

## GREEN STRUCTURAL CERAMIC WITH ADDITION OF RAW CLAY WASTE

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### Abstract

Raw clay waste is generated in the products conformation stage in the structural ceramic industry. Incorporation of raw clay waste is an alternative to make the structural ceramic sector more environmentally sustainable while reducing the consumption of clayey raw material. The Brazilian structural ceramic industry consumes 10.3 million tons of clay per month. This work aims to study the technical feasibility of raw clay waste addition in clayey mass used in the structural ceramic production. Samples of raw clay waste and clay were tested for chemical, physical and mineralogical characterization. Specimens containing waste contents, varying from 10% to 90% (wt.), were produced and burned in an industrial tunnel at 850°C. The technological properties evaluated were: water absorption, apparent porosity, apparent density, loss on ignition, firing shrinkage and mechanical strength. The results show that the addition of waste improves the evaluated properties significantly. With this, the reuse of raw clay waste in the clayey mass for production of ceramic roof tiles and blocks can contribute to the sustainability of ceramics sectors, reducing raw materials consumption and avoiding waste disposal in landfills. It becomes a feasible alternative to aim the ceramic industry comes to be a “green structural ceramic”.

### Introduction

The Brazilian structural ceramics industry has 6903 companies with the majority of micro, small and medium size operating in various technological levels, which generate 293,000 jobs according to ANICER - Associação Nacional da Indústria Cerâmica [1]. The sector presents a monthly production of 4.0 billion blocks and 1.3 billion roof tiles serving the building industry. Consumption of clay, the main raw material of the industry, is 10.3 million tons per month [1]. The extraction of clay to supply the industry is made, usually, in small mines, from 1,000 to 20,000 t/month, with low unit value of the raw material, but with high cost of transport [2]. The extraction and transportation activities generate significant environmental impacts [2]. The main problems faced by small and medium structural ceramics industries are: generation of waste without adequate treatment, lack of product quality control, high level of losses in mining and processing steps and lack of technology, among others [2]. The structural ceramic industry generates waste during the production of roof tiles and blocks causing environmental impact, which added to the impact of clay extraction, make the industry not sustainable environmentally. One of the ways to change this reality is to improve the technology involved in the productive process and the incorporation of waste in clayey mass.

The use of wastes may reduce consumption of non-renewable raw materials and the volume of waste disposed in landfills. There are many academic papers on the use of waste from various industries in the clayey mass production of structural ceramics, but the large-scale production of

products with incorporated waste is low. With this, technological innovation does not happen in the industry. This problem could be solved with the approach of academic research to the productive sector involved. This study aimed the interaction between research in the laboratory and the test industry to streamline the technological innovation process. The survey was conducted in a ceramics industry using the variables involved in the productive process of the ceramic products, such as local temperature and humidity conditions in the molding of the specimens. It was used the industry tunnel furnace, which utilizes a maximum temperature in the burning zone of 850°C for about 6 h with a total cycle of 24 h. In this sense, the aim of this research is to study the technical feasibility of the addition of raw clay waste to the clayey mass for structural ceramics production. The waste called as raw clay waste (Figure 1) is generated in the ceramic industry itself in the step of conformation the ceramic bodies. It consists of burrs of the pressing of roof tiles, and roof tiles and freshly pressed blocks discarded because of visual defects, such as cracks. The waste is taken out the process and stored in storage piles. It is estimated that the raw waste clay represents 40% of clay mass that enters the process.



Figure 1. Raw clay waste

In the literature, there are no studies (to our knowledge) on the characterization and the addition of raw waste clay (not burned) in the clayey mass production of structural ceramics. There are several studies [3, 4] about the use of "chamotte", which is burned ceramic waste. When the industries in Brazil incorporate raw clay in the process it is generally without any previous study of characterization of the waste clay and verification of its ceramics properties. The waste volume which returns to the process is not usually controlled, so products can be made from waste only when the disposal of waste clay is high.

