

COMPACTED CERAMICS INCORPORATING RECYCLED MARBLE PROCESSING RESIDUE

Asimina E. Domopoulou^{1*}, Xenofon D. Spiliotis², Konstantinos I. Ntampegliotis², Konstantinos H. Gudulas¹,
George A.-P. Papapolymerou², Vayos G. Karayannis¹

¹Department of Environmental Engineering, Technological Education Institute of Western Macedonia, Kila, 50100, Kozani, Greece

²Department of Civil Engineering, Technological Education Institute of Thessalia, 41100, Larissa, Greece

*Corresponding author: adomopo@teikoz.gr, Tel +30 24610 68122

Abstract

The recycling of marble processing residue as pore former into clayey mixtures for the development of lightweight thermal insulating ceramics can contribute both to sustainable management of this industrial secondary material and economic benefits. Indeed, use of ceramics as thermal insulators is one of the main applications for this category of materials.

In the present research, clay minerals incorporating 0-50 wt.% marble powdery residue were compacted into 5 cm disc-shaped specimens and fired at 950°C, a sintering temperature typically applied in standard ceramic manufacturing.

The characterization of sintered materials reveals successfully consolidated ceramic bodies even at 50 wt.% residue content, whereas both bulk density and thermal conductivity of sintered products clearly decrease as a result of an increased porosity attained with increasing the powder admixture percentage.

Keywords: marble residue, compacted ceramics, sintering, thermal conductivity, porosity

1. INTRODUCTION

The aim of the current research is the recycling of marble processing residue as an admixture in clayey raw materials, at various percentages (0, 12.5%, 25% and 50%), for manufacturing innovative engineering ceramics by employing powder metallurgy procedures, to contribute to the sustainable management of this industrial residue and also provide economic benefits to the production of ceramic materials.

Marble processing particularly in Greece is considered one of the most important industrial sectors. The marble mining sites are mainly located in northern Greece, including the region of Western Macedonia - Kozani. Marble ore cutting, grinding and polishing stages involve water recirculation in order to cool down the cutting and polishing equipment and to remove fine dust particles. From the produced sludge stream, significant quantities of solid marble residue are recovered.

On the other hand, recent trends in the ceramic manufacturing industry shows an increase in the use of thermal insulating ceramics (Hu, Wang & Huang 2010, Meukam et al. 2004, Akiyoshi et al. 2002, Kingery, Bowen & Uhlmann 1976). Actually, the usefulness of a material for such applications is largely fixed by the rate of heat conduction through it under a particular temperature gradient. The heat flow through a material being proportional to the temperature gradient applied, the thermal conductivity represents the proportionality factor and is a material constant.

So far, the addition of a variety of industrial and agricultural by-products as pore formers in standard clayey mixtures has been investigated, including the partial replacement of clay with bauxite, spent earth from biodiesel filtration and glycerine, recycled paper processing residues etc., in order to reduce the thermal conductivity and therefore to improve the thermal insulating behavior in fired clay ceramic production (Karayannis et al. 2013, Eliche-Quesada et al. 2012, Eliche-Quesada et al. 2011, Raut, Ralegaonkar & Mandavgane 2011, Sutcu & Akkurt 2009, Al-Amaireh 2006).

Another way of generating porosity in the clay ceramic body is by introducing marble waste, which is composed primarily of calcium carbonate. So far, most research has concentrated on using marble wastes in different applications like road construction, concrete and asphalt aggregates, cement, and other building materials. However, relatively little work is reported on the valorization of marble residues as efficient secondary resources than as wastes into clayey materials in order to appropriately tailor the properties of compacted ceramics. Nevertheless, the examination of different % powdery marble contents in the raw material mixture would allow to verify possible significant modifications in the properties of the ceramic products, with respect to the standard requirements for commercial use. Furthermore, potential utilization of recycled marble residues for the

production of engineering ceramics may provide significant benefits both from the economic and the environmental point of view (Bilgin et al. 2012, Eliche-Quesada et al. 2012, Montero et al. 2009a,b, Saboya, Xavier & Alexandre 2007).

