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Utilization of Estremoz marbles sawing sludge in ceramic industry – Preliminary Approach

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Abstract

Portugal is in forefront of world marble production, the marble quarries and processing industries in Estremoz region has an important role in economic life. The amount of waste produced by this activity is massive and cause several problems.

The aim of this study is to investigate the suitability and the effect of Estremoz marble sawing sludge in mixtures with clay to ceramic industry. Another main concern is the manufacture of environmental friend ceramics.

Plasticity behavior of clay mixtures with 2.5, 5, 10, 15 and 20wt% of marble powder were evaluated. The incorporation of waste reduces the liquid limit and plastic index of pastes.

Clay bodies were molded by uniaxial pressure and fired at maximum temperature of 950 ℃. The results reveal that the addiction of marble powder increases the water absorption, apparent porosity while the bulk density decreases. Due to their influence in the melted phase an improvement in mechanical strength characteristics was registered, namely in rupture modulus.

This preliminary study shows that the use such mixtures are promising in term of ceramics technological properties.

Keywords: Estremoz marbles, clay, reuse, ceramics.

1. Introduction

The natural stone is a well known construction material used in the historic heritage, monuments, buildings and sculptures. Their diversity and longevity allied to the high aesthetic value makes natural stone a valuable construction material. Portugal is one of the biggest world producers of natural stone (Martinez *et al.* 2008). For its abundance, variety, aesthetic properties and quality, the Portuguese natural stones have been used since ancient times. One of the best examples is the "Estremoz marble" from Alentejo, exploited in Estremoz region.

The oldest evidence of the use of this type of marble dates from 370 BC (Moura & Velho, 2011). During the Romanian times these marbles were widely used in buildings with structural and decorative purposes, e.g., the Roman Temple in Évora and the Roman Theatre in Mérida.

The 80 marble quarries at exploitation in 2007 (Moura & Velho, 2011) are located in Estremoz anticline which is a geological structure with a horizontal area of $280km^2$ (40 km x 7 km). The marbles are unique and reveal different patterns originated under the influence of Variscan Orogeny (Lopes & Martins, 2012).

Their excellent mechanical, physical properties and aesthetic beauty are a major reason for the 370.000 ton rock quarried in 2000, raising Portugal to the forefront of world marble production (Brilha *et al.* 2005). Today the Portuguese marble industry has leapt forward and mables are now exported worldwide (Brilha *et al.* 2005).

The exploitation and processing of marbles implies a huge production of waste. The sludge from marble sawing and polishing (figure 1) is generated in large amounts. This sludge is canalized from machinery to decanting deposits (figure 2). Usually, after sedimentation of marble particles in bottom, the water is reutilized and the powder has no utility.

Nearby quarries and processing industries are found countless heaps of waste marble powder. This leads to an occupation of a vast area of land and brings negative effects to the landscape. Bdour & Al-Juhani (2013) attribute several environmental problems to those amounts of waste marble powder: reduction in land productivity (decreased porosity, water absorption, and water percolation); severe air pollution with occupational health problems and possible damages to machinery and instruments; decrease of water quality and damage to aquatic life; negative effects in social and industrial activities since the heaps of powder remain scattered around the country which ruins the aesthetics of the region.

From the other side, with the increase of population demands and the decrease of non-renewable natural resources, the society is making an effort to reuse several types of waste in the production of new materials with different characteristics. After detecting their potentialities, the use of waste is considered an activity that can contribute to the diversification of materials, decrease in the final costs, besides providing alternative raw materials to several industrial sectors (Menezes *et al.* 2005). The construction field, which normally involves the use of large amounts of resources, is at the forefront on the reutilization of residues. The ceramic sector can incorporate different waste materials without significant process modifications (Alonso-Santurde *et al.* 2010), clay bricks can tolerate compositional fluctuations and raw material changes (Menezes *et al.* 2008).

Few authors evaluate the suitability of the reuse of different residues in clay mixtures to sintering clay bricks. Some interesting results have already been found in the incorporation of granite sawing waste from a Portuguese stone processing industry (Galhano & Ginja, 2010). The addiction of other types of wastes in clay raw material could be found in literature which emphasizes the interest of the society in reutilization of waste to bricks manufacture, a review investigation were made by Raut *et al.* (2011).

The selection of raw material for ceramics is made according to the specific application and performance criteria, which includes strength, durability and aesthetic requirements. Those parameters are mainly dependent on raw material characteristics, which in turn, should have suitable characteristics for manufacturing processes.

