

Using ornamental stone cutting rejects as raw materials for red clay ceramic products: Properties and microstructure development

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Abstract

The incorporation of various wastes in red clay-based ceramic products has been widely investigated, frequently with the aim of reducing the waste environmental impact. This work explores the not so obvious waste potentialities and describes the properties and microstructure development in a natural clay showing large processing limitations, upon the addition of two different ornamental stone cutting rejects, granite and marble + granite. All materials were collected at industrial sites and the behavior of mixtures containing 70 wt.% clay + 30 wt.% reject is detailed. Powder samples were uniaxially pressed under 20 MPa, sintered in air in an electric furnace for 2 h at a temperature in the range 950–1150 °C, and characterized. The experimental results obtained (firing shrinkage, porosity, flexural strength, microstructure) show that the rejects can be used to replace traditional fluxing agents, helping the sintering process, and simultaneously control the plasticity and shrinkage of an otherwise unusable clay, with obvious economical and environmental benefits.

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1. Introduction

Nowadays, industries of all kinds are looking for alternative, less expensive, raw materials and have optimized their processes in order to reduce the amount of waste they produce and the corresponding environmental impact. For a while, the ceramic industry, particularly the sector devoted to the fabrication of building products, has been the target for the incorporation of other industries rejects, particularly where the inertization of hazardous wastes is concerned [1–4]. Today, it is clear that some wastes are similar in composition to the natural raw materials used in the ceramic industry, and often contain materials that are not only compatible but also beneficial in the fabrication of ceramics [5–9]. Thus, upgrading industrial wastes to alternative ceramic raw materials becomes interesting, both technically and economically [10], and is becoming common practice. To this aim, waste materials have been classed in three categories [5]: (a) fuel wastes (those with high contents of organic or carbon-rich

substances, hence with high calorific added value), (b) fluxing wastes (which improve the ceramics sinterability), and (c) plasticity-controlling wastes (those likely to introduce changes in the green body preparation).

Ornamental stone cutting rejects (e.g. marble and granite) are inert and non-dangerous, but are becoming a worrying factor for industry owners and environmentalists alike. A growing amount of rejected mud is continuously discarded into rivers and lagoons, eventually leading to environmental degradation [11]. Granite has, as major constituents, feldspar, quartz and mica, and marble is basically constituted of calcite. The corresponding rejects can be classified as fluxes, as they have the potential to act as glassy phase formers during the sintering process, improving the sinterability of the clay material. The effect of small additions of such rejects to clay mixtures has already been investigated [7,8,12], and it was observed that the final properties of the fired products do not change drastically. It has also been shown [10] that higher contents of marble and granite rejects can be used to enhance the processing of clay products, enabling firing at lower temperatures. These materials also have a non-plastic character and, therefore, can play an important role as plasticity-controllers during fabrication.

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Table 1
Chemical composition of the raw materials used in this work (wt.%)

	Average particle size (μm)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	MnO	LoI
Clay	8.76	40.61	27.02	12.07	1.42	2.88	4.40	0.80	1.41	0.18	8.48
Granite	12.27	44.21	22.38	9.86	8.71	3.51	4.13	2.71	2.33	0.15	0.43
Margran	24.97	37.86	13.65	3.56	19.92	2.71	4.32	3.58	0.61	0.07	12.37

The objective of this work is to further investigate the use of granite and marble + granite rejects (hereafter referred to as margran) as full-fledged raw materials in the production of red clay ceramics, in conjunction with an otherwise unusable clay material. At a laboratory scale, the exact replication of the conventional industrial procedure (extrusion and slow firing) is not always easy to accomplish but such a study can also be carried out using different processing conditions and still produce valuable results.

2. Experimental procedure

A natural clay, with a plasticity index of 10.8% and poor firing characteristics, and two different ornamental stone cutting rejects, granite and margran, were collected as powders at industrial cutting works in the state of Rio Grande do Norte, Brazil, and used in this work. All materials are abundant and a viable intensive use is sought for them. Other than thorough drying at 120 °C, neither was subjected to any pretreatment before mixing.