### Materials and methods

The clay is extracted from a quarry located in Baixo Guandu-ES-Brazil. The raw clay waste is generated in a structural ceramic industry located in Colatina-ES-Brazil. Samples of clay and raw clay waste were collected in the storage of the structural ceramic industry located in the State of Espírito Santo using waste sampling procedures specified by ABNT – Brazilian Association for Technical Standards NBR 10007/2004 [5]. The raw clay waste consists of the clay and granite waste, both are raw materials used by the industry for the production of ceramic roof tiles and blocks. After that, the samples were air-dried, broken with the aid of a pounder, quartered and homogenized. Part of the material was used for characterization tests, and part for preparing the specimens. The materials were characterized by X-ray fluorescence (XRF) in a Philips PW2400 spectrometer; X-ray diffraction (XRD) with copper source (K  $\alpha$  radiation) in a Philips X- Pert MPD equipment; scanning electron microscopy (SEM) in a Philips XL-30 electron microscope; particle size analysis by laser diffraction in a Malvern Mastersizer 2000 equipment. The plasticity was evaluated using Atterberg's limits [6, 7]. The identification of the samples in XRD was made by comparison with the Crystallographic Open Database – COD standard files. Molded spheres specimens were made for evaluation of ceramic properties after firing at the ceramic industry. The spheres were made with a mixture of clay and raw clay waste (sieved in #

40 of ABNT). The specimens were manually molded with an average diameter of 2 cm, 10 g dry mass, with enough water to allow molding, according to the methodology developed in Laboratório de Materiais Não-Metálicos Prof. Persio Souza Santos (LPSS) of PMT/EPUSP/BR. The spherical specimens have been used in other studies [8, 9], which were compared to the results of pressed bars. The authors observed that the results found in ceramic properties of bars and spheres have coherence and often the values are similar. The spheres preparation method is simpler than the bars; and can be made in any structural ceramic industry for an initial analysis of low cost characterization of raw materials for use in ceramic bodies.

The raw clay waste content in the clayey mass varied from 10% to 90% (in weight) for making of specimens. The spheres were dried in a drying oven for 24 h at 110°C. Compressive strength was measured in part of the specimens, and part of the specimens was burned in an industrial tunnel-type furnace in a structural ceramic industry for 24 h, at a maximum temperature of 850°C in the burning zone for about 6 h. After firing, the following properties were evaluated: water absorption, apparent porosity, apparent specific mass, loss on ignition, according to the methodology proposed by Souza Santos [10], besides compressive strength.

### Results and discussion

The chemical analysis result (Table 1) is shown in terms of percentage through the weight of constituent oxides and loss on ignition. By analyzing the data, the clay was verified to present a typical chemical composition of common clay raw material, with 40.85% silica, 33.56% alumina; and 14.29% loss on ignition obeying ranges of values, from 6.80% to 38.00% for Al<sub>2</sub>O<sub>3</sub> and from 6.00% to 15.70% for the loss on ignition, respectively, as specified by Souza Santos [10] for ceramic raw materials. The silica content is located next to the range from 43.20% to 77.60% specified for SiO<sub>2</sub> [10]. The high value of loss on ignition of clay may cause porosity in the ceramic bodies. The percentage of 7.41% iron oxide is responsible for the reddish color after firing. The concentration of Na<sub>2</sub>O (0.16%) and K<sub>2</sub>O (0.77%) is not high; therefore, even being fluxing oxides, they contribute little to the formation of the glassy phase. Clays with these characteristics (aluminous silica, with high iron content and low content of fluxing oxides) demand high sintering temperature, as reported by Hildebrand et al. [11]. As seen in the table, the raw clay waste presents chemical composition similar to clay, with a high silica content (44.70%) and alumina (27.57%); and high value of loss on ignition (12.85%). These values obey to the specified by Souza Santos [10] for raw material of structural ceramic.

As the raw clay waste has granite waste in its composition, there is the presence of fluxing alkali oxides Na<sub>2</sub>O (0.65%) and K<sub>2</sub>O (1.56%), which may contribute for burning the ceramic bodies, reducing the need of high temperature in the formation of the glassy phase of the clay in question. The presence of Fe<sub>2</sub>O<sub>3</sub> is associated with steel shot, and CaO is associated with lime, both used in the mud from which the granite waste originates.

