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Sustainability in ceramics: The potential of residue from ornamental stone processing in clayey ceramic mass

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ABSTRACT
There is great concern about the generation and disposal of industrial solid waste. In the last years, solid waste has been incorporated into clayey masses, mainly for red ceramic manufacture. The incorporation of waste into clay mass can reduce environmental damage, which adds economic value to a material that would be discarded to produce a sustainable product. Therefore, the addition of residue from the processing of ornamental rocks into clay mass for the manufacture of red ceramics was studied, evaluating its potential in the ceramic industry. First raw materials were characterized by X-ray fluorescence spectroscopy, X-ray diffraction, and thermogravimetric analysis. Then, 10, 20 and 30% of the residue were added to the clay mass and specimens were made using extrusion. The specimens were fired at 850 and 950°C for 180 minutes, at a heating rate of 2°C/min. Then they were characterized in terms of firing shrinkage, water absorption, apparent porosity, apparent density, mass loss on ignition, and flexural strength. The results obtained showed that the firing temperature at 950°C contributed to a more efficient densification of the specimens. The addition of up to 20% of this residue to the ceramic mass showed similar mechanical properties to the formulation made only with clay. Therefore, it is possible to reduce the amount of clay used to make ceramic materials, using residue from ornamental stone processing as an alternative raw material.

KEYWORDS: Solid waste. Residue from ornamental stone processing. Ceramics.

1 INTRODUCTION

According to the Associação Brasileira de Cerâmica (ABCERAM, 2023), all non-metallic materials of inorganic origin are considered ceramics, generally obtained after firing at high temperatures, such as red and white ceramics, refractories, thermal insulators, abrasive materials, glasses, etc.

Red ceramics have a reddish color, as its name suggests. This coloring comes from the high percentage of iron oxide (Fe_2O_3) in its composition. It is generally used in the construction industry, as bricks, blocks, tiles, and ceramic tubes. It is common for ceramic materials to be formed through extrusion, which is one of the most used methods in the manufacture of red ceramics (WIECK & DUAILIBI, 2013).

The main raw materials used in the production of red ceramics are clay with high iron content (KAZMIERCZAK, 2017). Clay is used because of its plasticity, moldability, and good mechanical resistance associated with firing (VIEIRA; HOLANDA; PINATTI, 2000). However, according to a study carried out by Fonseca and Morais (2022), there are environmental impacts caused by clay extraction, such as air pollution, contamination of rivers and groundwater, deforestation and impacts on soil, as well as noise and visual pollution.

For this reason, a huge challenge for the ceramics industry is to reduce the extraction of clayey raw materials. In this context, solid waste can be used as an alternative raw material in the manufacture of red ceramics. Many studies discuss the ability of red ceramics to incorporate various types of waste, such as glass residue from glaze decanters (INOCENTE et al., 2018), water treatment sludge (SILVA & MACIEL, 2019), gypsum waste (ALMEIDA et al., 2020), Kraft pulp mill and flat glass cutting wastes (RODRIGUES et al., 2021) and walnut shell (BARNABAS et al., 2022).

Like other manufacturing processes, the ornamental stone processing generates residue that can cause environmental impacts when disposed of inappropriately. However, according to Taguchi et al. (2014), the composition of this residue is similar to the composition of clay, making it possible to incorporate it into the ceramic mass.

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Brazil has international prominence in the ornamental stone sector, according to the World Marble and Stone Report (MONTANI, 2020), it is one of the five largest global producers. In the Brazilian economy, great part of exports carried out in Brazil comes from this sector (ABIROCHAS, 2022).

Moreira, Freire, and Holanda (2003) studied the incorporation of ornamental stone residue into ceramic masses and selected important aspects, such as the chemical and mineralogical composition of the residue, similar to clay, in addition to the non-plastic nature of the residue, which can be beneficial to the clay mass.

