Development of tailored ceramic microstructures using recycled marble processing residue as pore-former

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Abstract. Recycling of marble processing residue is significant since marble processing constitutes an important industrial sector. Therefore, the sustainable management and the valorisation, in an economically profitable manner, of this industrial by-product should be considered. In this work, the potential use of marble residue as pore-former into clayey mixtures for the production of lightweight, porous and thermal insulating ceramics is investigated. Four samples consisting of clayey ceramic body incorporating up to 50 wt.% fine marble residue powder were produced. The final ceramic products were produced upon firing (sintering) at 950°C. Porosity and thermal conductivity measurements were carried out in order to assess the thermal insulating behavior of the produced sintered ceramics. The porosity of the sintered ceramics increases substantially by increasing the marble residue admixture loading. This, in turn, leads to a decrease in thermal conductivity. Consequently, the marble residue can be successfully employed as pore-forming agent, in order to improve the insulating behavior of the ceramic materials.

1. Introduction

Marble processing is currently regarded as one of the most important industrial sectors not only in Greece but also worldwide. In Greece the marble mining sites are mainly situated in the northern part of the country, including the Western Macedonia, Kozani region. The processing of marble ore includes various cutting, grinding and polishing stages that involve water recirculation, so as the cutting and polishing equipment to cool down. In this way, the fine marble dust particles are removed. In the end of the marble processing procedure, substantial quantities of solid marble residue are recovered from the resulting sludge stream.

On the other hand, the production and testing of ceramics for thermal insulating applications has attracted significant interest recently [1-4]. The success, in terms of applications, of an insulating material relies on its reduced heat conduction ability under a specific temperature gradient. The heat flow throughout a material is analogous to the applied temperature gradient. Thermal conductivity represents the proportionality factor (constant) and it is a material dependent property. Hence, in composite or multiphase materials, thermal conductivity can be modified by the modification of the materials constituents.
The addition of various constituents in the ceramic mixture that reduce the thermal conductivity, and consequently improve the thermal insulating behaviour, in fired clay ceramic production, is extremely important for the ceramic manufacturing industry. In practice, the decrease in thermal conductivity is usually achieved by the pore formation in the ceramic body. The incorporation of various pore-formers in standard clayey mixtures has been reported. The most important research efforts are related to the partial replacement of clay with bauxite in the ceramic material, the consolidation of used earth from biodiesel filtration and glycerine into the final ceramic material and the valorisation of paper processing residues, due to recycling, towards the production of novel ceramics [5-11].

Moreover, an alternative way for the porosity formation in the ceramic clay body is the incorporation of marble waste. Marble waste is mainly consisted of calcium carbonate (CaCO₃). The use of recycled marble residues (marble waste) for the engineering ceramics production could lead to significant benefits both from the environmental and economical point of view. Most works regarding marble wastes valorisation focused on rather conventional applications such as cement and concrete production, the production of asphalt aggregates used in road construction, and other building materials. However, not many works report the valorisation of marble residues to efficiently manipulate the properties of compacted ceramics [10,12-15]. Therefore, the investigation of the effect of various marble residue loadings, which are incorporated in the raw ceramic mixture, on the properties of the final ceramic product is important. Furthermore, the cautious examination of the properties of the final ceramic that incorporates waste assists to the correct evaluation of the ceramic material considering the standard requirements for commercial use.

In this work, the role of the marble processing residue as a pore-forming agent is investigated, by its incorporation in clayey raw materials as an admixture. Additionally, the possibility of employing powder metallurgy procedures for the production of innovative engineering ceramics is assessed. Moreover, the effect of the marble processing residue on thermal insulation behaviour (thermal conductivity) of the produced ceramics is also investigated. Furthermore, this work is expected to contribute to the sustainable management of this abundant industrial residue and also accentuate potential economic benefits regarding the production of novel ceramic materials.

2. Materials and Methods

2.1. Raw materials

In the present study, three different clays A, B and G were used. These clays were collected from Central Greece. Moreover, their composition is shown in table 1. The clay mixture (“Viokeral” mixture) used in this study consisted of 50% A, 33% B and 17% G clay type. The Viokeral mixture was utilized for manufacturing prototypes (Pr – blank samples, without marble residue) and samples incorporating various marble residue loadings.