Powder compacts (100 mm × 10 mm × 10 mm), obtained by uniaxially pressing (20 MPa) clay + reject mixtures were sintered in air, for 2 h, at 950, 1000, 1050 and 1100 °C (heating rate of 5 °C/min). Both raw materials and fired samples were fully characterized and, as explained later, particular emphasis will be given in this work to mixtures containing 70 wt.% clay and 30 wt.% reject, their microstructure features and the properties that control and are controlled by it. Raw materials chemical composition was obtained by X-ray fluorescence (XRF, Shimadzu EDX 700). The flexural strength of the sintered samples was determined in three-point bending tests (Shimadzu Autograph) with a constant crosshead speed of 0.5 mm/min, and open porosity was determined by Archimedes water displacement method. Microstructure characterization of fracture surfaces was carried out by scanning electron microscopy (Shimadzu SSX-550).

3. Results and discussion

Table 1 gives the average particle size and chemical composition of the raw materials. Both rejects present much coarser particle sizes than the clay and a non-plastic character. Small reject additions should translate into better particle packing and will likely contribute to a reduced drying shrinkage, as compared to the clay alone. Increasing reject additions will eventually produce higher porosities.

The clay presents the expected typical composition. It is rich in silica and alumina with minor contents of Mg, Ti, Ca, K and Na oxides, accompanied by a significant iron oxide content (12.07 wt.%), which will be responsible for the dark colour-

ing of the sintered bodies. The loss on ignition (8.48 wt.%) is within the usual range for red-clay materials and is associated with volatile components and organic matter burn-off [13–15]. In terms of mineralogy, the clay contains quartz and kaolinite and minor amounts of muscovite, rutile, iron oxide and illite [10]. During heat treatment, after the expected large shrinkage upon heating above 600 °C, this clay shows a shattering expansion above 800–900 °C (Fig. 1), which precludes its use without firing additives.

As expected, the rejects contain quartz, biotite, dolomite, albite, anorthite, calcite, rutile and orthoclase [10,16]. SiO₂ and Al₂O₃ contents in both rejects (and also those of the minor oxides) are comparable to those in the clay. On the contrary, in both the iron oxide content is significantly lower than in the clay, whereas the CaO content is much higher (particularly in margran, ~20 wt.%). Margran also presents the highest loss on ignition value, which is basically related to the decomposition of