Based on this, the objective of the present study was to evaluate the influence of incorporating residue from ornamental stone processing into clay mass for the manufacture of red ceramics through extrusion, in addition to verifying the possibility of reducing the amount of natural raw material used in the ceramic industry.

2 MATERIALS AND METHODS

2.1 Characterization of the raw materials

The raw materials used in this study were clay and residue from ornamental stone processing (ROSP). Clay was obtained from a deposit located in Nova Venécia, Espírito Santo, Brazil, while ROSP was donated by the Marmi Bruno Zanetti industry, located in Viana, Espírito Santo, Brazil.

After obtaining the raw materials, samples were prepared and placed in a laboratory oven at 110°C ± 5°C for 24 hours and were then used for characterization tests.

The mineralogical characterization was carried out using X-ray diffraction (XRD), performed on a Brucker diffractometer, model D8, with Cu-Kα radiation and diffraction angle 2θ. The crystalline phases present were identified using the DIFFRACPLUS® software, adopting patterns from the Joint Committee on Powder Diffraction Standards database.

The chemical analysis of clay and ROSP was conducted through X-ray fluorescence using the PANalytical equipment (model AxiosMax) with a 4 kW tube and rhodium target.

The thermal behavior of ROSP was measured through thermogravimetry (DSC/ATG), on the BP Engenharia equipment (model RB 3000), in a nitrogen atmosphere, at a heating rate of 10°C/min and a temperature range between 20 and 1050°C.

2.2 Formulations and specimens

To verify how the amount of residue added to the clay mass would influence the physical and mechanical properties of the specimens, four formulations were prepared. A formulation containing only clay was prepared to serve as a reference formulation (A0). For the other formulations, clay and ROSP were used, partially replacing the clay at levels of 10, 20 and 30%, as shown in Table 1.

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Table 1 – Composition of the formulations (% by mass).

Formulation	Clay (%)	ROSP (%)
A0	100	0
R1	90	10
R2	80	20
R3	70	30

Source: Prepared by the authors, 2023.

After defining the formulations, the raw materials were dried in a laboratory oven for 24 hours at a temperature of 110°C ± 5°C. They were then broken with a Marconi ball mill for 20 minutes and sieved using an ABNT n. 60 sieve with a mesh opening of 0.250 mm. Subsequently, the mixtures were homogenized, moistened with 25% (by mass) of water and placed in plastic bags for 24 hours.

The samples were then made using a Verdés extruder (model BR 051). The clayey masses were driven by an endless screw into the vacuum chamber (25 kgf/cm2), and exited through the rigid matrix continuously. For each formulation, 60 prismatic specimens were formed in dimensions of 95 mm x 30 mm x 15 mm.

All specimens were dried in a laboratory oven at 110°C ± 5°C for 24 hours. After, twenty specimens of each formulation were fired at 850°C, twenty specimens of each formulation were fired at 950°C and another twenty specimens of each formulation were not fired in order to determine the mechanical resistance. Firing was carried out in a muffle-type laboratory oven, at a heating rate of 2°C/min and a duration of 180 minutes. Afterwards, the specimens were cooled inside the laboratory oven by natural convection to room temperature.

2.3 Characterization of the specimens

To characterize the specimens, the dimensions and weights of the specimens were measured after drying and firing. Furthermore, the specimens were subjected to weighing of the immersed mass and wet mass. To obtain the immersed mass, the specimens were immersed in water for 24 hours and then weighed on a hydrostatic balance. After weighing the immersed mass, the excess water on the surface of the specimens was removed with a damp cloth. Then the specimens, which were previously saturated with water, were weighed again to determine the wet mass.

