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Reformulation of roofing tiles body with addition of granite waste from sawing operations

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Abstract

A ceramic body traditionally used to produce roofing tiles was reformulated by the addition of granite waste from sawing operations. The objective was to obtain a ceramic product with better technological properties. The main tool for the reformulation was the definition of the appropriate particle size of the raw materials as given by the Winkler diagram. The raw materials were characterized with respect to their mineralogical composition by X-ray diffraction, particle size distribution as well as chemical composition and plasticity. Specimens were made by extrusion and fired at temperatures from 850 to 1100 °C. The technological properties determined were: dry bulk density, linear shrinkage, water absorption and mechanical strength. Microstructural analysis of the fired samples was carried out by X-ray diffraction. The results showed that the granite waste contributes to reduce the plasticity and the linear shrinkage of the ceramic bodies. One reformulated ceramic body exhibited better values of water absorption and mechanical strength than the industrially used.

Keywords: Extrusion; Porosity; Plasticity; Tiles; Waste materials

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1. Introduction

Ceramic bodies industrially fabricated in Campos (the municipal area of Campos dos Goytacazes, north of the State of Rio de Janeiro, in Brazil) are still empirically elaborated using a mixture of local clays. These clays are predominantly kaolinitic mineral in nature, associated with high plasticity. Due to the excessive plasticity of the ceramic bodies, it is common to observe dimensional defects, which occur after drying and firing. Moreover, the kaolinitic nature and the presence of aluminum hydroxide (gibbsite) confer a refractory behavior to the local clays, which impairs sintering during the firing operation. In the case of clay ceramics for civil construction, this results in greater porosity associated with elevated values of water absorption and low mechanical strength.[1,2] To avoid these problems, it is necessary to reformulate the ceramic body composition. The addition of both non-plastic materials to reduce plasticity and fluxes to condition the refractoriness is a possible alternative.

One technological method, which is already being tested to decrease porosity, is the incorporation of granite wastes from the sawing process.[3,4] Granite is a rock with large amount of quartz, feldspars and mica. In the initial stages of firing, these minerals act as non plastic agents which permit the use of lower amount of water in body forming. This makes for an easier drying operation. During firing the quartz generally behaves as an inert material but may also partially dissolve in liquid phases, should they occur. Both the feldspars and mica favor the formation of liquid phases and contribute to lower the porosity of the final ceramic product.

Granite is readily available to the industries in Campos, from the municipal area of Cachoeiro de Itapemirim, south of the State of Espírito Santo and 150 km from Campos. Intense industrial activity related to ornamental stones, especially, granite is maintained in the region. After mining, the granite blocks are submitted to primary dressing, which consist of sawing, to obtain semi finished pieces such as plates and strips. This is followed by secondary dressing in which the sectioned pieces undergo polishing and surface finishing. During primary dressing, an estimated loss of 20–35% of the blocks occurs in the form of powder. This

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leftover powder is removed in a mixture with water and other residual materials such as metallic dust and lime, used as abrasive and lubricant, respectively. This sludge is commonly referred as granite waste. A monthly production of 400 tons of granite waste is estimated to be produced at Cachoeiro de Itapemirim. The final disposal of this waste has brought serious environmental problems. Since most industries do not have an adequate sludge treatment, the granite waste is contaminating the soil and underground waters as well as obstructing rivers and lakes.

Based on the need to improve the roofing tiles properties together with the availability of granite waste, the present work had as its main objective to reformulate an industrial ceramic body by waste addition. This would also bring an environmental advantage in terms of a final destination for the waste. The main parameter considered for this reformulation was a suitable particle size for the raw materials. This parameter is related to relevant properties of the ceramic body such as plasticity and mechanical strength.[5,6]

2. Materials and methods

The basic raw materials used in this investigation were two different local clays from Campos, as well as local sand and granite waste from Cachoeiro de Itapemirim. The clays are locally called "preta" (Portuguese for black) and "carolinho" (Portuguese for little lump). Here they will be referred, respectively, as clays **P** and **C**. Usually the clays are both mixed with sand to make roofing tiles at small plants, which produce around 50,000 pieces a month. The typical industrial ceramic body made at these plants, here named **IC** (industrial ceramic), is composed of 70% in mass of clay **P**, 20% of clay **C** and 10% sand.