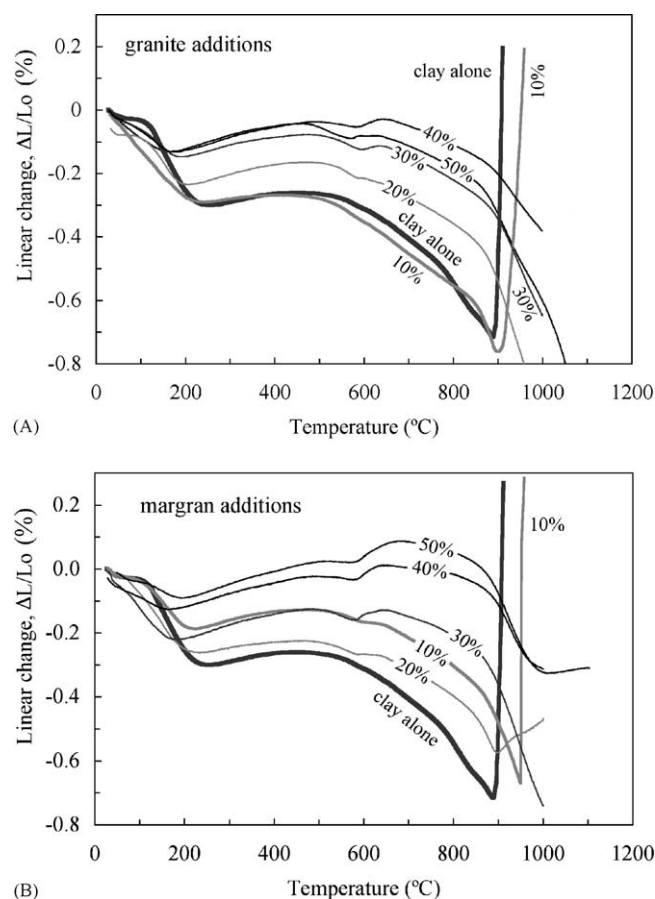


Fig. 1. (A) Dilatometric behavior of the clay alone and upon granite reject additions (10–50 wt.%). (B) Dilatometric behavior of the clay alone and upon margran reject additions (10–50 wt.%).

calcite, and the granite shows the lowest LoI value. The chemical composition of the mixtures of the clay with any of the rejects will show important changes only in terms of the secondary oxides, of which iron oxide will be the most abundant. Thus, the reject-added clay products are expected to present a lighter colouring than the clay alone. The higher alkaline and alkaline–earth oxide content (Na_2O , K_2O , CaO , MgO) present in both rejects (19.06 in granite and 30.53 wt.% in margran, compared to 9.50 wt.% in the clay), together with the iron oxide present in the clay, are expected to promote the liquid phase formation and development during firing (enhancing sintering and fired body mechanical strength). In the margran-added samples, however, gas evolution during firing (due to the carbonates decomposition) is expected to counteract the effect of a more abundant liquid phase (higher content of fluxing oxides), and they might end up being more porous and less strong.

More important, though, is the fact that the reject additions can help controlling the shrinking/expansive firing behavior displayed by the clay alone, given that the packing of larger particle sizes brought in by the rejects (Table 1) can provide the extra pore space needed to accommodate the liquid phase without disrupting the microstructure. This is illustrated in Fig. 1 for granite and margran additions in various contents (10–50%). It can be seen that the mixtures start to present a manageable dilatometric behavior upon additions of at least 20% reject: the high temperature expansion disappears and shrinkage becomes successively lower. The usual fluxing effect only becomes apparent for additions greater than 40%. From this content onwards, the firing shrinkage at any given firing temperature, is expected to increase, particularly for the granite-added compositions, given the smaller particle sizes (lower initial porosity) and absence of carbonates.

Based on these findings and the results of related works [10], the discussion that follows will give particular emphasis to mixtures containing 70 wt.% clay and 30 wt.% reject. Fig. 2 shows the changes in linear firing shrinkage of samples containing 30% reject, as a function of the firing temperature. It can be observed that, at any given firing temperature, the firing shrinkage of the granite-added composition is higher than that of the margran-added composition, particularly so for firing temperatures above

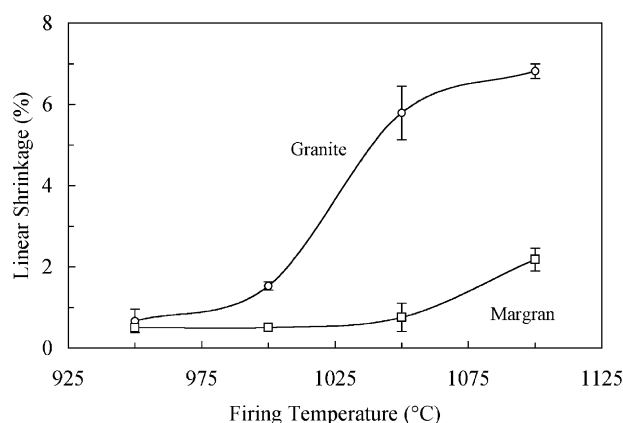


Fig. 2. Changes in the linear sintering shrinkage of reject-added samples (30 wt.% reject), as a function of the sintering temperature.