The characterization of specimens was performed using linear burning shrinkage (LBS), apparent porosity (AP), water absorption (WA), apparent specific mass (ASM), fire loss (FL) and flexural strength (FS), obtained from Equations 1, 2, 3, 4, 5 and 6, respectively.

$$LBS(\%) = \frac{Ls - Lq}{Ls} \times 100$$ (Equation 1)

$$AP(\%) = \frac{mu - mq}{mu - mi} \times 100$$ (Equation 2)

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$$WA(\%) = \frac{mu - mq}{mq} \times 100$$ (Equation 3)

$$ASM(g/cm^3) = \frac{mq}{mu - mi}$$ (Equation 4)

$$FL(\%) = \frac{ms - mq}{ms} \times 100$$ (Equation 5)

$$FS(MPa) = \frac{3 \times P \times L}{2 \times b \times h^2}$$ (Equation 6)

Where *Ls* is the length of the specimens after drying in the laboratory oven; *Lq* is the length of the specimens after firing (mm); *ms* is the mass after drying in the laboratory oven (g); *mq* is the mass after firing (g); *mi* is the immersed mass (g); *mu* is the wet mass (g); *P* is the force applied for rupture (N); *L* is the distance between the supports (mm) set at 70 mm; *b* is the width of the specimen (mm); and *h* is the thickness of the specimen (mm).

3 RESULTS

3.1 Characterization of the raw materials

Table 2 presents the results of the chemical characterization of the clay and residue from ornamental stone processing (ROSP). It is possible to verify that the raw materials used consist mainly of SiO_2 and Al_2O_3, corresponding to approximately 80.50% of the composition of the clay and 84.28% of the ROSP.

Table 2 – Chemical composition of raw materials.

Chemical components (%)	Clay	ROSP
SiO_2	55.61	65.75
Al_2O_3	24.89	17.53
Fe_2O_3	5.97	4.62
K_2O	2.33	5.39
TiO_2	1.1	0.40
MgO	0.62	0.74
Na_2O	0.42	1.70
CaO	0.15	3.23
P_2O_5	0.12	0.32
MnO	<0.05	0.06
SO_3	-	0.21
SrO	-	<0.05
ZnO	-	<0.05

Source: Prepared by the authors, 2023.

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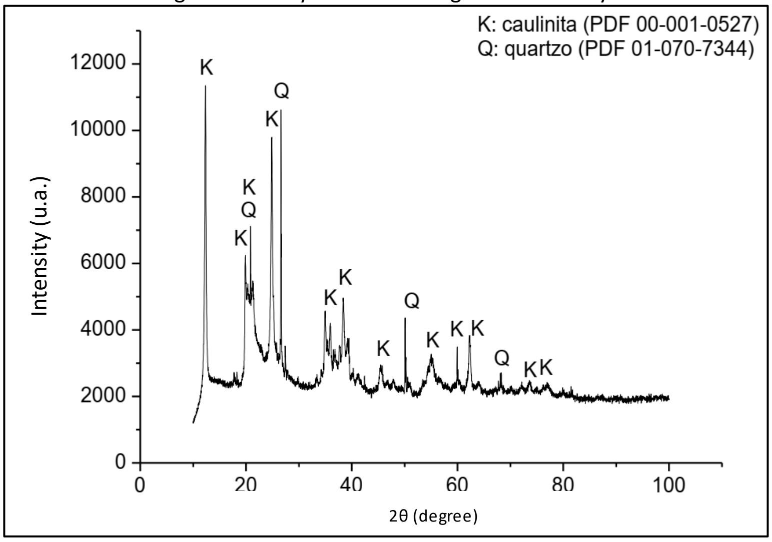
Moreover, although in low concentrations, levels of K_2O, CaO and MgO were identified, they can act as melting elements in ceramic masses. This fact can reduce the temperature required for particle consolidation during the firing process, due to the formation of the liquid phase (MANHÃES et al., 2009).

ROSP presented a significant concentration of SiO_2 in relation to the other components. This can be considered an indication that the ornamental stones that originated the residue are predominantly granitic stones (NEVES et al., 2021).