2. MATERIAS AND METHODS

2.1 Raw materials

Three different clays A, B and C, collected from Central Greece, were used in the present study and their chemical analysis is presented in Table 1. The clay mixture ("Viokeral" mixture) used in this research consisted of 50% A, 33% B and 17 % C clay type. The Viokeral mixture was utilized for manufacturing prototype (pr) specimens and specimens with various % marble residue content.

Table 1. Chemical analysis of clays

CLAY	PARAMETER (%)										
	Loss on Ignition (LOI)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	CaCO ₃ (eq)	CO ₂
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	-	-
C	16.5	51.0	8.5	4.7	11.6	3.9	1.5	1.4	0.6	24.5	10.7

The marble residue used in specimen preparation was derived from the treatment of marble processing wastewater originating from the region of Western Macedonia, one of the main sources of marble in Greece, characterized by a broad variety of white and colored marbles and other stones that are used today in the marble industry (Domopoulou, Gudulas & Papastergiadis 2013). Particularly, the mineralogical composition of marbles from Tranovalto - Kozani area is composed of calcite (98%), dolomite (1%), quartz (0.5%) and muscovite (0.5%). The chemical composition of these marbles is given in Table 1.

Table 2. Chemical composition of marbles

ELEMENT	CaO	MgO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	K ₂ O	Na ₂ O	MnO	CO ₂
CONTENT (%)	53.50	1.52	0.25	0.18	0.25	0.02	0.04	0.01	44.4

Both raw materials used (clay mixture and marble residue) were crushed and sieved, resulting in fine aggregates (particle size <0.63mm).

2.2 Fabrication of compacted ceramic specimens

The marble residue/clay samples were produced by mixing 0, 12.5, 25 and 50 % wt. marble residue and 5-6% wt. water in the aforementioned clays. A schematic diagram of the proposed method is shown in Figure 1.

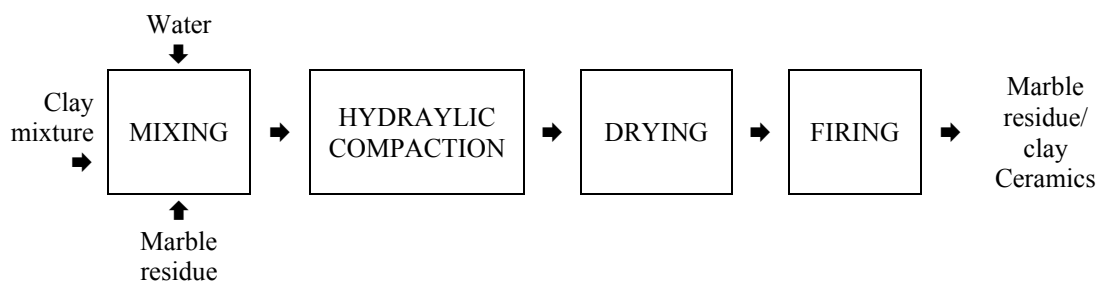


Figure 1. Schematic diagram of the procedure followed for the production of clay ceramics.

The wet mixture was uniaxially cold pressed in a stainless steel die using a hydraulic press to form a series of 5cm diameter disc-shaped green compact specimens. All compacts obtained at 20 tn load had a reasonable green strength for the subsequent fabrication step. Afterwards, the green disks were weighed for moisture determination and then exposed to natural (for 12 h) and then forced drying (at 110°C) until reaching a constant weight. Dried test pieces were fired following a protocol of gradual temperature increase up to the peak temperature of 950°C for 2h in a programmable electric chamber furnace.

2.3 Ceramic specimen characterization

The determination of specimen shrinkage, weight loss upon sintering (LOS) and physical properties, including density, water absorption capacity and porosity was conducted on fired ceramic specimens according to the ASTM C67: Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile.

The thermal conductivity coefficient (k) was measured at 25°C by the Anter Unitherm Model 2022, which applies the guarded heat flow meter method. The tests are in accordance with the ASTM E1530 Standard (ASTM E1530: Test Method for Evaluating the Resistance to Thermal Transmission of Thin Specimens of Materials by the Guarded Heat Flow Meter Technique).

All the results presented hereunder are the mean value of ten specimen measurements.

