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The use of a calcium carbonate residue from the stone industry in manufacturing of ceramic tile bodies

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ABSTRACT

The substitution of clayey raw materials for other wastes, in this case sludge rich in calcium carbonate, in the production of traditional ceramics could give rise into cost savings due to the utilisation and recycling of wastes as a secondary raw material. At the same time, it can be helpful for solving environmental problems associated with such wastes. This research shows the results of the addition to a clay of a calcium carbonate residue in different proportions (15, 20, 25, 30 and 35%) in a ceramic body. The most suitable products were selected regarding the mineralogical composition of the resulting ceramic material and its technological behavior. In order to evaluate the ceramic properties of the obtained material, several properties of processing and product (linear contraction, water absorption capacity, bending strength) have been determined. With regard to the technological properties of the final ceramic bodies, there seems not to be any clear relation between the values of linear contraction and the percentage of residue. However, the increase in water absorption with the increase in the residue percentage is evident. The addition of residue gives rise to a decrease in the bending strength. The selection of the adequate percentage of sludge to be added to the ceramic body will be controlled by the usual standards applied to specific construction materials.

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1. Introduction

In Spanish natural stone industry, about 70% of the processing wastes are being disposed locally. The marble dust is usually dumped on the riverbeds and this possesses a major environmental concern. In dry season, the marble powder/dust dangles in the air, flies and deposits on vegetation and crop. All these significantly affect the environment and local ecosystems. The marble dust disposed in the riverbed and around the production facilities causes reduction in porosity and permeability of the topsoil and results in water logging. Further, fine particles result in poor fertility of the soil due to increase in alkalinity.

Attempts are being made to utilise marble wastes in different applications like road construction, concrete and asphalt aggregates, cement, and other building materials. It is evident that there is a great potential for recycling of wastes released from different marble industrial processes.

In recent years residues have been constructively applied to resources in recycling research, and related achievements are seen in engineering applications. Different authors have been investigating the incorporation of different types of residues in the manufacture of traditional ceramic materials in recent years (Hauser, 2000; Dondi et al., 1997, 2002). However, very little research has focused on ways to improve the properties of clay tile. It is well known that mechanical properties of ceramics are an important parameter for defining their use and applications (Zweben, 1991). It is obvious also that raw materials in ceramics manufacturing have an important influence on the properties of the ceramics.

Following this trajectory, a study with residues of a different nature is being carried out in order to improve different behavior and defects in traditional ceramic products like bricks and roofing tile. From the economic and environmental point of view, the use of such residues would suppose as secondary raw material additional advantages.

In this work first results are shown when partially substituting ceramic pastes of a clay type rich in silica throughout residue rich in calcium carbonate. The ceramic pieces have been molded by pressing method and the mineralogical characterization has been carried out after firing process.

2. Materials and methods

2.1. Characterization of raw materials

Ceramic clay and one representative sample of a residue rich in calcium carbonate (sludge) coming from different marble plants of the natural stone industry of Alicante province (Spain) was selected. In

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Table 1
Mineralogical composition (%) of the clay used in the experience

Raw material						Clay fraction				
Q	F	Phy	Cc	Do	Hm	I	K	C	I/S	C/S
35	x	45	5	x	10	45	25	10	15	5

Q: quartz; F: feldspars; Phy: phyllosilicates; Cc: calcite; Do: dolomite; Hem: hematites; I: illite; K: kaolinite; C: chlorite; I/S: illite/smectite; C/S: chlorite/smectite; x: present (<5%).

fact, this selected clay is used nowadays for manufacturing of roofing tiles.

The mineralogical analysis of clay samples was carried out by XRD on aggregate oriented (normal, heated to 550 °C during 2 h and treated with ethylenglycol) using a Siemens D-500 with Bragg-Bretano geometry. Infrared spectroscopy was used as complementary technique for a correct differentiation of kaolinite and chlorite and a scanning electron microscope (SEM/EDX) to confirm the presence of interstratified and montmorillonite. The chemical analysis of major and minor elements was made by X-ray fluorescence (XRF) using conventional techniques. The chemical characterization of the residue employed was done by X-ray fluorescence (XRF) with a PW2400 X-ray spectrometer with rhodium target X-ray tube, controlled by SuperQ/Quantitative version 1.1 software.

The size distribution determinations were performed by laser dispersion using a Malvern Mastersizer 200E (100 nm-1000 μ m range).



Fig. 1. IR absorption spectroscopy. Cl: chlorite; K: kaolinite.

Table 2

Composition (wt.% oxides) of the clay used and the residue for the compositional design of the body

%	Clay	Residue
CaO	1.07	75.70
MgO	2.93	0.26
Al ₂ O ₃	14.52	0.36
SiO ₂	62.40	1.00
Fe ₂ O ₃	4.06	-
K ₂ O	3.64	-
LOI	9.31	22.60
SrO	-	0.01
SO ₃	-	0.06
P ₂ O ₅	0.18	0.01
TiO ₂	0.78	-
MnO	0.04	-
Na ₂ O	1.07	-

LOI: loss of ignition.

2.2. Design of the green body

The body (with a humidity of 15%), once dried in a stove at 105 °C, was grinded and passed through a 500 μ m sieve. A reference sample (Gr) and compositions A, B, C, D and E were tested with 15, 20, 25, 30 and 35% of added residue, respectively.

The test bodies were pressed with a laboratory Mignon-S Nanetti uniaxial press, at 40 MPa, and shaped on discs of 20 mm diameter, 5 mm thick and an approximate weight of 3.5 g. The usual industry sector firing cycles were designed (0–500°C: 2 h; 500–650°C: 2 h; 650–Tmax: 2 h; Tmax: 4 h), and maximum temperatures (Tmax) of 975, 1000, 1025 and 1050 °C were reached. The mineralogical analysis of the fired test bodies was carried out by XRD using the usual conditions and techniques.

The evaluation of the presence or absence of "*caliches*" in the conformed fired test bodies was evaluated at low magnification in a binocular microscope.

2.3. Determination of linear contraction and water absorption capacity

The linear contraction has been calculated in both dried (D.L.C.) and heated (H.L.C.) samples. The linear contraction was determined following the conventional techniques.

The water absorption capacity (%) has been determined in ceramic tile bodies following the ISO-10545-3 (AENOR, 1997).

2.4. Bending strength

With the aim of determining the extent to which the residue introduction in the ceramic paste affects the mechanical properties of the product, the bending strength of both dried and heated samples has been carried out using INSTRON 1011 equipment using a 3-point loading method.



Fig. 2. Size distribution curve of the marble dust residue.

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