Regarding the mineralogical characterization of clay, it is possible to infer that the clay used is the kaolinite type, since the presence of kaolinite accounts for the majority material. The existence of quartz in the mineralogical analysis corroborates the significant content of SiO_2 detected in the chemical characterization. Figure 1 illustrates the clay X-ray diffraction peaks that correspond to kaolinite and quartz.

Figure 1 – X-ray diffraction diagram of the clay.



Source: Prepared by the authors, 2023.

In the mineralogical characterization of ROSP, the predominance of quartz is evident, corroborating the fact that the residue studied comes from stones with a silicate composition, therefore granitic stones (NEVES et al., 2021). Quartz can reduce the plasticity of clay mass, reducing the amount of water required for extrusion. In addition, it can increase the hardness and promote the densification of ceramic products (ALMEIDA et al., 2020). Diffraction peaks in ROSP corresponding to microline, albite, and calcite were also identified, as shown in Figure 2.

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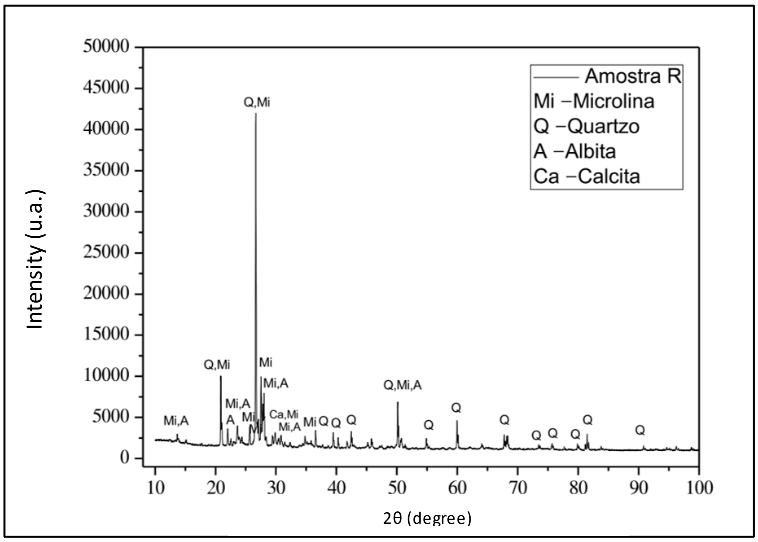
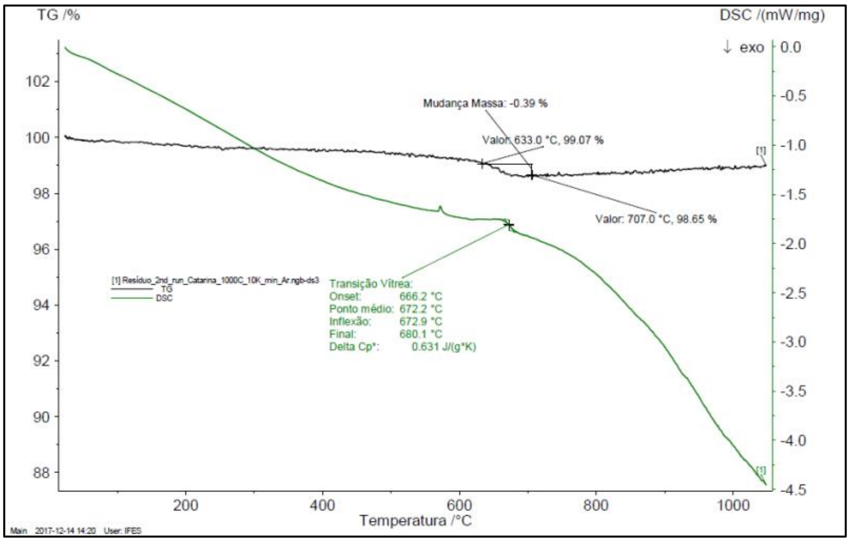
Figure 2 – X-ray diffraction diagram of the ROSP.