3. RESULTS AND DISCUSSION

3.1 Ceramic specimen preparation and appearance

Figure 2 depicts the change in the specimen appearance/coloring resulting from the incorporation of marble residue into clay mixture sintered at 950 °C. From this Figure, it is obvious that fired specimen color turns from red to brown for 12.5% marble addition and to pale brownish for higher residue percentages, up to 50%, in the clayey raw material mixture. Furthermore, visual inspection of the sintered specimens obtained shows that the disk geometry is practically unaffected by the marble residue incorporation in the clay mixture and its volume slightly increases only for the higher waste percentage considered (50%).

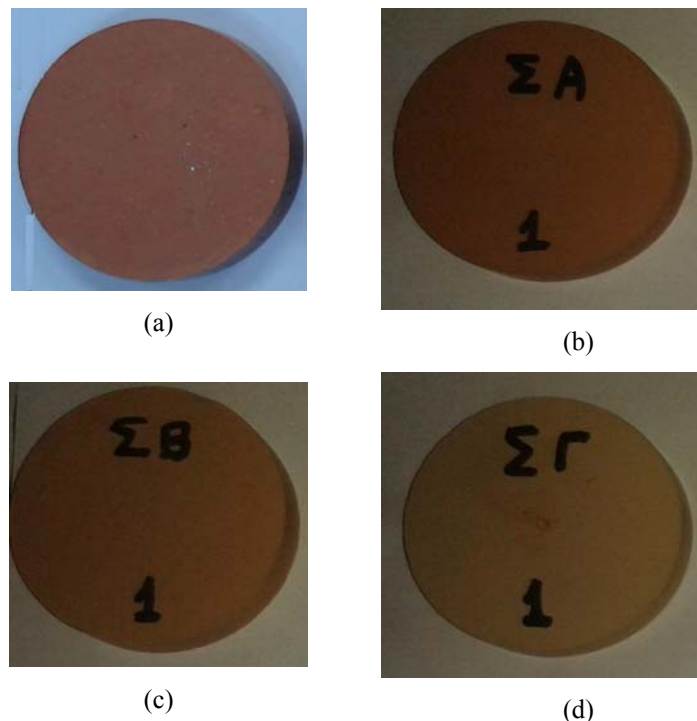


Figure 2. Appearance of the ceramics specimens fired at 950°C, with different marble residue content: (a) prototype:0%, (b) ΣA:12.5%, (c) ΣB:25%, (d) ΣΓ:50%.

Figure 3 depicts the specimen weight loss (LOS) variation resulting from the incorporation of marble residue into clay mixture sintered at 950 °C. According to the results, weight loss is increased rapidly by the marble residue addition (by almost 48%, 112%, 237% for 12.5%, 25% and 50% marble residue respectively), apparently due to CaCO_3 decomposition during firing.

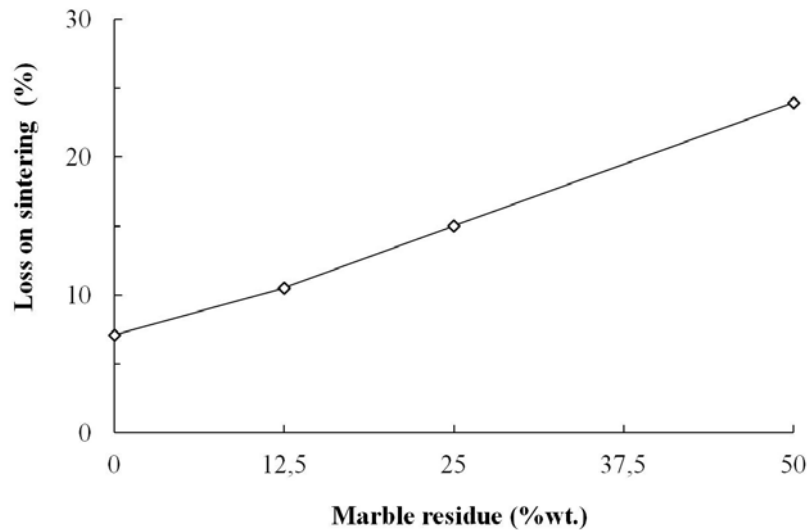


Figure 3. The effect of % marble residue addition on weight loss on sintering (LOS) of clay ceramics sintered at 950 °C.