This work aims the characterization of sawing sludge obtained from “Estremoz marbles” processing. As well, the characterization of mixtures clay/marble powder at different percentages. The suitability of those mixtures in the processing of ceramic bricks will be preliminarily evaluated.

Figure 1 – Primary cut of a marble block in processing industry.

Figure 2 – Decanting deposit of marble sawing sludge.

2. Materials and Methods

The clay material for this investigation was taken from a ceramic manufacturing industry in Beira Litoral region in Portugal. The sludge from sawing of “Estremoz marble” was taken from a dimension stone processing industry in Estremoz. Both materials were dried in oven at 60 ℃.

Chemical composition of the clay and marble powder was obtained through SEM analysis (JEOL JSMT330A).

Mixtures with the sludge content of 2.5, 5, 10, 15 and 20wt% were made. In order to characterize and evaluate the behavior of mixtures, plasticity tests were performed by the Atterberg consistency limits in accordance with the Portuguese standard NP-143.

The clay bodies were molded by uniaxial pressure using a hydraulic press and a load sensor (Centor Easy R Andilog). The load applied in the moist mixtures was of 2.6 kN. After 24 hours at room temperature the clay bodies with 120x20x10mm were de-molded and placed at 110 ℃ for 24 hours.

The dried samples were fired in an electric kiln under oxidizing conditions at temperature of 950 ℃. The temperature increases was at a rate of 2.5 ℃/min and at 950 ℃ a plateau of 1 hour were made.

Changes in the linear shrinkage were evaluated using a caliper in green bodies and after the firing process.

The determination of bulk density, apparent porosity and water absorption in the samples were made according ASTM C373. Mechanical characteristics were studied by flexural tests made in a Ceramic Instruments Press, according to ASTM C1161.

3. Experimental and Discussion

3.1. Raw material

Table 1 exhibit the chemical content in oxide form of clay, marble powder and for all used mixtures. The clay is mainly composed of silica (61.5%) aluminum (21.9%) and calcium (8.7%). When compared with other similar investigations, the used raw clay had small amounts of Fe_2O_3 (3.7%). The marble powder is homogeneous in their composition and is extremely fine grained.

The iron is the main coloring agent, usually raw materials with higher percentages (5-7%) produces reddish ceramics, while lower iron contents produces whiter ceramics.

Estremoz marbles has a carbonated composition with values between 94 and 99% of calcite ($CaCO_3$) (Lopes & Martins, 2012). Chemical analysis in the marble powder reveals 83.6% of CaO which is lower than expected. Such discrepancy could be attributed to sludge impurities result from saw erosion, lubrification fluids and other particles captured in the drainage channels.

The addiction of carbonated compounds changes the course of the thermo reactions in the firing process which generates other crystalline phases. Usually the carbonates in raw material promotes whiter ceramics, however the iron contained in the marble powder could play an important role in the color characteristics of the ceramic. The increasing of marble waste content in mixtures produces a slight increase in Fe_2O_3.

The calcium carbonate isolate decomposes between 600 and 1000 ℃ according the reaction:

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

Further, the calcium oxide reacts with silica and alumina from the clay minerals desidroxilation (Barba *et al.* 2002). Because of those reactions, the moderate presence of calcite allows the formation of amorphous material which promotes the creation of new phases (Martirena *et al.* 2006).

Table 1 – Chemical composition in terms of oxide content.

	Clay	Marble Waste	2.5% mixture	5% mixture	10% mixture	15% mixture	20% mixture
SiO_2	61.48	3.20	60.02	58.57	55.65	52.74	49.82
Al_2O_3	21.89	1.67	21.38	20.88	19.87	18.86	17.85
CaO	8.73	83.57	10.60	12.47	16.21	19.96	23.70
Fe_2O_3	3.74	4.73	3.76	3.79	3.84	3.89	3.94
K_2O	1.85	1.34	1.84	1.82	1.80	1.77	1.75
TiO_2	1.61	2.02	1.62	1.63	1.65	1.67	1.69
MnO	0.47	2.46	0.52	0.57	0.67	0.77	0.87
P_2O_5	0.08	0.02	0.08	0.08	0.07	0.07	0.07
Na_2O	0.07	0.02	0.07	0.07	0.07	0.06	0.06
MgO	0.06	0.95	0.08	0.10	0.15	0.19	0.24
ZrO_2	0.01	0.03	0.01	0.01	0.01	0.01	0.01

The clay paste must have essential features to allow a proper shaping process. Problems such as body decomposition, cracking or laminations occur in shaping processes and are detected in the clay bodies after their drying or after sintering. The raw material composition is quite important in paste plastic behavior. This behavior is normally characterized by the Atterberg limits - liquid limit describes the transition from a viscous liquid to a plastic state in amount of water terms; plastic limit determines the transition from a plastic to a semi-solid state in amount of water terms and the index of plasticity is the water content between plastic and liquid limit. It describes the sensitivity of raw material to changes in water content.