Source: Authors, 2023.

Figure 3 shows the thermal analysis of ROSP, using DSC/ATG, which reveals the events linked to mass loss during heating up to 1050°C. There is an endothermic event between the temperature of 633°C and 707°C, approximately, associated with a small loss of mass, of 0.39%. This loss of mass can be attributed to the glass transition, which occurs at temperatures close to 670°C, considering the presence of K2O, CaO and MgO in its chemical composition.

Figure 3 – ROSP DSC/ATG graph.



Source: Prepared by the authors, 2023.

3.2 Characterization of the specimens

Figure 4 illustrates the specimens used in the physical and mechanical tests. The specimens that were not fired (A) are brown. The specimens fired at 950°C (C) acquired a redder color compared to those fired at 850°C (B).

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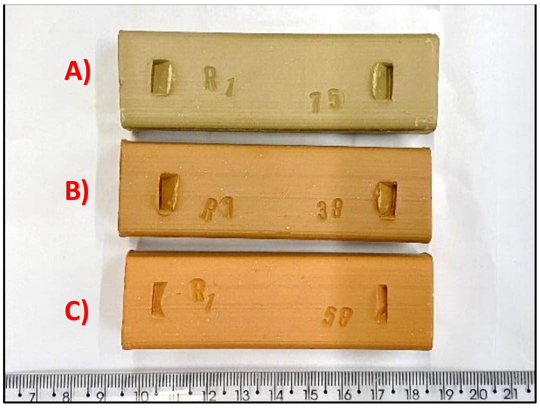
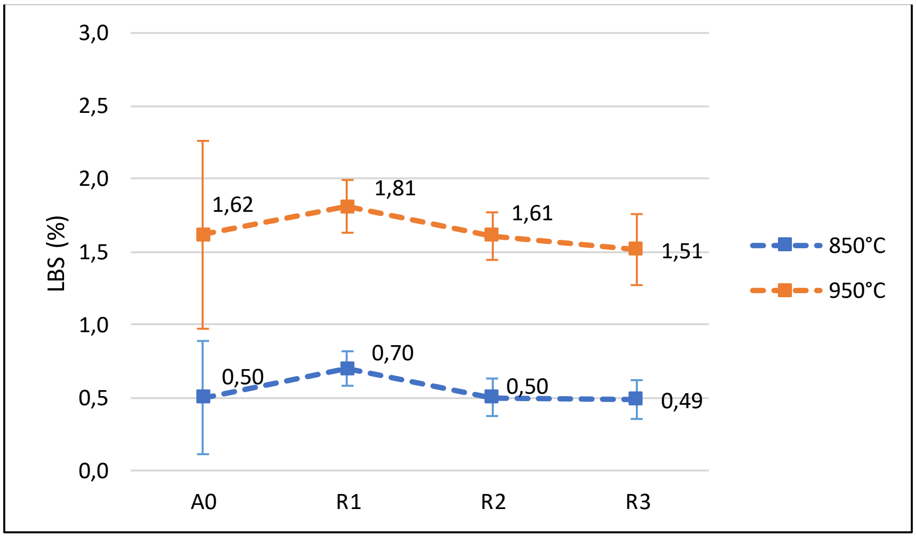
Figure 4 – Extruded specimens.



Source: Prepared by the authors, 2023.

Using linear burning shrinkage (LBS), it is possible to verify the effectiveness of the sintering process, because greater retraction is an indication of greater particle densification. The specimens fired at 950°C presented higher LBS than those fired at 850°C for all formulations. Formulations A0, R1 and R2 obtained the highest LBS values, indicating that the addition of ROSP to the clay mass reduced LBS (Figure 5).

Figure 5 – Linear burning shrinkage of the tested formulations.



Source: Prepared by the authors, 2023.