Table 1. Chemical composition of materials by XRD (wt%)

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	K <sub>2</sub> O	MgO	CaO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MnO	LOI
Clay	40.85	33.56	7.41	1.51	0.77	0.63	0.21	0.16	0.14	<0.05	14.29
Waste	44.70	27.57	8.96	1.22	1.56	0.72	1.01	0.65	0.16	0.06	12.85

Note: LOI – loss on ignition

Figure 2 shows the X-ray diffraction of the clay and the raw clay waste. The XRD analysis of clay indicates that the predominant minerals are kaolinite, quartz, illite and goethite. The analysis of the X-ray diffractogram of the raw clay waste identifies the presence of crystalline phases associated to mica, feldspar and quartz; the latter confirms the high value of SiO<sub>2</sub> (44.70%) in the

XRF detected. In addition, orthoclase was also detected. The raw clay waste also shows characteristic peaks of kaolinite and quartz, originated from clay.

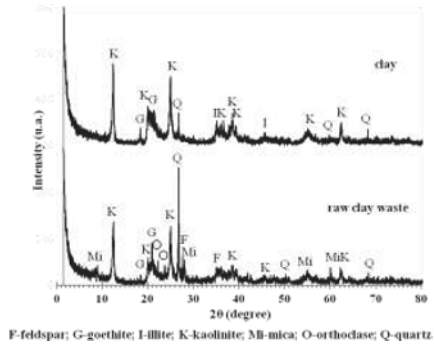


Figure 2. XRD of materials

Figure 3 presents images showing the material morphology and particle size obtained by electron microscopy. The images indicate that the grains of materials are irregular in shape tending to form lamellar and slender particles, some scattered and others in clumps forming larger particles. The formation of these clumps between very thin particles may increase the porosity. The particles size ranged from 2  $\mu\text{m}$  to 45  $\mu\text{m}$  in the clay; and from 2  $\mu\text{m}$  to 50  $\mu\text{m}$  in raw clay waste.

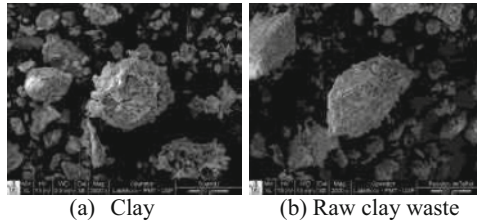


Figure 3. SEM of materials

Atterberg limits of the raw materials are presented in Table 2. The clay plasticity index (PI) is 25.46% and the raw clay's waste is 20.75%, above 15.0%, indicating high plasticity, which makes them suitable for molding by extrusion. Regarding the plasticity limit (PL) of clay, the 42.00% value is within the range from 9.0% to 56.0% specified by Souza Santos [10] for kaolinitic clay, confirming the predominance of the kaolinite mineral identified in XRD. It is found that the values of the Atterberg limits of the raw waste clay are within the ranges suitable for the structural ceramic products, 30 to 60% for the LL, 15 to 30% PL and 10 to 30% for PI [12]. Thus, it can be said that the raw clay waste has adequate plasticity for extrusion.

Table 2. Atterberg limits of materials

	Plasticity Limit-PL (%)	Liquid Limit-LL (%)	Plasticity Index-PI (%)
Clay	42.00	67.46	25.46
Waste	29.45	50.22	20.75

The particle size distribution of the clay and the raw clay waste are shown in Figure 4. The effective diameter of the clay is 2.06  $\mu\text{m}$  and the raw clay waste is 2.10  $\mu\text{m}$ . These are very close

values, indicating that both raw materials have similar particle size distribution. The clay and the raw clay waste have about 25% grains larger than 20  $\mu\text{m}$ ; 64% grains between 2  $\mu\text{m}$  and 20  $\mu\text{m}$ , and less than 11% grains smaller than 2  $\mu\text{m}$ . The clay and raw clay waste have low "clay fraction" (grains smaller than 2  $\mu\text{m}$ ), presenting plasticity due to the organic matter contained in the clay and the raw clay waste.