The obtained results are plotted in the graphs of figures 3 and 4. The Casagrande diagram (after Gippini, 1969) in figure 3, defines the area set to extrusion. The samples located in zone A and B, have optimum and adequate characteristics for extrusion, respectively. The clay workability chart of Bain and Highley (1979) in figure 4, defines two ranges where the workability is optimum (C) and good (D).

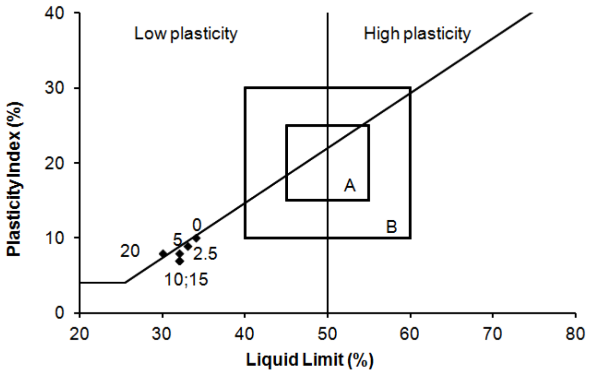

Figure 3 - Casagrande diagram with domains (after Gippini, 1969) relative to extrudability of raw materials.

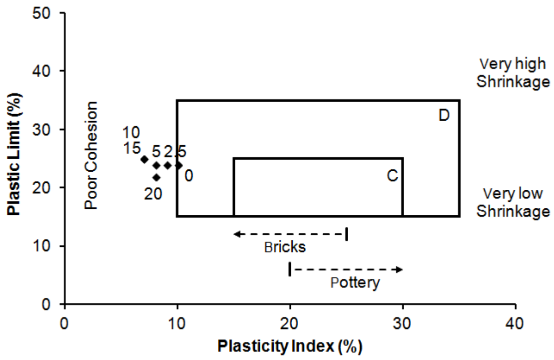

Figure 4 - Clay Workability Chart (after Bain and Highley, 1979).

According to the results the used clay, without marble powder, does not present appropriate features to extrusion. Liquid limit and plasticity index tends to decrease with the incorporation of marble waste causing their deviation from extrusion zone. The plastic limit value remains constant in mixtures until 5%, while higher amounts produce some fluctuations in this limit. In any case, it seems that all mixtures containing marble present worse cohesion and less workability features.

In fact, those results are extremely influenced by the clay properties, in this case the utilization of marble waste is negative. However, their effect is obvious, in raw materials with high plasticity index it could be used as an addictive to improve their workability or manage the material plasticity for specific types of shaping.

3.2. Technological Properties

Figure 5 display the linear dimension measured in green bodies and fired samples. It is possible to observe that the green bodies made of clay have a linear shrinkage of 3%. With the incorporation of increasing amounts of marble powder linear shrinkage tends to decrease until 1.5% in 20% mixtures. This reveals that the addition of marble waste provides dimensional stability and reduces the probability of clay bodies cracking during the drying process. After the green bodies sintering the linear shrinkage trend is similar, samples without and with small amounts of marble waste reveals the highest dimensional reduction. In fact, after the firing those samples expand after sintering process. In such cases, it will be expected an increase in samples porosity.

Despite being difficult to identify in figure 6, a visual inspection of fired samples note a slight tendency to darkening with the increasing of marble waste. This could be attributed to the small amounts of Fe_2O_3 added or/and to a generation of other crystalline phases.

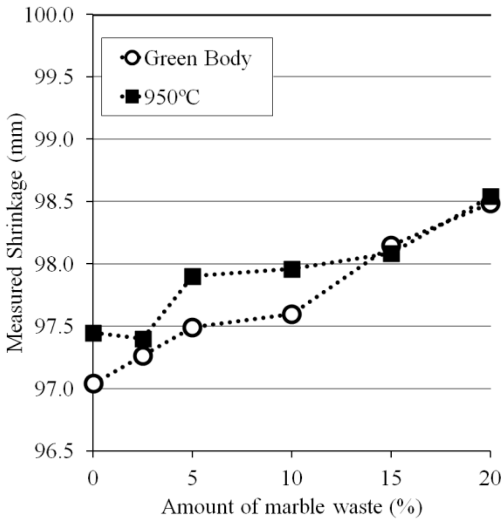

Figure 5 – Linear Shrinkage of the green and fired bodies.