Water absorption (WA) and apparent porosity (AP) are associated with LBS. As expected, formulations R1, R2 and R3 obtained the lowest WA and AP values. Therefore, the addition of ROSP to the ceramic mass reduced the WA and AP values in relation to the reference formulation (A0). It is possible to conclude that the specimens fired at 950°C recorded the best results for WA and AP (Figure 6 and Figure 7).

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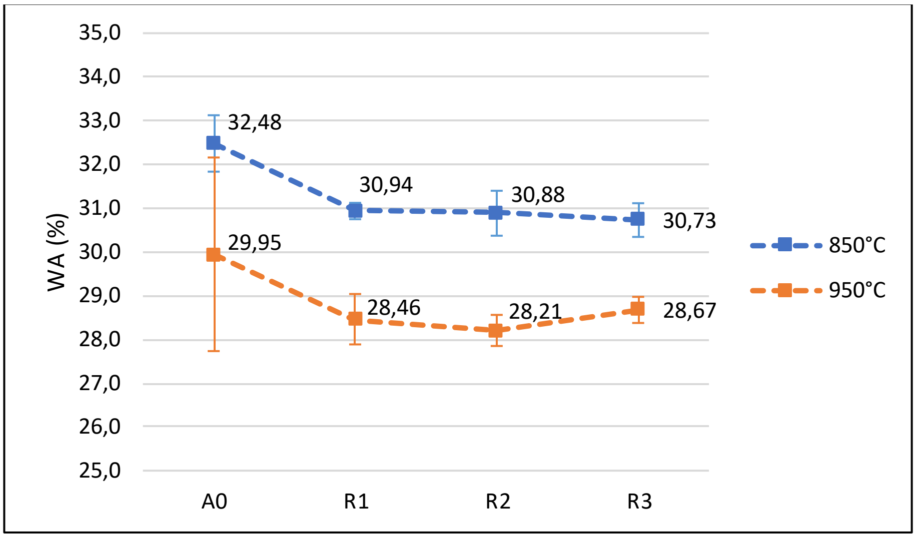
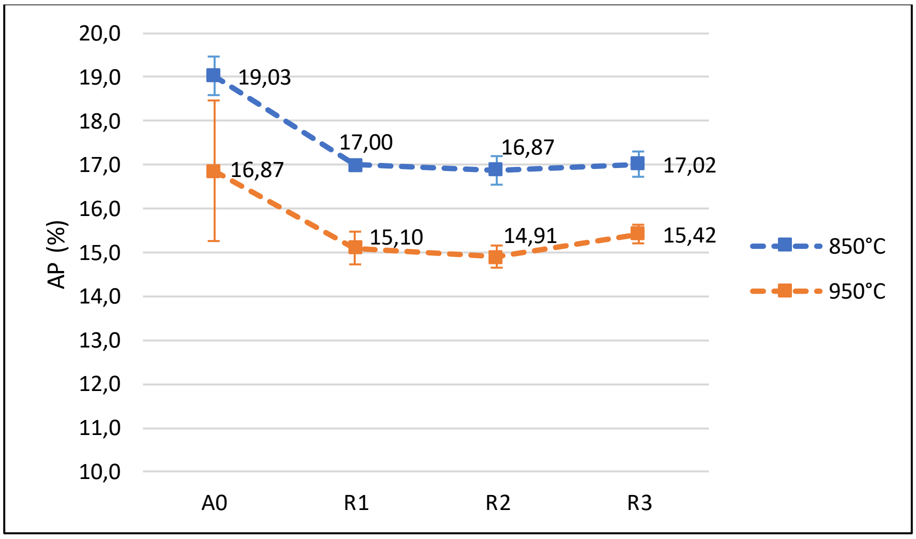
Figure 6 – Water absorption of formulations after firing.



Source: Prepared by the authors, 2023.

Figure 7 – Apparent porosity of formulations after firing.



Source: Prepared by the authors, 2023.

