Original Article

Development of ceramic paver with ornamental rock waste

Lucas Fonseca Amaral, Juliana Peixoto Rufino Gazem de Carvalho*, Bertácia Mendes da Silva, Geovana Carla Girondi Delaqua, Sergio Neves Monteiro, Carlos Maurício Fontes Vieira

Advanced Materials Laboratory – LAMAV, State University of the North Fluminense Darcy Ribeiro – UENF, Av. Alberto Lamego 2000, Campos dos Goytacazes, RJ 28013-602, Brazil

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ABSTRACT

In attempt to give a nobler destiny of ornamental rock residue, in order to expand the use of ceramic paver, clayey bodies were formulated with 0, 10, 20 and 30 wt.% of waste by uniaxial pressure at 34 MPa. The samples were fired at 900, 950, 1000 and 1050 ºC and some technological properties were evaluated. The results indicated that the residue addition adjusted the clayey body plasticity and increased the dry bulk density, indicating a higher packing. The linear shrinkage suffered a decline with increasing residue content, configuring a good result, because it is important for products dimensional control. Although there was a decrease in mechanical resistance, the water absorption presented a small decrease with the addition of residue. The use of ornamental rock residue allowed improvements in yellow clay of Campos dos Goytacazes, besides being an appropriate way of disposal.

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1. Introduction

The ornamental rock industry represents an important market for Brazil, being among the largest producers in the world, to occupy the 4th place with 5.9% of world production in 2015 [1]. The ornamental rock is widely used in construction and is also used for other purposes, as sculptures [2]. Another interesting fact reflects the importance of this sector to the Brazilian economy through the exportation, generating a revenue of approximately US$ 1.10 billion in 2017.

However, all this production reflects a huge problem regarding the generation of solid waste. This waste represents a huge environmental impasse, since, due to the costs involved in its correct destination, many companies end up depositing them in an inappropriate way. Its generation occurs in large quantities in the form of mud, which when dries resulting in a very fine powder. The inappropriate disposal may cause environmental damages, such as the streams and rivers contamination and human health impact by inhalation [3,4]. Due to all these impacts, the importance of recycling this residue is evident.

* Corresponding author.
E-mail: julianarufino@pq.uenf.br (J.P. Carvalho).
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A technical and economical solution to this scenario is the use of this residue as raw material for the clayey based ceramics industry. The ceramic industry, especially the red ceramic segment, has great potential for solid waste reuse. This potential is based on basically two characteristics of this industrial branch, the raw materials characteristics and the high production volume [5,6].

The Brazilian red ceramic industry has great importance for the country, representing 4.8% of the national industrial production with approximately 7400 industries [7]. However, most of these companies have some obstacles that hinder the improvement of red ceramic segment that are hand labor disqualified, lack of business management and outdated technology. In addition to this, most manufactured products have low added value as sealing blocks, for example.

In this scene, the improvement of the red ceramic industry can get along with the diversification of production with the manufacture of high value added products such as tiles, structural blocks and ceramic pavers. The last one, is a clayey pavement which the manufacturing process is still spreading in Brazil, used in architecture and buildings.

The ceramic paver offers benefits such as long life, high mechanical strength, exuberant natural colors and facility of deployment and repair. However, for the manufacture of this product in the Campos dos Goytacazes industries is need to correct the deficiencies of the clays of this region, as low flux content, high plasticity and high loss on ignition, with the use of alternative raw materials.

In this sense, the ornamental rock waste contains K₂O and Na₂O that may act as fluxing agents, which, in reaction with silica and alumina, promote liquid phase formation by eutectic reaction, that improve the sintering process. In addition, this residue has coarse granulometry, which in mixture with the clays are capable of increasing the packaging of the shaped products. Finally, this waste is generated in sufficient quantities to supply the demand and for coming from the beneficiation of ornamental rocks of Santo Antônio de Pádua, that is located in an economically viable distance for use in the Campos dos Goytacazes ceramics.

Due to the presented reasons, this work aims to study the physical and mechanical properties of yellow clay with the ornamental rock waste incorporation, as well as determine a suitable composition for ceramic paver production. In this way, the ornamental rock waste may act in order to correct the deficiencies of clays from Campos dos Goytacazes and provide correct disposal environmentally appropriate and advantageous.