As already mentioned, the granite waste was obtained in the form of a sludge that, in addition to granite powder and water, contained small amounts of metallic dust and lime. This waste was collected from the primary dressing sector of a stone sawing industry located in Cachoeiro do Itaperirim.

Upon receipt, the raw materials were dried at 110 °C, manually disintegrated with a crusher and then sieved to 20 mesh (0.840 mm). The following tests were used to characterize the raw materials:

- X-ray diffraction (XRD), performed with powder samples in a Sheifert URD 65 equipment using Cu-K_α radiation for 2θ angles varying from 5 to 65°.
- Chemical composition, carried out by fluorescence spectrometry in a related X-ray equipment.
- Particle size and distribution, obtained by wet sieving and Andreasen pipette sedimentation method.
- Plasticity, determined by the Atterberg indices: Lower plastic limit (LPL), Upper Plastic Limit (UPL) and Plastic Index (PI).

After the raw materials characterization, a reformulation of the industrial ceramic body, **IC**, was undertaken using the Winkler diagram. This is a ternary diagram in which the vertices represent different granulometric ranges (<2 μm; 2–20 μm; $>$ 20 μm). A parameter of 35% in weight of particles <2 μm was established for the reformulations. This is the fraction of clay minerals corresponding to ceramic bodies that are within the field for roofing tiles in the diagram. Based on this parameter, three experimental ceramic bodies were formulated. They were denominated **XC1**, **XC2** and **XC3**. Table 1 displays the amount of different clays, sand and granite mixture for each reformulated ceramic body as well as that for the **IC**. The reason for choosing these experimental compositions will be explained latter in this paper.

In order to determine the technological properties of the ceramic bodies, 10 cm long rectangular specimens with 1.1 cm × 3.0 cm in cross section, were shaped by extrusion, using a laboratory piston extruder. Initially the specimens were dried at room temperature for 24 h and than oven-dried at 110 °C to constant mass. Finally, the specimens were fired at a maximum temperature, which varied from 850 to 1100 °C in an electric laboratory kiln with a 180 min socket at maximum temperature, using a heating/cooling rate of 4 °C/min. The measured technological properties were: dry bulk density, measured by the dimensional method dividing the dry mass by the external volume; drying and firing linear shrinkage; water absorption and mechanical strength, obtained by the flexural rupture stress, using the three points method.

The phase composition of the fired bodies at 1050 °C was determined by X-ray diffraction (XRD). The 2θ scanning was from 5 to 65°, at intervals of 0.05°, with an accumulation time of 2 s.

3. Results and discussion

Fig. 1 shows the X-ray patterns of the raw materials. The patterns indicate that both clays are predominantly

Table 1
Batch composition (mass%) of the tested bodies

Ceramic bodies	Raw materials			
	Clay C	Clay P	Sand	Granite waste
IC	20	70	10	–
XC1	80	–	–	20
XC2	45	25	–	30
XC3	15	45	–	40

kaolinitic with the presence of quartz, mica and gibbsite. As expected, the sand displayed only peaks for a quartz crystalline structure. In the granite waste, the presence of quartz, mica, plagioclases and microcline was observed. Mica and microcline are sources of alkaline flux materials, such as K_2O and Na_2O, which favor the formation of a liquid phase above 700 °C.[7] The results from Fig. 1 confirm the tendency of both clays, **P** and **C**, to have high loss of ignition and refractoriness due to the presence of $Al(OH)_3$ in the form of gibbsite. The fluxing capacity of the granite waste, which is associated with lower porosity after firing, is also confirm by the presence of K_2O and Na_2O containing minerals.

Table 2 shows the chemical composition of the raw materials. One can notice, for both clays, a relatively low amount of SiO_2 and high amount of Al_2O_3. This indicates and elevated fraction of clay minerals. The black color that gives the name to clay **P** is due to the relatively high level of organic matter in its composition. Moreover, the significant amount of Fe_2O_3 in both clays will be responsible for the reddish color of the roofing tiles after firing. It should be noted in Table 1 that clays **P** and **C** have a relatively low content of alkaline oxides (K_2O and Na_2O), which act as fluxes to improve the sintering mechanisms. The content of alkaline earth oxides (MgO and CaO) is also low, indicating a negligible amount of carbonates. Additionally