| CLAY | CLAY Loss on Ignition (LOI) | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | K₂O | Na₂O | TiO₂ | CaCO₃ (eq) | CO₂ |
|------|-------------------------|------|-------|-------|-----|-----|-----|------|------|-----------|-----|
| A    | 11.9                    | 49.4 | 12.9  | 7.1   | 8.6 | 4.9 | 2.9 | 1.6  | 0.8  | 14.7      | 6.5 |
| B    | 9.9                     | 52.8 | 13.5  | 7.6   | 6.3 | 4.3 | 3.2 | 1.6  | 0.9  | -         | -   |
| G    | 16.5                    | 51.0 | 8.5   | 4.7   | 11.6| 3.9 | 1.5 | 1.4  | 0.6  | 24.5      | 10.7|

Table 1. Chemical analysis of clays
The marble residue used in this work resulted from the treatment of marble processing wastewater, from the Western Macedonia region. This region is one of the largest sources of marble in Greece. The Western-Macedonian marble is characterized by a large variety of white and coloured species of marble, and other stones as well, which are nowadays used in the marble industry [16]. The mineralogical composition of marbles from Tranovalto, Kozani area is: Calcite (98%), Dolomite (1%), Quartz (0.5%) and Muscovite (0.5%). The chemical composition of these marbles is given in table 2.

Prior to the sample preparation the clay mixture and the marble residue were crushed and sieved so as fine aggregates (with particle size <0.63mm). is received.

| Component | CaO | MgO | SiO<sub>2</sub> | Fe<sub>2</sub>O<sub>3</sub> | Al<sub>2</sub>O<sub>3</sub> | K<sub>2</sub>O | Na<sub>2</sub>O | MnO | CO<sub>2</sub> |
|-----------|-----|-----|----------------|----------------|----------------|--------|---------|-----|-----------|
| Composition (%) | 53.50 | 1.52 | 0.25 | 0.18 | 0.25 | 0.02 | 0.04 | 0.01 | 44.4 |

### 2.2. Fabrication of compacted ceramic specimens.

The ceramic samples consisting of marble residue and clay samples were produced by mixing 0, 12.5, 25 and 50 % wt. marble residue in the aforementioned clays, and adding 5-6% wt. water in the mixture. A full list of the samples fabricated in this work is given in table 3.

| sample name | clay (%wt) | marble residue (%wt) |
|-------------|------------|----------------------|
| Pr          | 95         | 0                    |
| SA          | 72.5       | 12.5                 |
| SB          | 70         | 25                   |
| SG          | 45         | 50                   |

The constituents shown in the table 3 were initially formed in wet mixtures. Subsequently, the wet mixture was uniaxially cold pressed in a stainless steel die using a hydraulic press. In that way a series of disc-shaped, with 5 cm diameter, green compacted samples were produced. All ceramic compacts were obtained by applying a 20 tn load and they had a reasonable initial strength for the subsequent fabrication step. Thereafter, the green disks were weighed in order to determine the moisture. Then the disks were dried naturally for 12h and then forced dried, at 110°C, until no additional weight loss is observed. Dried sample pieces were fired, following a gradual temperature increase protocol up to the temperature of 950°C. This sintering temperature typically applied in standard ceramic manufacturing. The sample pieces remained at 950°C for 2h. The whole firing procedure took place in a programmable electric chamber furnace. A comprehensive schematic diagram of the proposed production method is shown in figure 1.

![Schematic diagram of the proposed production method](image_url)

Figure 1. A schematic representation of the procedure followed for the production of marble residue/clay ceramics.

### 2.3. Ceramic specimen characterization.
The fired ceramic sample’s shrinkage, weight loss upon sintering (LOS), density, water absorption capacity and open porosity was determined according to ASTM C67. The thermal conductivity coefficient (k) was measured at 25°C by using an Anter Unitherm device (Model 2022), based on the guarded heat flow meter method. The thermal conductivity measurements were performed according to ASTM E1530. All the measurements presented hereunder are the mean value of ten specimen measurements.

Morphological examination and elemental analysis of the ceramic sample surfaces was carried by means of Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) using a JEOL 6610LV microscope carrying a large area (80mm²) silicon drift detector (X-Max 80, Oxford Instruments). All ceramic sample surfaces were coated with carbon prior observation, using a Quorum 150R E device. The elemental maps shown in this work were acquired and analysed using AZtech Nanoanalysis software (Oxford Instruments).

In order to gain further insights into the porosity of the ceramic samples produced, a well-established methodology, based on SEM and image analysis, was used. In brief this method includes pixel binarization and counting [17]. The porosity was calculated from the ratio of the total pore area to the net area of the image. This image analysis method has been already successfully used in food and polymer science [17,18]. The SEM images, used for the porosity measurements, were recorded using the backscattered electron (BSE) detector of the microscope in order to achieve higher pixel contrast [19]. At least five images of each sample were recorded and analysed for the porosity determination.