2. Materials and methods

2.1. Raw materials preparation

The ornamental rock residue and yellow clay were dried for 24 h in an oven of Odontobrás brand, model EL-1.5, at a temperature of 110 °C. After drying, the raw materials were manually crushed and sieved through 42 mesh.

2.2. Raw materials characterization

The particle size distribution of the clay was performed according to the NBR 7181-84 (ABNT) standard, which combines sieving and sedimentation techniques [8]. The plasticity was evaluated through the Atterberg limits, and to determine the liquidity limit, the method standardized by Arthur Casagrande in accordance with ABNT NBR 6459 [9] was applied, while the plasticity limit determination was performed according to the standard ABNT NBR 7180 [10].

The dilatometric test was realized on the Netzsch DIL 402 PC equipment, with a heating rate of 10 °C/min and a final temperature of 1050 °C. For test, two samples of 2 g, one without waste and the other with 30 wt.% of waste, were made in cylindrical format pressed with 1 ton.

In order to obtain X-ray diffraction results of 0 and 30% of the residue at all temperatures, the XRD7000 diffractometer of the Shimadzu brand was used, and it was operated with Cu Kα radiation for a 2θ range from 5° to 60°, with step of 0.02° and time of 5 s. The XRD peaks observed in the diffractogram were assigned with reference to the 2θ values and corresponding d-spacing, it was identified with the use of PDXL2 software (Rigaku) by comparison with ICDD – Powder Diffraction Files (PDF-2013) standards.

2.3. Composition preparation

Compositions were made with additions of 0, 10, 20 and 30 wt.% of waste. The compositions were homogenized in a dry mixer for 15 min, moistened with 8 wt.% with water and sieved on 20 mesh. Rectangular specimens were made with dimensions of 115 mm × 25 mm with a weight of 60 g of the mixture, and uniaxial pressing at 34 MPa. These were the conformation parameters selected so that the laboratory specimens reached an apparent dry density similar to those products obtained industrially.

After preparation, the specimens were put into an oven at 110 °C, where it has been drying for 24 h. After drying, they were weighed, measured and sent to the laboratory muffle furnace MAITEC brand, FL 1300 model, and sintered at 900, 950, 1000, and 1050 °C at a constant heating rate of 2 °C/min maintained the threshold temperature for 3 h and cooled by natural convection.

2.4. Properties evaluation

After sintering and cooling, the samples were again weighed and measured with a Mitutoyo digital caliper and the following physical and mechanical properties were determined: dry bulk density, linear shrinkage, water absorption, flexural rupture strength and compressive strength.

The dry bulk density was measured dividing the specimens dry/sintered weight by the external volume (dimensional method) according to Eq. (1).

\[
DD = \frac{\text{Sintered weight (g)}}{\text{Volume (cm}^3\text{)}} \times 100
\]  

(1)
The linear shrinkage (LS) was calculated by the length determination of the samples before and after sintering, according to Eq. (2).

\[
LS = \frac{\text{length}_{\text{final}} - \text{length}_{\text{initial}}}{\text{length}_{\text{initial}}}
\]  

(2)

The water absorption (WA) was obtained according to ASTM standard procedure [11], according to Eq. (3).

\[
WA = \frac{\text{weight}_{\text{humid}} - \text{weight}_{\text{dry}}}{\text{weight}_{\text{dry}}} \times 100
\]  

(3)

The prismatic specimens were used for flexural test, while to determine the compressive strength, a new samples were obtained by cutting the originals specimens with dimensions of 25 mm × 25 mm. The flexural strength (FS) test was performed by loading three points with the load applied by the

Fig. 1 – X-ray diffraction patterns of sintered specimens.
upper cut at a speed of 0.5 mm/min until the specimen was ruptured, the results was calculated according to Eq. (4); the same machine (Instron 5582 universal test machine with 100 kN capacity) was also employed to the compressive resistance (CR) determination by using two parallel protection plates, with cross bar moving at 0.1 mm/min, the results was calculated according to Eq. (5).

$$FS = \frac{3 \times P \times L}{2 \times b \times d^2}$$  \hspace{1cm} (4)

where $P$ = rupture strength (N); $L$ = distance between supports (mm); $b$ = width (mm); $d$ = height (mm).

$$CR = \frac{\text{compressive strength (N)}}{\text{Area (mm}^2\text{)}}$$  \hspace{1cm} (5)

In Brazil, there is no norm to establish standards for ceramic paver, making it necessary to use international norms. In Table 1 are American standards ASTM [12,13].