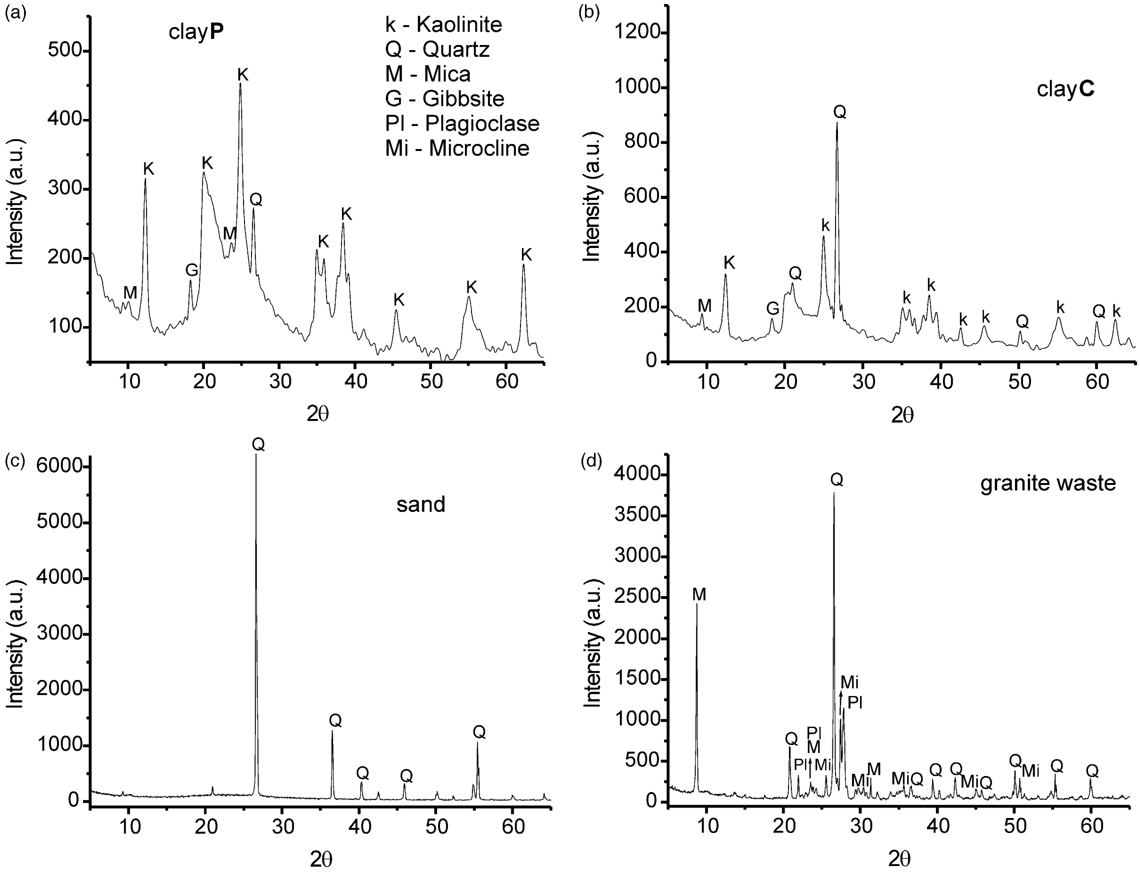

Fig. 1. X-ray diffraction patterns of the raw materials: (a) clay **P**; (b) clay **C**; (c) sand; and (d) granite waste.

Table 2
Chemical composition of the raw materials (mass%)

Raw materials	Compositions									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	LOI	OM[a]
Clay **C**	50.79	29.15	3.63	1.83	1.83	0.22	0.15	0.96	11.84	0.10
Clay **P**	48.73	29.20	2.22	1.61	0.61	0.27	0.41	0.58	16.34	1.24
Sand	92.19	3.31	1.02	0.89	1.02	0.49	0.33	0.25	0.45	–
Granite waste	64.14	13.25	8.18	0.96	4.40	2.55	3.56	1.65	1.60	–

[a] OM, organic matter.

to the high amount of clay minerals, the loss of ignition is also related to the presence of organic matter and gibbsite.

As far as the sand composition is concerned, only silica is a major constituent. The other oxides are minor components and are probably due to contamination. The main impurity appears to be mica.