The apparent specific mass (ASM) of the specimens fired at 850°C was lower compared to the specimens fired at 950°C, therefore, a higher temperature favored the densification of particles (Figure 8). The incorporation of the residue into the clay mass also contributed to greater densification of the specimens, as the formulations with residue obtained a higher ASM compared to the reference formulation (A0).

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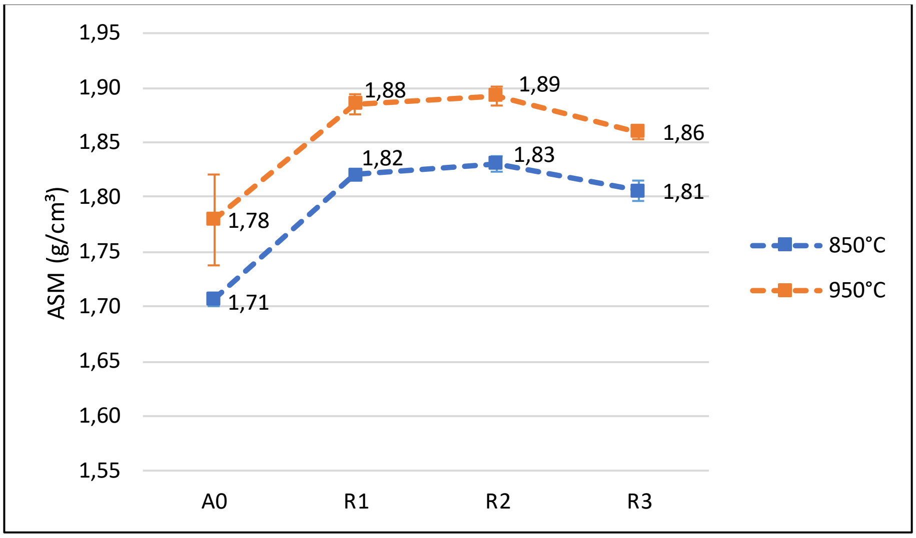
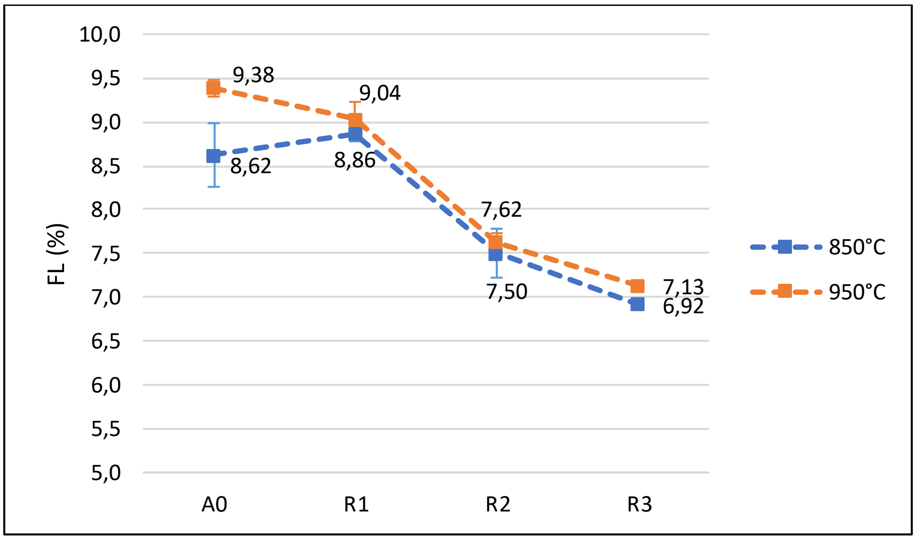
Figure 8 – Apparent specific mass of formulations after firing.



Source: Prepared by the authors, 2023.

In terms of fire loss (FL), the specimens fired at 950°C demonstrated higher FL compared to those burned at 850°C. However, with the addition of residue, FL tended to reduce considering all formulations with residue, as shown in Figure 9. FL of the specimens may be linked to the low mass loss of ROSP, since the addition of the residue decreased FL.