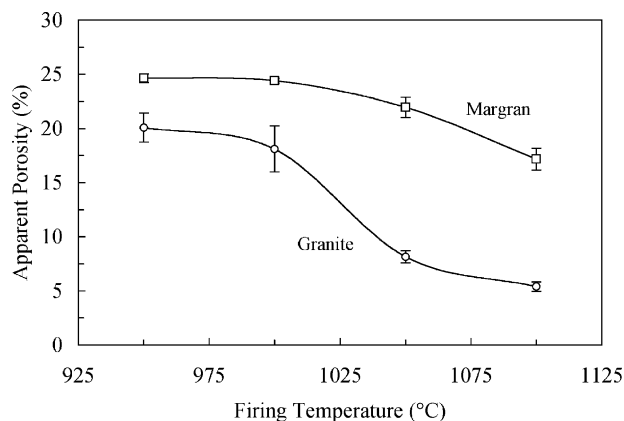


Fig. 3. Changes in the apparent porosity of sintered reject-added samples (30 wt.% reject), as a function of the sintering temperature.

~1000 °C. This means that the less efficient packing of larger particles and gas evolution during firing can compensate, and even dominate, the effect of high flux contents on the shrinkage behavior.

Figs. 3 and 4 show the observed changes in porosity and flexural strength of fired samples containing 30% reject, as a function of the sintering temperature. Both properties, for both rejects, showed the usual dependence on the temperature, namely, porosity decreased when the firing temperature increased and flexural strength increased with it. As expected, the sample containing margran showed, at all firing temperatures, higher porosity than that containing granite. Nevertheless, at lower firing temperatures (below ~1000 °C), the margran-added sample showed higher flexural strength than that containing granite, which might be explained by a stronger glassy bond, due to the presence of a more abundant liquid phase during firing.

At firing temperatures above ~1000 °C, as the microstructure becomes more compact, the effect of microstructural features of a critical size (particles or pores) should become dominant and dictate the sintered body mechanical strength. The originally larger particle size in the margran-added sample and its higher porosity at this high firing temperature range might explain its poorer flexural strength.

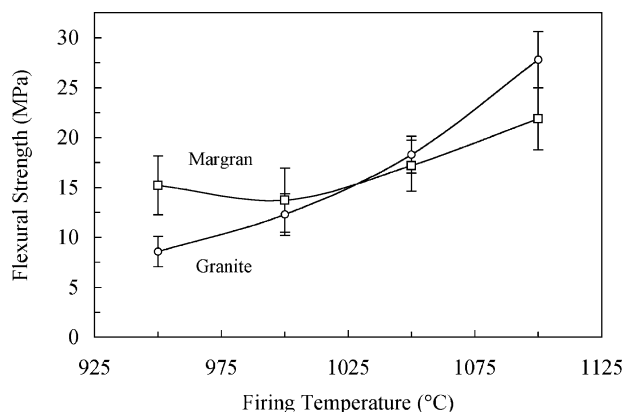


Fig. 4. Changes in the flexural strength of sintered reject-added samples (30 wt.% reject), as a function of the sintering temperature.

Table 2

Comparison between the property values obtained in this work and the specified property range for red-clay hollowed bricks [14]

	Porosity (%)	Flexural strength (MPa)
Clay + granite	5–20	9–26
Clay + margran hollowed	17–25	15–20
Specified for red-clay hollowed bricks [14]	≤25	≥5.5

Table 2 summarizes the property values obtained in this work and compares them to those commonly specified for red clay hollowed bricks. Although the latter are usually produced by extrusion, hence not directly comparable, it can be seen that the former are within the specified range, suggesting that it is possible to fabricate clay-based bricks using the clay and any of the rejects as raw materials.

Fig. 5 shows the fracture surface, as seen on SEM, of granite-added samples sintered at 950, 1000, 1050 and 1100 °C. The micrographs show the evolution of the sintering process with the rise in the sintering temperature. At 950 °C, the material shows a rough microstructure, with insignificant bonding between particles and a lot of interconnecting porosity (gaps between particles), an indication that the sintering process has barely started. At 1000 °C, more particles are bonded (grain growth) and the presence of a liquid phase at the firing temperature is obvious (rounded, smooth surfaces are characteristic of the presence of liquid during the sintering process). This is a clear sign that the sintering process is underway. At 1050 °C, there are signs of transgranular fracture (strong interfaces, glassy bonds between grains) and well-defined grain boundaries, and many isolated rounded pores can be observed, i.e. the material reached the

final sintering stage at this temperature. At 1100 °C the samples present a structure with few pores and signs of vitrification, in agreement with the values observed in Figs. 2–4.