The chemical composition of the granite waste, presented in Table 2, in addition to SiO_2 and Al_2O_3, shows a relatively large presence of alkaline and alkaline earth oxides. This confirms the idea that the granite wastes could produce a fluxing action if added to clay ceramic bodies.

Fig. 2 shows the particle size distribution of the raw materials. One may note that both clays have an elevated % of clay minerals, considered as that with particle size below 2 μm. Clay **P** and clay **C** present 63% and 44% in mass of clay minerals, respectively. On the other hand, the sand and the granite waste have only small amount, about 1%, of particles with <2 μm, that are associated probably with fine particles of mica. Furthermore, both non-plastic sand and granite waste present significant differences. The size of the sand particles is relatively coarse and concentrated in the range from 50 to 500 μm. On the other hand, the granite waste has a finer size with a better granulometric distribution.

The plasticity parameters of the clays, in terms of the Atterberg indices, are shown in Table 3. For both clays, the values of these indices, characterize highly plastic materials. As already mentioned, the elevated plasticity of the clays is related to the large amount of particles with size below 2 μm, that are associated with clay minerals. Among the indices presented in Table 3, the lower plasticity limit, **LPL**, gives a value of great technological interest. This value represents the minimum % of water that is needed in a clay body to reach the plastic condition for its forming process by extrusion. Clays with high **LPL**, such as clay **P** with 33%, will present difficulty for drying. Ceramic bodies made from these kinds of clays display low permeability as well as excessive linear shrinkage both from drying and firing operations. These conditions could result in serious defects in ceramic pieces.

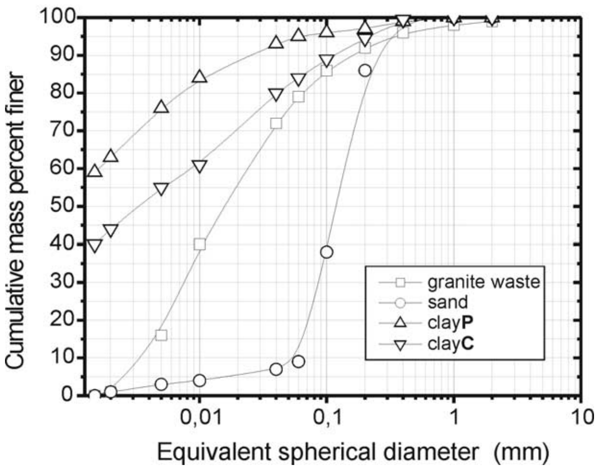

Fig. 2. Particle size distribution of the raw materials.

Table 3
Atterberg limits of the clays (% mass)

Clays	Atterberg limits (%)		
	LPL	UPL	PI
C	24	51	27
P	33	81	48

Fig. 3 shows the Winkler diagram with four fields, I, II, III and IV, commonly associated with major classes of clay ceramic products. For instance, field II corresponds to that which is adequate for roofing tiles and, as such, is of interest in the present work. The definition of different classes of ceramic products in the Winkler diagram is based on the particle size of the material. For extruded clay ceramics, the fraction of particles with size <2 μm is the one with greatest technological interest because is associated with the plasticity of the ceramic body.

The granulometry of the clays used in this work allows them to be categorized to the Winkler diagram. According to Fig. 3, clay **C** with 44% of particles size with <2 μm constitutes an almost natural ceramic body for roofing tiles. On the other hand, clay **P** with 63% is far from any class for clay ceramic products. The sand with 94% of particle size greater than 20 μm, is very close to the corresponding vertex of the Winkler triangle. The granite waste is half way between the 2–20 μm and >20 μm vertices.

As far as the industrial, **IC**, and experimental, **XC**, ceramic bodies are concerned, Fig. 3 also depicts their

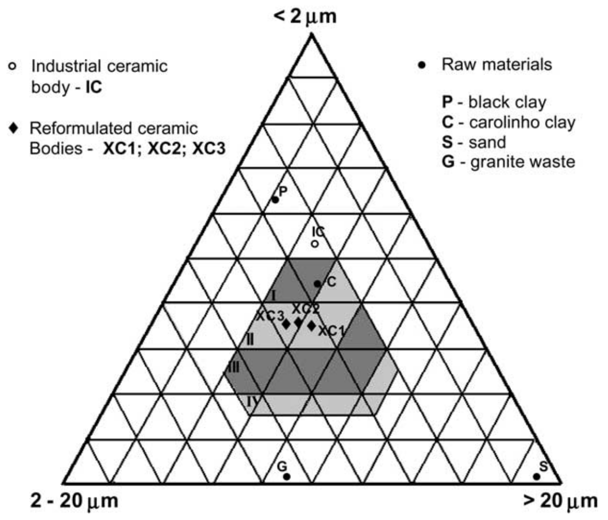

Fig. 3. Particle size distribution of the clays and ceramic bodies (mass%) in the Winkler diagram.