Figure 9 – Fire loss of formulations after firing.



Source: Prepared by the authors, 2023.

Regarding the flexural strength (FS) tests, the firing temperatures influenced the mechanical resistance of the specimens, since the specimens burned at 950°C indicated a higher FS in relation to those burned at 850°C (Figure 10). Formulations R1 and R2 fired at 950°C showed better mechanical resistance, presenting results close to the reference formulation (A0). However, according to the recommendations of Santos (1989), for the manufacture of masonry

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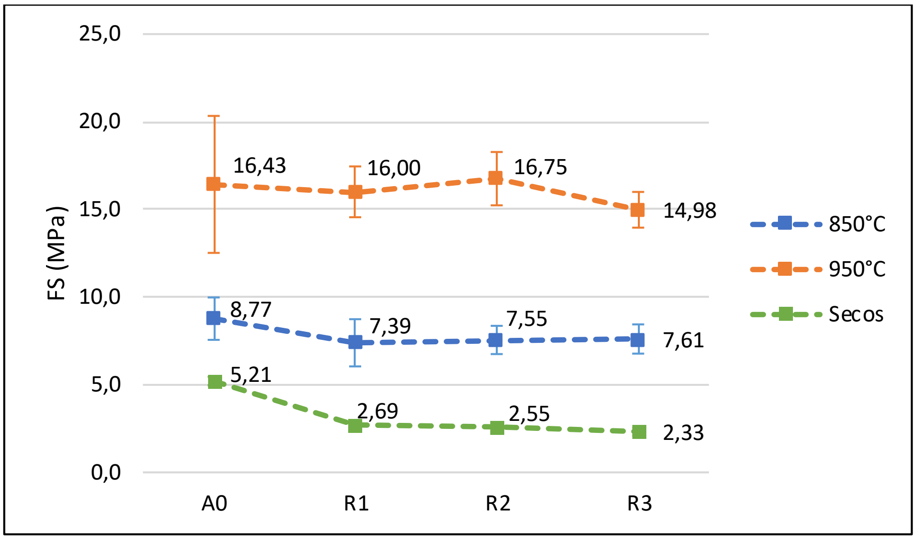
bricks, the minimum FS limit after firing is 2.0 MPa. Therefore, all formulations, regardless of the burning temperature, met the recommendation.

Figure 10 – Flexural strength of the specimens.



Source: Prepared by the authors, 2023.

4 CONCLUSIONS

This study investigated the feasibility of using residue from ornamental stone processing (ROSP) as an alternative raw material in the manufacture of red ceramics. From a chemical point of view, ROSP predominantly has SiO_2 and Al_2O_3, as does clay. Moreover, the main mineralogical constituent of the residue is quartz, showing that the residue comes from granitic stones. Quartz in the clay mass helps maintain the plasticity necessary for extrusion.

The firing temperature significantly influenced the physical and mechanical characterization of the specimens, considering that firing at 950°C presented the best results. The incorporation of up to 30% of ROSP into the clay mass reduced apparent porosity, water absorption, and fire loss. The addition of ROSP also contributed to greater densification of the specimens, corroborated by the linear burning shrinkage and apparent specific mass.

The incorporation of up to 20% of residue into the ceramic mass showed mechanical properties similar to the reference formulation, which contains only clay. However, it is essential to keep in mind that all formulations with residue met the recommendations of Santos (1989) for flexural rupture stress.

Therefore, the results attest that it is possible to reduce the amount of natural raw material used in the manufacture of red ceramics. With the incorporation of up to 30% of ROSP into the clay mass, the amount of clay in the ceramic mass formulation can be reduced by up to 70%.

Furthermore, the use of waste, which is generated in large amounts and is normally disposed of in landfills, can add value to the ceramics industry, aiming to produce more sustainable materials for trading.

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