The sintered specimens microstructure was analyzed by scanning electronic microscopic (SEM) in a Shimadzu model Superscan SSX500-50.

### 3. Results and discussion

In Fig. 1, the X-ray patterns of specimens containing 0 and 30% of residue are shown for sintering temperatures of 900, 950, 1000 and 1050 °C. It can be observed that quartz is very present in all samples and for all temperatures, the quartz is considered a residual mineral, originating from both the clay and residue and acts as a plasticity reducer. However, in excessive quantity, this mineral may cause a decrease in mechanical resistance. This fact is due to the micro-cracks generated in its allotropic transformation at 573 °C. In addition, this mineral has some thermal stability up to temperatures around 1700 °C. Therefore, the quartz does not contribute effectively to the sintering.

It is interesting to note that the presence of mica muscovite is not only present at 1050 °C and at 1000 °C, without residue, and also at 1050 °C containing 30% of residue. This is a mineral with lamellar morphology, which can cause the appearance of defects in ceramics. Since it presents reduced particle size, mica muscovite can act as a phase liquid former due to the eutectic reaction by the presence of alkali oxides.

The hematite is responsible for the reddish color of the pieces. At 950 °C, without residue addition, the rutile appears in small amounts. However, with residue addition the cordierite may be found in small quantities. The mullite is a very important phase for the ceramic industry, because it has excellent mechanical properties, this phase formation was only shown at 1050 °C, this phase is formed by the metakaolinite decomposition, and only occurs at higher temperatures [14,15]. It also may be noted the presence of feldspars, such as an albite, anorthite and orthoclase. The feldspars may act as important fluxes agents by means of eutectic reactions, which may favor sintering and decrease porosity.

Figs. 2 and 3 represent the behavior of the dilatometry curves with 0 and 30% of residue, respectively. Between 100 and 200 °C the curves show a slope, representing a contraction due to the elimination of moisture water. From 200 °C the curves stabilize to 500 °C, when they suffer a sudden fall due to the transformation of the kaolinite to metakaolinite, increasing the density of the particles that have been transformed or the bonding of the metakaolinite particles just formed, generating contraction. A change in inclination of the curves

### Table 1 – Technical specification for ceramic paver according to ASTM.

<table>
<thead>
<tr>
<th>Norms</th>
<th>Technical specifications</th>
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<tr>
<td>ASTM</td>
<td>WA (%)</td>
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<tr>
<td>C 1272</td>
<td>Type R</td>
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<tr>
<td>C1272</td>
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<td>C 902</td>
<td>MX</td>
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<td>C 902</td>
<td>NX</td>
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WA, water absorption; CS, compressive strength; AI, abrasion index; AV, volume of abrasion; R and F, implementation systems hard and flexible, respectively; SX, floors suitable for outdoor subjected to freezing and thawing conditions; MX, indicates outdoor use and not exposed to cold temperatures; NX, suitable for interiors.
is observed, occurring in higher values for the formulation with 0% residue (around 650°C). This occurs due to the formulation with residue having greater quantity of quartz that suffers allotropic transformation from 573°C, generating an expansion. In this interval, there is a concurrence between the sintering of the material, initiated by the transformation of the metakaolinite, generating contraction and the transformation of the quartz, generating expansion. The sintering process stands out, but the quartz transformation is able to retard the contraction, which is even more present in the mass with 30% of the residue. At temperatures around 900°C, the curves return to present a sudden slope that may be related to the end of the allotropic transformation of the quartz, which slowed the contraction and the formation of the liquid phase, responsible for the sintering.

Fig. 4 shows the particle-size distribution of the clay and the residue. The fraction below 2 μm represents the clay fraction, between 2 μm and 20 μm the silt fraction and above 20 μm, sand fraction. The residue presents granulometry distributed in 54.5% of silt, 44.2% of sand and only 1.3% of clay, presenting a coarser granulometry when compared to that of the clay, that has 44.1% of clay, 26% of silt and 29.9% of sand. Despite of the residue has a coarser granulometry than the clay, it has enough fine granulometry to be used in the formulation of the masses. The ornamental rock waste is a non-plastic material, which may improve the packing of the samples and decrease the linear shrinkage.