Table 4
Chemical composition of the ceramic bodies (mass%)

Ceramic bodies	Compositions									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	LOI	OM[a]
IC	53.49	26.60	2.38	1.58	0.90	0.28	0.35	0.62	13.85	0.89
XC1	53.46	25.97	4.54	1.66	2.34	0.69	0.83	1.10	9.79	0.08
XC2	54.28	24.39	4.64	1.51	2.30	0.93	1.24	1.07	9.89	0.36
XC3	55.20	22.82	4.82	1.38	2.31	1.17	1.63	1.07	9.77	0.57

[a] OM, organic matter.

Table 5
Technological parameters of the ceramic bodies

Ceramic bodies	Technological parameters		
	Dry bulk density (g/cm^3)	Fraction <2 μm (%)	LPL (%)
IC	1.77	53	27.9
XC1	1.80	35.4	19.2
XC2	1.79	35.85	19.0
XC3	1.77	35.35	18.5

position in the Winkler diagram. It is interesting to notice that the industrial ceramic body, **IC**, traditionally used for roofing tiles in Campos is not located in the proper field II fort this class of material. Apparently, for industry, it would be considered more convenient to have an excessively plastic body rather than to be in the proper field of the Winkler diagram. In terms of the extrusion operation, this could be an advantage with less wear of the components and better mechanical strength of the pieces. On the other hand, however, a more plastic ceramic body will make difficult the drying process and will present an elevated linear shrinkage after the drying and firing stages. The reduction of clay minerals fraction, which is one of the objectives of this work, can be obtained by increasing the amount of sand. However, it would not bring the mixture to the center of field II in Fig. 3.

Granite waste is possibly a better solution for conditioning of the **IC**. The present work analysed the effect of granite waste in different formulations located at the center of field II in Fig. 3. The idea was to investigate the changes that occur in properties and technological parameters of quite different compositions for ceramic bodies. At the same time, these experimental ceramic bodies were formulated to be closely located in the Winkler diagram, with 35% of clay minerals fraction, at 65% to the 2 μm vertex, and equidistant from the two other vertices.

In any case, it is expected that the granite waste could be a better alternative to sand. The finer granulometry of the granite waste reduces the risk of contraction cracks and favors the dissolution of quartz during the firing stage. As also mentioned, the granite waste has alkaline fluxes, $K_2O + Na_2O$, that promote fusion from around 700 °C due to eutetic formation with SiO_2–Al_2O_3. This decreases the porosity of the products.

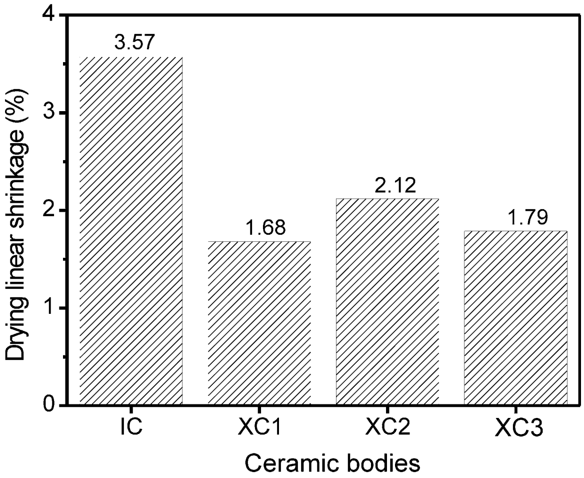

Fig. 4. Drying linear shrinkage of the ceramic bodies.