Fig. 6 shows the fracture surfaces, as seen on SEM, of margran-added samples, as a function of the sintering temperature. The presence of carbonates in the margran reject (Table 1) is expected to play an important role in the microstructure development. The fracture surfaces of samples fired at 950 and 1000 °C are rather similar. There is a large amount of homogeneously distributed small rounded pores (in agreement with the porosity values shown in Fig. 3), which appear to form communicating channels. This temperature range includes the carbonate decomposition temperature and those channels might be the escape routes of the ensuing gas. Again, at 1000 °C, the microstructure already shows the presence of a liquid phase (in agreement with the chemical composition, Table 1), which is very obvious at 1050 and 1100 °C. Nevertheless, the presence of a liquid phase during sintering is not enough to cause a sharp decrease in porosity (i.e. densification) from 1000 to 1100 °C (as seen in Fig. 3). The presence of small rounded pores (narrow cylindrical channels) is an indication that gas evolution (carbonate dissociation) occurs during first melting. The persistence of those pores at higher temperatures suggests that the liquid phase is very viscous and gas evolution prevents pore closure. As the microstructure becomes more compact (at higher temperatures), pores become isolated rather than as channels (decreased open porosity). Despite the higher porosity and larger grain size, the margran-added sample shows flexural strength values not much lower than those of the granite-added sample. Although the better mechanical performance of calcite-bearing bodies is usually ascribed to the formation during firing of calcium aluminium silicates, such as anorthite, gehlenite or wollastonite, the strengthening of porous microstructures can

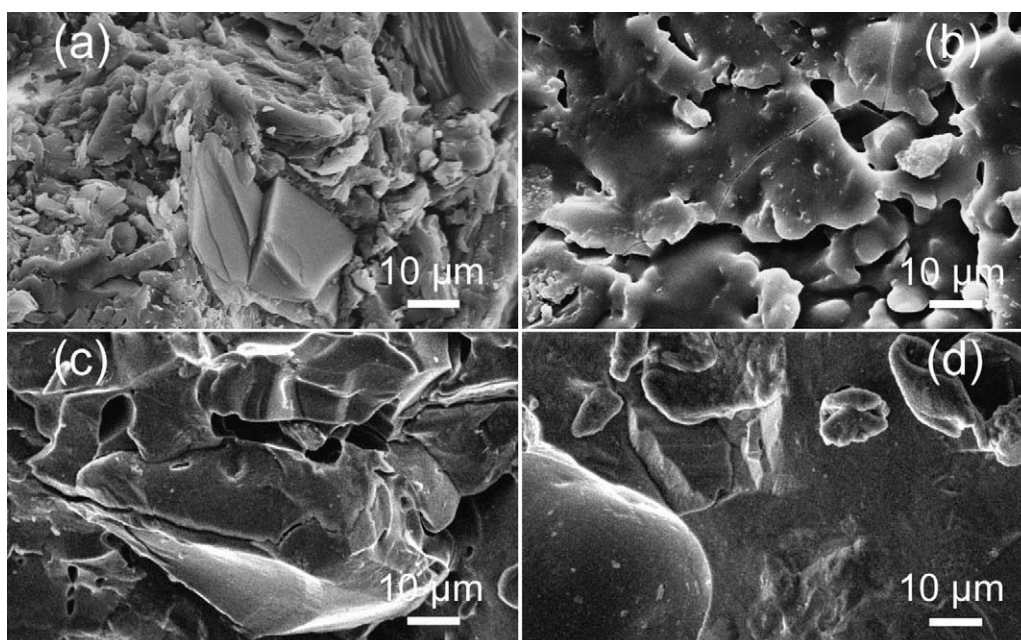


Fig. 5. Fracture surfaces, as seen on SEM, of 30 wt.% granite-added samples sintered at: (a) 950 °C, (b) 1000 °C, (c) 1050 °C, and (d) 1100 °C.