Fig. 5 presents the location of the clays within the Winkler Diagram. This diagram is based on the granulometry of raw materials to delineate regions suitable for the manufacture of certain products such as solid brick (region 1), hollow brick (region 2), tiles (region 3) and shackles (region 4).

In this figure, it can be observed that the yellow clay presents a more distributed granulometry, being located in the region suitable for the manufacture of tiles, while the residue presents concentrated particle size in the intervals of 2-20 μm and >20 μm, being located outside the regions for viable products. However, combinations of these raw materials could produce bodies inside practical regions.

Fig. 6 presents a prognostic of the extrusion of the masses with 0 and 30% of residue by means of the Atterberg limits.

Fig. 7 presents the dry density according to the content of ornamental rock residue incorporated in specimens sintered at 900, 950, 1000 and 1050°C.
[16]. The Atterberg method determines the interval of moisture that a clay or clay mass can be moldable. For this, a plastic limit, that indicates the minimum amount of water to achieve the plastic state and liquid limit, which indicates the maximum amount of water that the material without changing its plastic state. Above this limit, clay or clay mass is not consistent enough to be moldable. The plastic index is defined as the difference between the liquid limit and plastic limit. It is considered in the literature that clay or clay mass have a minimum plastic index of 10% [17].

Both the clayey body without residue and with 30% of residue have plastic index above 10%. The plastic limit of both is outside the recommended limit for an optimal extrusion (18–25%), presenting higher values. However, the addition of the residue decreased the plastic limit of the clay, locating the clay mass in the region of acceptable extrusion. This happens due to the deplasticizing action of the residue, which has a coarse granulometry. The apparently unsuitable behavior of the sample 0% has, however, practical advantages, such as less wear of the equipment, and also by the fact than it can increase the production and the mechanical strength of the pieces.

The apparent dry density results are shown in Fig. 7, it can be observed that the values of the ceramics with 0 and 10% of residue are statistically similar. With the addition of 20% this property presents an increase, being similar to the specimens containing 30% of residue. This increase, in favor of the amount of waste incorporated, is explained by the coarser particles presented by the ornamental rock residue when compared to the clay, this characteristic contributes to
the packaging increase and as consequence increases the density [18].

In Fig. 8 are represented the water absorption results as function of the residue incorporation content at all the employed sintering temperatures. It is generally agreed that increasing the sintering temperature leads to a reduction in water absorption, this fact is explained by the more efficient sintering at high temperatures, resulting in the closure of porosity and consequently the reduction of water absorption occurs. The water absorption values present small decrease as the residue content is increased, except for the temperature of 1050 °C. Although the ornamental rock waste contains fluxing oxides such as Na2O and K2O, which may cooperate with the liquid phase formation, the factor that most contributed to the water absorption reduction was the specimens apparent dry density increase as the residue is added, which may be observed in Fig. 9. With the exception of the sintering temperature of 1050 °C, the others temperatures were not enough to reach a good level of sintering by liquid phase formation.

Fig. 12 – Compressive strength according to the content of ornamental rock residue incorporated in specimens sintered at 900, 950, 1000 and 1050 °C.

Fig. 13 – Specimens optical micrographs (a) sintered at 950 °C, without waste with 430× magnification; (b) sintered at 950 °C, with 30 wt.% of waste with 430× magnification; (c) sintered at 1050 °C, without waste with 216× magnification; (d) sintered at 1050 °C, with 30 wt.% of waste with 216× magnification.

Fig. 14 – SEM image of ceramic containing 0% residue and sintered at 900 °C.
Fig. 15 – (a) SEM image of ceramic containing 30% residue and sintered at 900 °C; (b) typical EDS of mica muscovite.

Fig. 16 – (a) SEM image of ceramic containing 0% residue and sintered at 1050 °C; (b) typical EDS of mica muscovite – point 1; (c) EDS of amorphous matrix – point 2; (d) typical EDS of sodium feldspar – point 3.

Formulations involving all studied waste contents and sintered at 1050 °C are indicated, based on the ASTM standard, for MX-type ceramic pavers production, which are indicated for external areas and whose concern with freezing is not considered. The NX type, suitable for indoor use, has no limits for water absorption.