Table 4 presents the chemical composition of the investigated ceramic bodies. One should notice that the experimental bodies (**XC**'s), show a decrease in the loss of ignition as well as an increase in the SiO_2/Al_2O_3 ratio (**XC1** = 2.06; **XC2** = 2.23; **XC3** = 2.42) as compared to the industrial ceramic body (**IC** = 2.01). This is due to the decrease in the clay mineral fraction. A substantial increase was also observed in the % of alkaline fluxes with granite waste addition. The relative amount of Fe_2O_3 was also raised with respect to the **IC**. This should darken the typical color of the roofing tiles.

Table 5 presents some relevant technological parameters for the ceramic bodies investigated. It can be observed that the experimental bodies show a decrease in the plasticity limit as compared to the industrial ceramic body. This is also due to the decrease in the clay mineral fraction. The reformulation did not change the packing of the particles, since all ceramic bodies presented similar dry bulk density.

Fig. 4 shows the values of the drying linear shrinkage for the ceramic bodies investigated. A significant reduction in these values was observed in the **XC**'s bodies, as

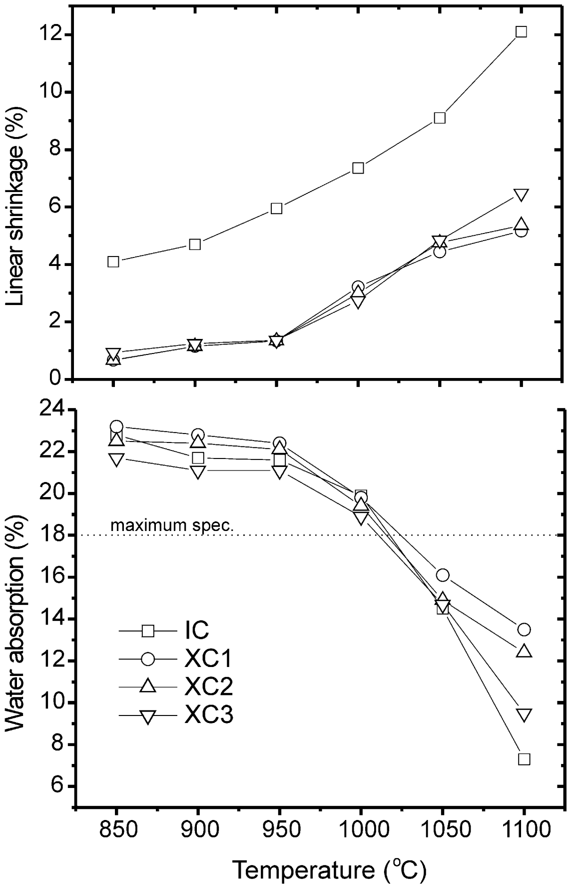

Fig. 5. Gresification diagram of the ceramic bodies.

compared with that of the **IC** body. This behavior is due to the lower plasticity of the reformulated bodies, which resulted in a lesser amount of water being required for the extrusion process. The reduction in the drying linear shrinkage brings several advantages. These are: faster drying process, decrease in energy consumption and smaller risk of developing cracks and dimensional defects.

Fig. 5 shows the gresification diagram with the behavior of the ceramic bodies in terms of water absorption and linear shrinkage as a function of the firing temperature. It can be seen that all ceramic bodies present a decrease in water absorption and an increase in linear shrinkage, with increasing firing temperature. This is a consequence of the vitrification, which occurs during the sintering process helping to reduce porosity. Vitrification is a phenomenon associated with formation of liquid phase, which surrounds the solid particles.[8] By the action of capillarity and surface tension these particles undergo a rearrangement that promotes densification and contraction of the internal structure.

The decrease in the water absorption for all ceramic bodies is approximately the same up to 1000 °C. For higher temperatures, the **IC** has a tendency for a sharper decrease. Even though this ceramic body has a lower content of fluxing oxides, Table 4, this behavior can be attributed to its elevated % of fine particles and relatively low amount of quartz. It should also be mentioned that, from a practical point of view, the recommended values for water absorption, ⩽18%[9] was only attained above 1000 °C for all ceramic bodies.

