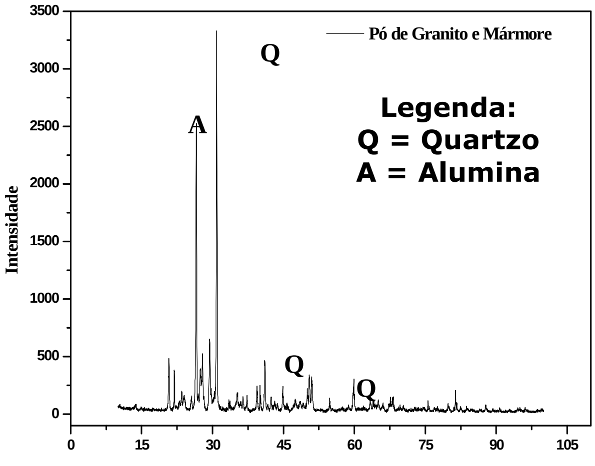


Figure 5: X-rays diffraction of the marble and granite reject.

The most intense peaks correspond to alumina and silica, while the less intense peaks to the other oxides present, confirming the chemical compositions present in the analysis of EDX.

As Table 3 to 6 show, respectively, Apparent Porosity of the standard samples and samples with Scheelite reject and marble and granite reject after sintering. Note that there was a change, however not significant in porosity with the addition of mineral rejects.

Table 3 – Apparent Porosity of the samples sintered at 850ºC, during 1 hour.

Samples	Dry Mass (ms)	Humid Mass (mu)	Immersed Mass (mi)	$PA = \frac{mu - ms}{mu - mi}$
A	10,39 g	12,04 g	6,75	0,31
B	10,62 g	12,10 g	6,77	0,28
C	10,64 g	12,08 g	6,72	0,27
D	10,54 g	12,12 g	6,69	0,29
E	10,15 g	12,07 g	6,68	0,36

Table 4 – Apparent Porosity of the samples sintered at 900ºC, during 1 hour.

Samples	Dry Mass (ms)	Humid Mass (mu)	Immersed Mass (mi)	$PA = \frac{mu - ms}{mu - mi}$
A	10,65 g	12,20 g	6,77 g	0,28
B	10,71 g	12,06 g	6,76 g	0,25
C	10,67 g	12,00 g	6,67 g	0,24
D	10,74 g	12,02 g	6,64 g	0,23
E	10,77 g	12,00 g	6,60 g	0,22

Table 5 – Apparent Porosity of the samples sintered at 1000ºC, during 1 hour.

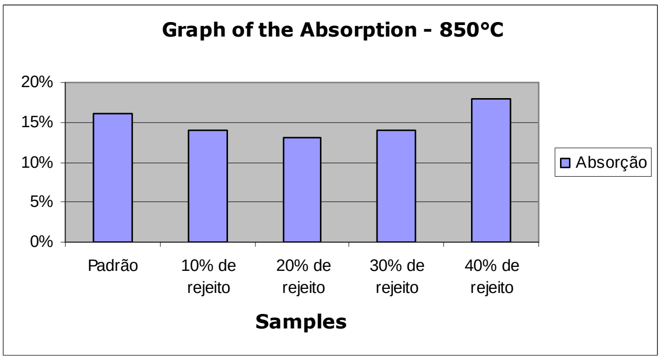
Samples	Dry Mass (ms)	Humid Massa (mu)	Immersed Mass (mi)	$PA = \frac{mu - ms}{mu - mi}$
A	10,84 g	12,20 g	6,81 g	0,25
B	10,78 g	12,06 g	6,69 g	0,23
C	10,76 g	12,04 g	6,66 g	0,23
D	10,74 g	12,02 g	6,40 g	0,22

E	10,78 g	12,08 g	6,38 g	0,22

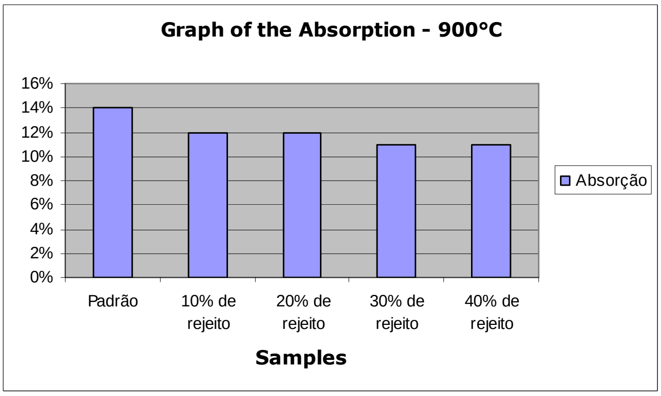
Table 6 – Apparent Porosity of the samples sintered at 1100ºC, during 1 hour.