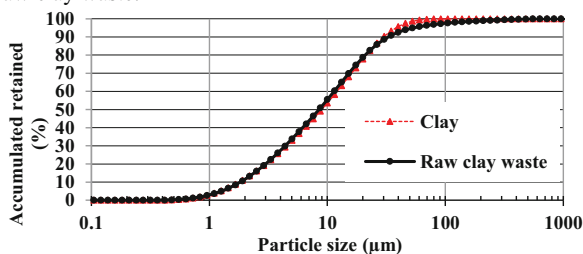


Figure 4. Particle size distribution curve of materials

The results of ceramics properties from the spheres made with solely clay and with mixture of clay and raw clay waste are shown in Table 3. For the fired spheres the highest value of compressive strength (2.93 MPa) was obtained with the 90% content of waste, which resulted in improvement of this property, since the clay without waste presented a lower value (2.16 MPa). The highest compressive strength value (0.69 MPa) in dry spheres also occurred for 90% of waste content. The values of water absorption, apparent porosity, loss on ignition and firing shrinkage decreased by increasing the raw clay waste content, while the value of apparent density increased with the waste content, indicating that the raw clay waste promotes the densification of ceramic bodies. The fluxing oxides contained in waste helped burn the specimens, because they minimize the effects of adverse conditions, such as, the low temperature 850°C practiced in the industry and the use of the kaolinitic clay, which is more refractory. And the fine granulometry of the waste promoted the filling of the interstices between the clay grains promoting the physical packaging; and with that, there was the increase of strength in the specimens.

Table 3. Average values of the ceramic properties of spheres

Waste(%)	LOI(%)	WA(%)	AP(%)	AD( $\text{gcm}^{-3}$ )	FS(%)	$\sigma_D$ (MPa)	$\sigma_B$ (MPa)
0	14.34	25.38	37.92	1.54	12.03	0.61	2.16
10	14.35	24.93	39.25	1.54	10.45	0.56	1.50
20	13.76	24.83	38.19	1.54	9.34	0.56	1.54
30	13.32	23.97	37.60	1.57	9.09	0.56	1.69
40	13.14	23.86	37.39	1.57	8.79	0.59	2.00
50	12.26	22.47	36.47	1.64	8.39	0.65	2.07
60	12.21	22.13	36.25	1.64	7.95	0.65	2.27
70	11.65	21.65	35.99	1.64	7.39	0.68	2.35
80	11.65	21.41	35.31	1.67	7.21	0.68	2.52
90	11.35	21.09	34.76	1.67	6.83	0.69	2.93
Reference*	6.00 to 15.70	$\leq 25.00$	$\leq 35.00$	1.50 to 2.00	2 to 17	-	-

Note: LOI= loss on ignition; WA= water absorption; AP= apparent porosity; AD= apparent density; FS=firing shrinkage;  $\sigma_D$ =compression strength after drying;  $\sigma_B$ = compression strength after burning.

Note: \*Souza Santos [10].

Considering the referential limits [10] described in Table 3, the water absorption, apparent density, loss on ignition and firing shrinkage values met the limits at all the raw clay waste

contents. The porosity met the limit with 90% of waste. The porosity values were influenced by the properties of clay (main component of waste), such as, high value of loss on ignition.

### Conclusions

Chemical and mineralogical characterization showed that clay is predominantly kaolinitic, containing adequate amounts of quartz and iron. The clay and the raw clay waste may be considered silica aluminous materials. In all the compositions studied, the values of ceramic properties (less apparent porosity) meet the requirements for structural ceramic. Apparent porosity only meets these limits with 90% of waste content. The results show that the addition of waste improves the evaluated properties significantly. It can thus be concluded that the raw clay waste especially influences the formation of the glassy phase of the ceramic body, reducing water absorption, increasing the densification, including the comparison of the values obtained from clay without waste. The reuse of raw clay waste in the clayey mass can contribute to the sustainability of ceramics sectors, reducing raw materials consumption and avoiding waste disposal in landfills. It becomes a feasible alternative for the ceramic industry becomes a green industry. The paper shows the technical feasibility of using spheres, and industrial firing, in studies about the incorporation of industrial wastes in the ceramic industry.

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