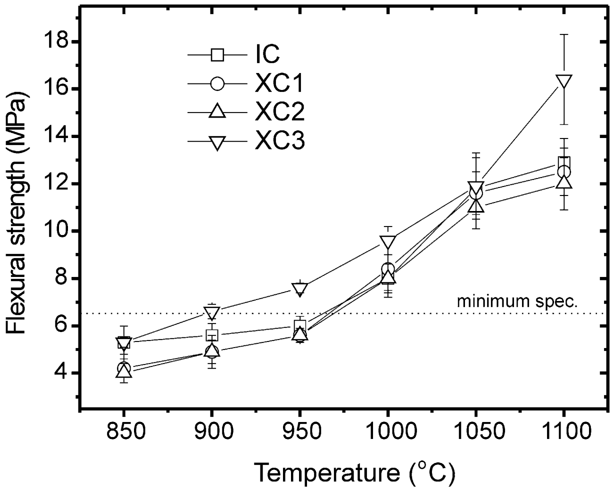

Fig. 6. Flexural strength of the ceramic bodies against the firing temperature.

Regarding the firing linear shrinkage, it can be seen in Fig. 5 that the **IC** has values significantly above those for the **XC**'s. Again, the finer particles and lower amount of quartz contributes to this behavior as well as to the higher loss of ignition, shown in Table 4, of the **IC**. The practical consequences for roofing tiles are cracks, distortion, bending and outside caliper. For red ceramic products this could be very serious since, in general, there is a temperature gradient inside the industrial furnaces.

Fig. 6 shows the variation of the flexural strength as a function of the firing temperature. All ceramic bodies increase their flexural strength with temperature in approximately the same way. There is a tendency toward higher strength values for the experimental ceramic body **XC3**, which has the greater amount, 40% in Table 1, of granite waste. This could be explained by taking into account the brittle nature of red ceramics for civil construction. For this class of materials, such as roofing tiles, the mechanical strength is determined by the stress concentration in structural defects such as pores, voids and microcracks. According to the fundamentals of fracture mechanics,[10] the larger the defect the lower the material's strength.

In Fig. 5 one can notice that **XC3** has the lower water absorption, which means lower open porosity, of all the ceramic bodies up to 1000 °C. Therefore, with less pores acting as defects, **XC3** should have the greatest mechanical strength as shown in Fig. 6. However at 1100 °C, Fig. 5, **IC** has the lowest open porosity, as inferred by its water absorption, but not the highest strength. A possible explanation for the still higher