Samples	Mass Dry (ms)	Humid Mass (mu)	Immersed Mass (mi)	$PA = \frac{mu - ms}{mu - mi}$
A	10,69 g	12,18 g	6,54 g	0,26
B	10,66 g	12,10 g	6,47 g	0,25
C	10,72 g	12,10 g	6,42 g	0,24
D	10,74 g	12,08 g	6,40 g	0,23
E	10,82 g	12,12 g	6,33 g	0,22

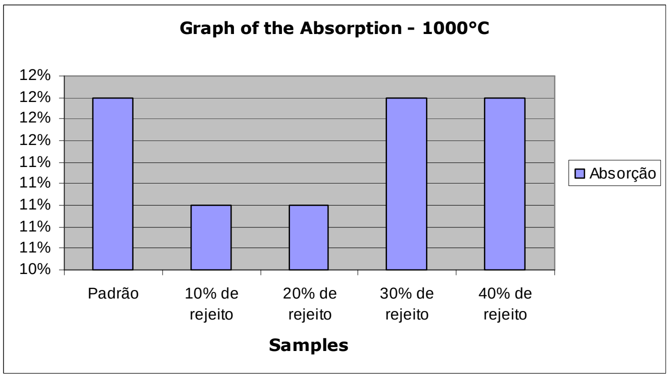
In Graphs 1 to 4 We have the level of water absorption depending on the mineral reject content and temperature sintering.



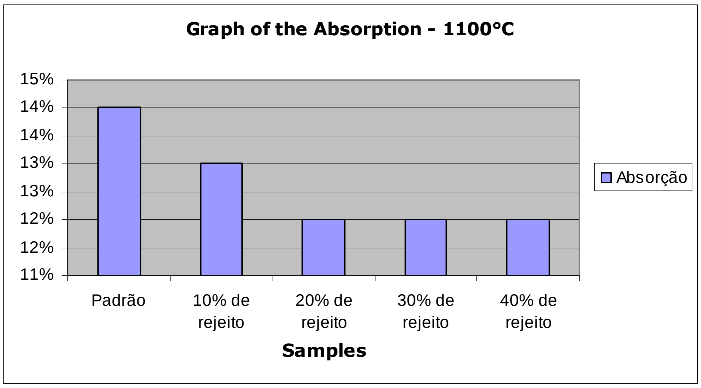
Graph 1: Absorption of water in the samples sintered at 850ºC , during 1 hour.



Graph 2: Absorption of water in the samples sintered at 900ºC , during 1 hour.



Graph 3: Absorption of water in the samples sintered at 1000ºC , during 1 hour.



Graph 4: Absorption of water in the samples sintered at 1100ºC , during 1 hour.

It is perceived that there was a small variation in the level of water absorption with the incorporation of mineral reject, however most water uptake occurred in the standard samples.

In tables 7 to 10 have the test result re Retraction Linear performed in standard samples and samples with the mineral reject.

Table 7 – Assay Results of linear retraction in the temperature sintering at 850ºC.

Samples	Lenght of the Green (Lo)	Lenght After Burns (Li)	$\Delta L = \frac{Lo - Li}{Lo}$ x100
Standard	60,62 mm	60,24 mm	0,62%
10% de rejeito	60,61 mm	60,30 mm	0,51%
20% de rejeito	60,55 mm	60,36 mm	0,31%
30% de rejeito	60,61 mm	60,42 mm	0,31%
40% de rejeito	60,60 mm	60,44 mm	0,26%

Table 8 – Assay Results of linear retraction in the temperature sintering at 900ºC.

Samples	Lenght of the Green (Lo)	Lenght After Burns (Li)	$\Delta L = \frac{Lo - Li}{Lo}$ x100
Padrão	60,57 mm	60,30 mm	0,44%
10% de rejeito	60,57 mm	60,34 mm	0,37%
20% de rejeito	60,55 mm	60,41 mm	0,23%
30% de rejeito	60,55 mm	60,44 mm	0,18%
40% de rejeito	60,52 mm	60,50 mm	0,03%

Table 9 – Assay Results of linear retraction in the temperature sintering at 1000ºC.

Samples	Lenght of the Green (Lo)	Lenght After Burns (Li)	$\Delta L = \frac{Lo - Li}{Lo}$ x100
Padrão	60,44 mm	60,03 mm	0,67%
10% de rejeito	60,43 mm	60,11 mm	0,52%
20% de rejeito	60,58 mm	60,28 mm	0,49%
30% de rejeito	60,64 mm	60,36 mm	0,46%
40% de rejeito	60,76 mm	60,55 mm	0,34%

Table 10 – Assay Results of linear retraction in the temperature sintering at 1100ºC.