The specimens sintering linear shrinkage results are represented in Fig. 9. It is possible to note the reduction of this property as it adds higher residue content. This fact is justified by the more inert characteristic of the residue compared to the clay. Thus, by partially replacing the clay with the residue, it will also be reducing the content of clay minerals which are the main responsible for sintering linear shrinkage of the ceramics. With increasing residue content, linear shrinkage decreases at all temperatures. For example, the samples with 30 wt.% of residue and sintered at 1050 °C had a linear shrinkage decrease of approximately 27% compared to the samples without waste. This property is an important parameter for ceramic industry, as this is one of the most critical stages of the process, where there is a greater probability of generating defective products. In Fig. 10 an optical micrograph of a sintered specimen is shown, clearly demonstrating a micro-crack generated during the sintering process. If the shrinkage is too excessive, the sintered ceramic matrix may not withstand the stresses generated by it generating critical cracks in the parts.

Figs. 11 and 12 show the results of flexural rupture strength and compressive strength, respectively. The increase in temperatures favors sintering kinetics, and generally, benefits
the mechanical resistance resulting in product consolidation improvement.

Contrary to what has been demonstrated by Vijayaragavan et al. [19], a reduction in mechanical strength is observed with the increasing residue content. This occurs because the ornamental rock residue has a large amount of quartz. Due to its allotropic transformation at 573 °C, tensions are generated inside the pieces and resulting in micro-cracks that act as stress concentrators contributing to the reduction of mechanical resistance [18].

Despite of compressive strength reduction, which reaches 42% at 1050 °C when comparing the formulations containing 30 and 0 wt.% of waste, virtually all formulations at all sintering temperatures are satisfactory, according to ASTM, for some type of ceramic paver production.

Fig. 13 shows the optical micrographs of specimens without residue and with 30 wt.% of residue. It is possible to note that there is an increase in the amount of quartz particles and their size, being able to prove the aforementioned discussion.

The scanning electronic micrographs (SEM) of the compositions containing 0 and 30% of the residue and sintered at 900 °C, the lowest temperature used in this study, are shown in Figs. 14 and 15. It is possible to observe in both micrographs a rough texture with still lamellar appearance of the particles. This indicates the low microstructural consolidation of these sintered ceramics at 900 °C due to the lack of liquid phase formation. In Fig. 15 it may be observed a possible muscovite mica particle, proven by EDS. In this case, it is verified that the coarser granulometry of this particle shows failure of consolidation with the amorphous ceramic matrix, emphasizing that the coarse granulometry of the residue may have contributed to the mechanical resistance reduction.

Figs. 16 and 17 represent the SEM obtained from ceramics containing 0 and 30% residue and sintered at 1050 °C, the highest temperature employed in the study. In view of these images, it is possible to notice a microstructure with a less rugged and more consolidated texture, and there are also fewer pores. In both figures some points were still selected for the realization of EDS in order to investigate some mineralogical phases present. In Fig. 16, a probable muscovite mica particle in its lamellar form is also identified, a particle of a potassium feldspar and the chemical composition of the amorphous ceramic matrix. While in Fig. 17 the EDS was also performed only to identify the chemical composition of the amorphous ceramic matrix.

4. Conclusion

- The residue adjusted the plasticity of the yellow clay and enabled, by coarse granulometry, a greater packing, increasing the dry density.
- The pieces when submitted to the higher firing temperatures suffer a better sintering, presenting improvement in all investigated properties.
- The increase in the residue content resulted in a minor linear retraction, which is of extreme importance for the dimensioning of the pieces.
- In the absorption of water, the residue caused minor changes, decreasing it.
- Due to the probable cracks generated by the large quantity of quartz present in the residue, there was a significant reduction in the mechanical resistance with the increase of the residual content.
- The use of ornamental rock residue is viable for some types of ceramic pavers. Due to the results of water absorption and compressive strength obtained, MX and NX type pavers with a firing temperature of 1050 °C, according to ASTM, can be produced.
- In addition to improvements in some properties of ceramics, the use of this residue for this purpose allows the recycling of a material that could be disposed of unduly and causing damage to the environment.

Conflicts of interest

The authors declare no conflicts of interest.

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