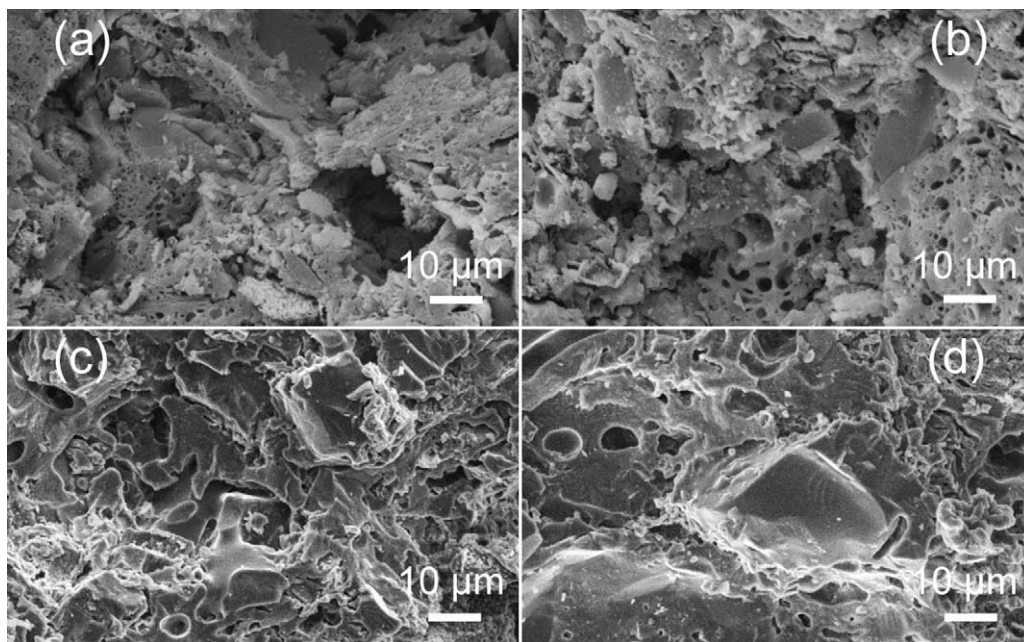


Fig. 6. Fracture surfaces, as seen on SEM, of 30 wt.% margran-added samples sintered at: (a) 950 °C, (b) 1000 °C, (c) 1050 °C, and (d) 1100 °C.

be further understood by the formation and development of a viscous liquid phase during firing, and was also observed in alumina bodies with additions of a similar granite reject [16].

These results are in agreement with those presented in Fig. 2 (firing shrinkage), Fig. 3 (apparent porosity) and Fig. 4 (flexural strength), which show that the margran reject is particularly well suited for a forgiving fabrication process, i.e. one in which fluctuations in firing temperature and/or mixture composition do not entail sharp changes in properties (see the dilatometric curves in Fig. 1).

4. Conclusions

This work describes the properties and microstructure development in an clay with poor firing characteristics to which two different ornamental stone cutting rejects, granite and margran (marble + granite), were added. All materials were collected at industrial sites and were used as such. The experimental results obtained for mixtures with 70 wt.% clay and 30 wt.% reject (linear shrinkage, porosity, flexural strength, microstructure) show that both rejects can be used to replace traditional fluxing agents with the added benefit of controlling the plasticity and shrinkage of the otherwise unusable clay. Moreover, the margran rejected was found to be particularly suited for a forgiving fabrication process, i.e. one in which fluctuations in firing temperature and/or mixture composition do not entail sharp changes in properties. Thus, the use of significant amounts of non-beneficiated

granite and/or marble reject is rather promising and has the potential to ameliorate and minimize the cutting mud negative impact on the environment.

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