3. Results and discussions

3.1. Ceramic specimen appearance and weight loss on sintering.
Photographs of the fired ceramic samples produced are shown in figure 2. The apparent change in the appearance and the color of the samples is attributed to the incorporation of marble residue into the clay mixture, which was sintered via firing at 950°C. Specifically, the sample color changes from red (Pr sample) to brownish (SA sample) and subsequently to pale brownish (SB and SG samples) by increasing the marble residue loading up to 50%. Moreover, by visually inspecting the samples we noticed that the disk geometry is not affected by the marble residue incorporation and that disk volume slightly increases only for the ceramic samples that incorporate higher waste loadings (50%).

The effect of the marble residue incorporation on the weight loss (LOS) of the fired samples is presented in figure 3. The weight loss substantially increases, almost proportionally to the marble residue addition. This increase in the weight loss should be ascribed to the calcium carbonate (CaCO₃) decomposition during firing.
3.2. SEM-EDS Mapping

In order to assess the dispersion of the marble residue inside the ceramic body, as well as to observe the morphology of the samples, SEM-EDS analysis was used. In figure 4, SEM images with EDS maps of prototype (without marble residue) ceramic samples (figures 4a and 4b) and also ceramic samples with 50% marble residue (figures 4c and 4d) are presented. The addition of marble residue fine particles increases the surface roughness of the ceramic sample. Calcium (magenta colored) appears to be evenly spread on the elemental map (figure 4d), indicating a satisfactory dispersion of marble residue into the clay matrix upon specimen preparation.
Figure 4. SEM images and the corresponding elemental maps of the Pr sample (a and b), and the SG4 sample (c and d). The scale bar is set to 50 μm.

3.3. Bulk density/ Open porosity

The effect of the marble residue addition into the clayey mixture on the bulk density (d) and open porosity (OP) of sample disks sintered at 950°C was also investigated (figure 5). The experimental data in Figure 5 show that the open porosity increases significantly while the bulk density decreases respectively with the marble residue incorporation into the clayey raw materials (by 17% and 83% respectively for 50% residue percentage). This finding suggests that, marble residue acts as pore forming agent when it is incorporated inside bulk ceramic bodies, which are subjected to firing in high temperatures (950°C).

Figure 5. The effect of the marble residue addition on the bulk density (d) and open porosity (OP).
3.4. Porosity calculation from SEM micrographs.

SEM images of the ceramic samples surfaces are shown below (figure 6).

Figure 6. SEM micrographs of four representative samples studied in this work. (a) Pr (0% marble residue), (b) SA3 (12.5% marble residue), (c) SB4 (25% marble residue) and (d) SG4 (50% marble residue). Scale bar is set to 100 μm.

The addition of the marble residue increases the (dark colored) voids observed on the surface of the ceramic samples. In figure 7, the % porosity (as calculated from the SEM micrographs) versus the marble residue (%wt.) content is shown. The error bars in the graph correspond to the standard deviation from the average value. The addition of the marble residue significantly increases the porosity of the ceramic samples. This also confirms the pore-forming capabilities of the marble residue. Moreover, the % porosity values calculated from the SEM micrographs appear to be in good agreement with the open porosity (OP) values.

Figure 7. Porosity % (calculated from the SEM micrographs) versus marble residue (% wt.).

3.5. Thermal conductivity

Thermal conductivity measurements were conducted in order to verify the ability of marble residue to improve the insulating behaviour of the produced ceramics.
The thermal conductivity coefficient (k) of compacted specimens fired at 950°C as a function of the marble residue (% wt.) content is shown in figure 8. The incorporation of high loadings (up to 50%) of marble residue inside the clayey body substantially reduces (up to 35%) the thermal conductivity. In that sense the insulating behaviour of the ceramics is improved. This finding is in agreement with the porosity measurements. The presence of pores inside the ceramic body is expected to reduce the thermal conductivity, due to the very low thermal conductivity values of air which exists in the pore volume. Therefore, the porosity determination of the ceramic materials destined to thermal insulation application is rather significant.

4. Conclusions
Ceramics loaded with different % marble processing residue content were successfully produced upon firing at 950°C. Up to 50 wt.% residue content was successfully consolidated in the clayey ceramic body, by employing an established powder metallurgy procedure. SEM-EDS results suggest that the fine particles of marble residue were evenly incorporated and dispersed into the clayey ceramic body, even for higher admixture percentages. The characterization of the ceramic samples by means of porosity and thermal conductivity measurements reveals that, by increasing the marble residue loading, the porosity of sintered ceramic products increases, which, in turn, leads to a decrease in thermal conductivity. Consequently, the marble processing residue can be employed as an efficient pore former, in order to improve the insulating behavior of the ceramic materials.

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