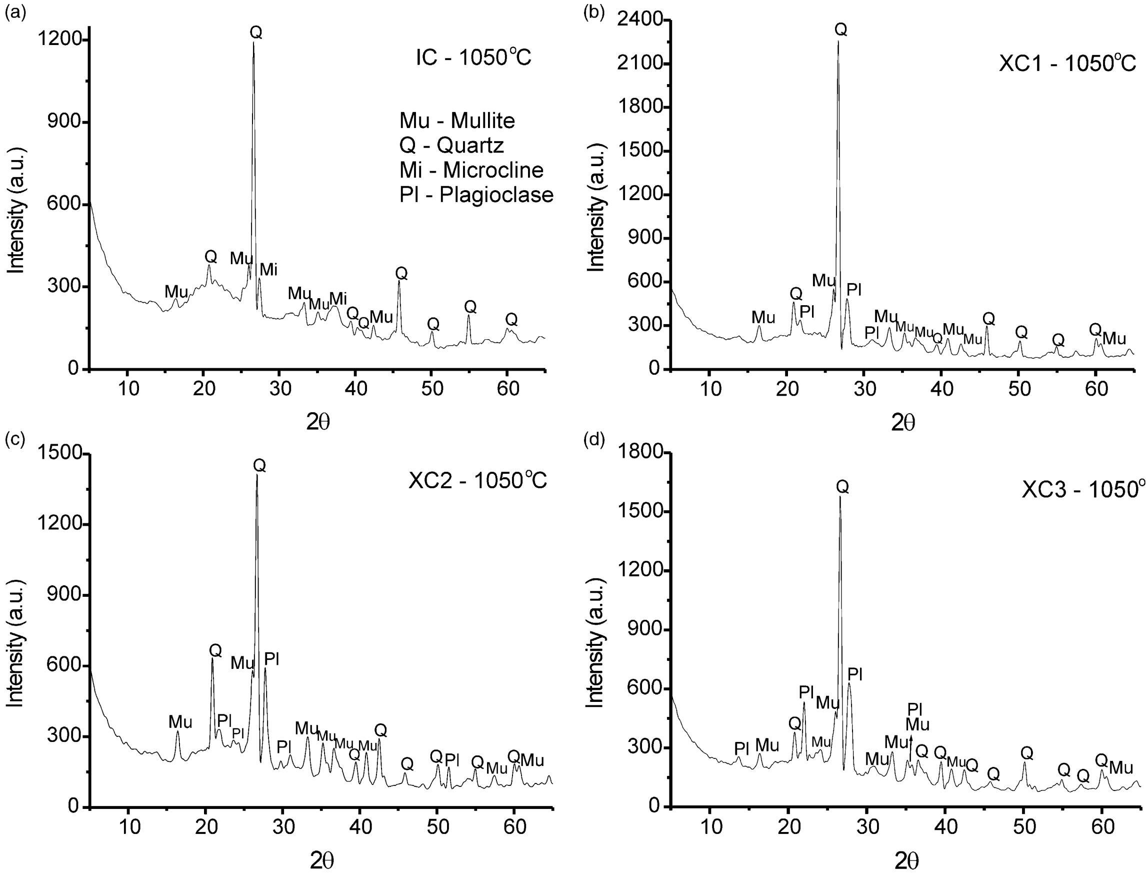

Fig. 7. X-ray diffraction patterns of the ceramic bodies fired at 1050 °C: (a) **IC**; (b) **XC1**; (c) **XC2**; (d) **XC3**.

value of ceramic body **XC3** at 1100 °C, Fig. 6, could be the comparatively finer particle size, Fig. 2, of the quartz from the granite waste as compared with the sand existing in **IC**. A finer structure would also imply smaller pores and thus a more difficult crack propagation.

For practical purpose, Fig. 6, shows that the recommended value of mechanical strength, $\geqslant 6.5$ MPa, for roofing tiles[11] is attained by **XC3** at 900 °C and above. The other ceramic bodies, including **IC**, need a minimum of 1000 °C to reach the required strength.

Fig. 7 shows the XRD patterns of the ceramic bodies fired at 1050 °C. This temperature corresponds to that in which all bodies obtained satisfactory technological properties. One should notice from the XDR pattern in Fig. 7(a) that the crystalline phases identified in the industrial ceramic body **IC** are associated with potash feldspar (microcline), quartz and mullite. It should also be mentioned that experimental bodies (**XC**'s) present similar crystalline phases. The following phases were determined: plagioclases (essentially anorthite and albite), quartz and mullite. As the granite waste addition increases, the peak intensities of plagioclases also increase. The main difference between the experimental bodies as compared to the industrial ceramic body is the type of feldspar detected. By contrast to the industrial ceramic body **IC**, in the experimental bodies (**XC**'s) the microcline phase was not detected. Plagioclases phases were detected in all **XC**'s due to their melting points higher than 1050 °C.[12] The common crystalline phases between **IC** and **XC**'s are quartz and mullite. While quartz is a residual phase, mullite results from spinel phase, with an approximate composition of $2Al_2O_3 \cdot 3SiO_2$, formed at temperatures around 925 °C.[13,14]

4. Conclusions

The reformulation of an industrial ceramic body traditionally used in Campos dos Goytacazes, Brazil, by adding fine particle granite waste from sawing operation, has led to the following conclusions:

- The industrial ceramic body has an elevated fraction of clay minerals, which locates it outside of the proper field in the Winkler diagram. This results in excessive plasticity and loss of ignition.

Consequently, the body shows elevate linear shrinkage at the drying and firing stages, which is associated with defects and non-conformity of the final product.

- The reformulated ceramic bodies, in which sand was replaced by different amounts of granite waste, presented lower plasticity as compared to the industrial ceramic body. This would bring practical advantages such as easy drying operation as well as lower drying and firing linear shrinkage that decrease the risk of dimensional defects.
- In the specific case of the reformulated ceramic body with the greatest amount of 40% of granite waste addition, good technological properties were obtained. Up to 1000 °C it has the lowest water absorption, which could be associated to low porosity. Moreover the mechanical strength is the highest at all temperatures.
- The experimental bodies (**XC**'s) with granite waste addition fired at 1050 °C presents plagioclase, quartz and mullite as crystalline phases. In the industrial ceramic body fired at this same temperature, the phases detected by XRD were microcline, quartz and mullite.

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