3.2 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 disk specimens sintered at 950 °C is presented in Figure 4. The experimental data in Figure 4 show that the open porosity rapidly increases and 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 verifies that, in fact, marble residue acts as pore forming agent in the bulk of the compacted materials.

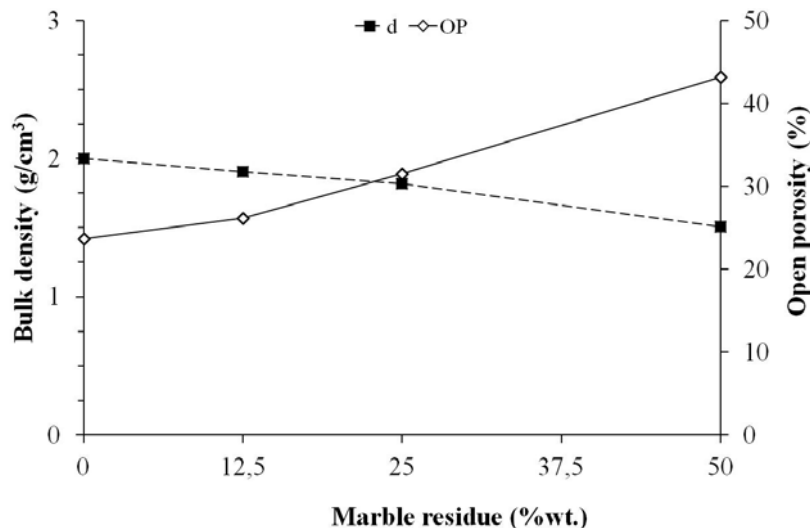


Figure 4. The effect of % marble residue addition on bulk density (d) and open porosity (OP) of compacted ceramics sintered at 950 °C.

3.3 Thermal conductivity

Figure 5 shows how the thermal conductivity coefficient (k) of compacted specimens fired at 950 °C is influenced by the % marble residue presence in the clay mixture. It is apparent that the embodiment of marble residue in high proportions reduces k by approx. 13% and 35 % for 25% and 50% marble residue content respectively, thus improving the insulating behavior of the compacted ceramics. This finding is expectedly in accordance with the porosity trends presented in Figure 4, thus confirming that porosity plays an important role on the thermal behavior of ceramic materials.

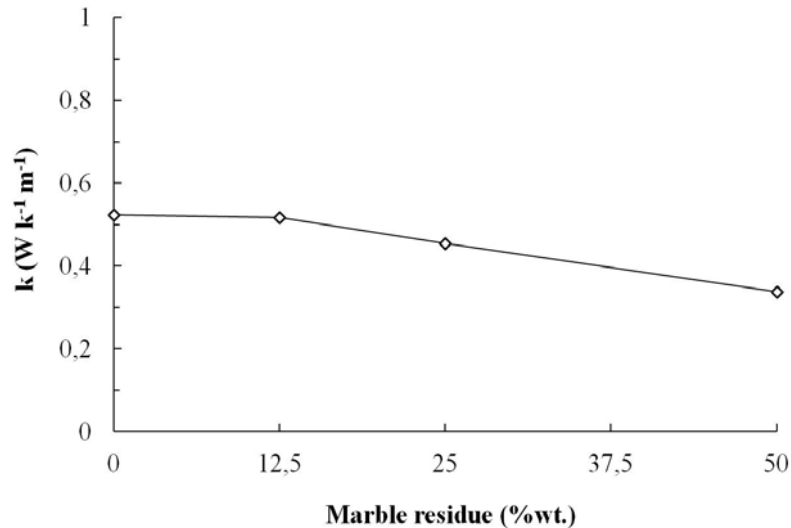


Figure 5. The effect of % marble residue addition on thermal conductivity coefficient (k) of compacted ceramics sintered at 950 °C.

4. CONCLUSIONS

- Compacted ceramics incorporating 12.5, 25 and 50 wt.% recycled marble processing residue as secondary resource are successfully produced upon firing at 950°C.
- The experimental results of properties characterization on fired materials reveal effectively consolidated ceramic bodies even at 50 wt.% residue content.
- By increasing the marble powder admixture percentage, the porosity of sintered products increases leading to decreased thermal conductivity, which is promising with regard to a potential significant gain in thermal insulation capability of the produced ceramics.

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