Figure 6 – Visual appearance of the fired samples.

Table 2 exhibit the values obtained in physical and mechanical tests in fired samples. Those parameters were plotted in figure 7 to a better interpretation of patterns. Quite interesting results were obtained in modulus of rupture - the use of amounts up to 15% significantly improves the mechanical strength. Mixtures with 15% marble waste show an increase of 33% in modulus of rupture. Such results are in accordance with some statements found in literature (Soares *et al.* 2010).

This behavior is related to the already mentioned modifications in thermo reactions associated with the presence of carbonated material. The formed CaO can react with silica and alumina to create crystalline calcium based phases. The new phases also affect the formation of melted material and thus the vitrification degree of the fired body. It is consensual that vitrification degree has a major role in ceramic mechanical strength performance.

In porous materials an increase in mechanical strength is associated to a decrease in porosity, in this case this is not verified. With the increasing amount of marble waste the apparent porosity and water absorption values also increases. As has already been seen, the retraction of the fired bodies decreases with CaO content due to the formation of silicates and aluminosilicates of calcium promoting a delay on ceramic densification (Sousa & Holanda 2006). During the firing process the release of CO_2 in gaseous form coming out of the samples may have influence in their porous structure. It is also observed a decrease in bulk density which is coherent with the porosity and water absorption values.

Table 2 – Mechanical and physical characteristics of the fired bodies.

	0	2.5	5	10	15	20
Modulus of Rupture (MPa)	9.88	10.57	11.61	11.54	13.12	12.94
Water Absorption (%)	18.85	18.20	19.76	20.08	20.69	22.21
Apparent Porosity (%)	31.69	30.46	32.25	32.24	32.84	34.59
Bulk Density (g/cm^3)	1.68	1.67	1.63	1.61	1.59	1.56

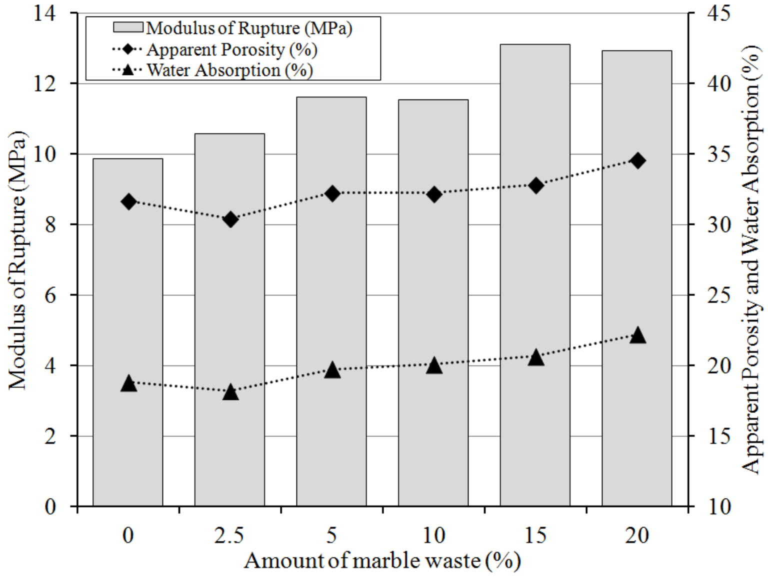

Figure 7 – Mechanical and physical behavior of the fired bodies made with different marble powder amounts.

4. Conclusions

The present study shows that it is possible to produce ceramics having as raw material mixtures of clay and significant amounts of marble sawing waste.

The marble powder has CaO as main component which is associated to calcite, other impurities such Fe_2O_3 were found. The sludge reveals good homogeneity and is composed by extremely small the particles.

The addiction of marble powder to raw materials affect their plastic behavior, in clays with high liquid limit their use could be beneficial. It also contributes to a dimensional stability in green and fired body.

At firing temperature of 950 ℃ an increase in marble waste produces an increase in mechanical strength due to their influence in the melted phase. From the other side, the water absorption and the apparent porosity are negatively affected.

The results in this preliminary study show that the use of such mixtures is promising in term of ceramics technological properties. The amounts between 2.5 and 15% reveal the best compromise between those properties.

Hopefully, further work will focus the study on other types of clays as main raw material and other firing temperatures. Also accelerated aging tests are going to be considered to understand their durability.

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