Samples	Lenght of the Green (Lo)	Lenght After Burns (Li)	$\Delta L = \frac{Lo - Li}{Lo}$x100
Padrão	60,49 mm	60,17 mm	0,52%
10% de rejeito	60,50 mm	60,25 mm	0,41%
20% de rejeito	60,52 mm	60,36 mm	0,26%
30% de rejeito	60,55 mm	60,39 mm	0,26%
40% de rejeito	60,57 mm	60,43 mm	0,23%

Notably, the values of linear retraction lowest were obtained for the temperature around 900^{0}C. Higher temperatures resulted in increased shrinkage in the presence of 20 and 30% reject this. The addition of mineral reject in the mass ceramic standard provided a marked reduction in linear retraction of all samples, while the samples C, D and E had lower rates of linear retraction.

Figure 6 illustrates the variation of the tensile strength of the standard samples with varying concentrations of mineral reject.

	Fmax.	FBreak
Nr	MPa	MPa
A11	2,40	1,20
B11	1,51	-
C13	3,66	3,05
D12	3,18	2,95
E13	3,53	1,75
A22	4,99	4,06
B21	6,99	6,42
C22	5,65	4,40
D21	4,62	3,34
E21	4,33	3,08
A32	20,14	5,68
B32	11,46	9,22
C33	12,95	19,96
D33	6,45	10,72
E31	6,90	6,05
A41	4,02	2,98
B41	3,77	3,60
C41	7,23	6,04
D42	3,89	2,87
E42	5,44	2,69

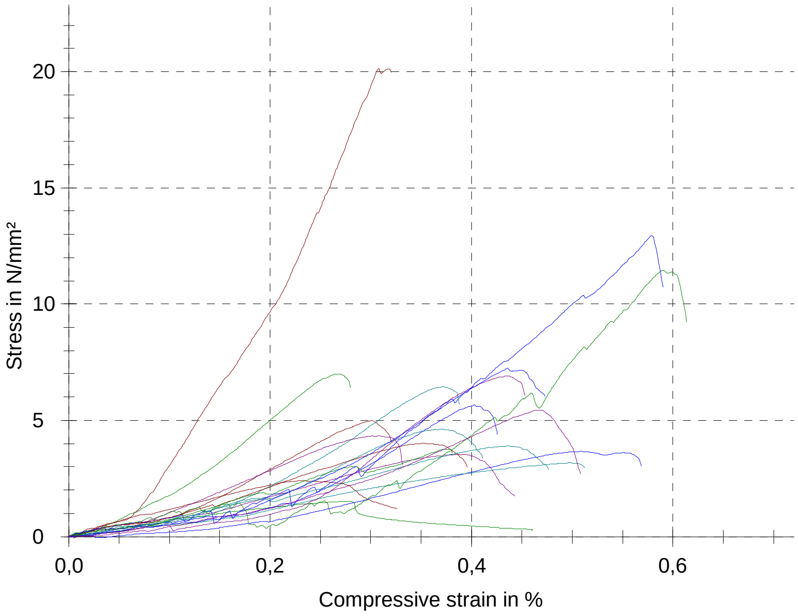


Figure 6: Assay of strength in Three Points performed in the samples sintered at 850^0, 900^o, 1000^0 E 1100^{0}C, durante 1 hora.

It is perceived that the higher the sintering 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, with a peak temperature sintering DE 1000^{0}C. High levels of reject have caused a weakening in the samples, consistent with the standard samples (composition D and E).

Conclusions

Increases high mineral reject will affect the conventional ceramic processing, since, in general, are produced via extrusion (tiles, bricks ,...). This is because of the differences in behavior between the plastic clay and the reject (reducing plasticity), which would certainly hinder the process of manufacture. Moreover, high levels of rejects will provide a reduction in mechanical strength of the final product. It is noticed that the sintering temperatures used the results were higher than those of ceramic mass standard used, suggesting that the use of mineral reject with percentages around 20-30% is technically feasible and economically interesting. Another reason is to redirect and better use of natural resources, providing alternative destination to reject this mineral, in addition to adding value to the material produced by improving their physical and mechanical properties. Regarding porosity there was no significant variation in the rate of absorption for different percentages of reject clay mineral aggregate. However, the linear retraction showed a decrease of their values with the addition of the percentage of reject. The results presented in this paper show that it is possible to add mineral concentrates reject granite and marble and scheelite the ceramic mass with percentages around 20-30%, without sacrificing quality and physical and mechanical properties of the final product.

It was evident that research on the use of mineral reject the incorporation of clay, it is possible and very important, in addition to reusing the waste discarded by the mining industry, contributing to climate change.

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