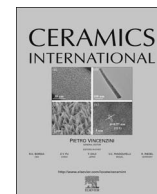




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Usage of marble wastes in traditional artistic stoneware clay body

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ABSTRACT

Recycling of industrial wastes aids environmentally friendly production and has the advantage of lowering costs. Marble production generates large amounts of waste. Recycling of such wastes by incorporating them into ceramic industry is a practical solution for pollution problem. The aim of this work is to assess the possibility of the recycling of marble wastes in the production of stoneware clay bodies as a raw material for ceramic artwork production. Five different clay body mixes containing marble waste up to 27% were prepared and evaluated for firing color, water emission, morphology, microstructure, thermal expansion coefficient and thermal behavior. The results of the tests show that the utilization of marble waste in stoneware body is feasible for ceramic artwork production.

1. Introduction

Industrial waste management constitutes one of the major global problems of our times. Recycling of non-biodegradable waste is particularly difficult. Ceramic waste has been classified in this group [1,2].

Ceramic waste are hard, durable and extremely resistant to chemical, physical and biological degradations and highly thermally. It has been estimated that about 30% of the daily production in the ceramic industry goes to waste. Nowadays, the ceramic industry creates a significant amount of waste for disposal. These solid waste lead to severe environmental pollution and significant land occupation. Huge amount of ceramic waste (in the form of pellets and powder) is produced in different stages such as grinding, cutting, dressing and polishing inside the industrial plant. Wastes can be used to produce new products or can be used as admixtures so that natural sources are used more efficiently and the environment is protected from waste deposits. Recycling and reuse of waste materials suggest energy saving, cost reduction, possibly superior products and less or no hazards to the surrounding environment [3–6].

Marble is a metamorphic rock, such as limestone, that contains largely calcium carbonate (CaCO_3). Furthermore, in marble, small amounts of silica, feldspar, iron oxide, mica, fluorine and organic matters may be found [7]. It is one of the most extensively used aesthetic stones [8]. Marble waste dust is an inert material which is obtained as an industrial by product [9]. A 90% of dried marble slurry having very fine dust is smaller than 200 μm in size [10].

Turkey has large deposits of high quality marble and is one of the leading producers. Large quantities of wastes are produced in different stages of marble quarrying and processing operation [11].

There are many studies on the use of natural stone (marble and dolomite) wastes as reinforcement material or raw material in various areas and applications [12–19]. Natural raw materials used in the fabrication of clay-based ceramic products show a wide range of compositional variations and the resulting products are very heterogeneous. Therefore, such products can tolerate further compositional fluctuations and raw material changes, allowing different types of wastes to be incorporated into the internal structure of ceramic tiles and bricks as part of their own matrix. Some wastes are very analogous in composition to the raw materials used, moreover they often contain materials that can also be helpful in improving the fabrication of ceramic products. Many attempts were made to incorporate solid wastes into raw materials mixtures in order to produce different ceramic products. Recent studies demonstrated the possibility of incorporating marble and granite sludge slime as additives into clay-based ceramic products [20–22].

A key issue for the recycling of solid waste material as an alternative raw material in the ceramic field is the knowledge of its chemical, mineralogical, and physical characteristics [23]. In this work we mainly focused on the recycling of waste generated by marble industries. The aim of this work is to study the possibility of the use of marble powder waste generated in the Afyonkarahisar -Merdivenci Mermer Inc. of Turkey, in ceramic mixtures, for manufacturing of stoneware clay bodies. The effects due to the use of waste marble powder were

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Table 1

Recipes of the standard (STD1) and marble waste added bodies.

Raw Material	STD	R1	R2	R3
Sodium-feldspar	15	15	15	15
Potassium-feldspar	8	8	8	8
Quartz	7	7	7	–
Kaolin	20	10	–	–
Marble Waste	–	10	20	27
Fire Clay	10	10	10	10
Clay	40	40	40	40

investigated in laboratory experiments and discussed in terms of firing behavior and main physical–microstructural properties.

2. Materials and methods

The typical stoneware clay body recipe (STD) that used by ceramic artists in their works was prepared with dry marble waste. In this study very fine marble powder was used. It was obtained as a by-product of marble sawing and shaping. Marble wastes were supplied from the facility in the form of sludge and then milled and sieved through 100 mesh. After drying, they became ready to use as raw material.

Firstly, XRF analyses of marble waste and the other raw materials in the recipe were conducted in order to determine the chemical compositions. Also XRD (X-ray powder diffraction), particle size and hot stage microscope analyses of marble wastes were performed.

Throughout the whole study 3 different groups of clay body recipes in terms of waste content from 10, 20 and 27 wt% of marble waste was selected and prepared. Standard and waste added stoneware body recipes were coded as STD, R1, R2 and R3 and their composition are given in Table 1.

In order to prepare stoneware clay bodies suitable amounts of Na-feldspar, K-feldspar, quartz, kaolin and marble waste with water were ground in a ball mill for 1 h and sieved through 100 mesh. This mixes were dewatered by leaving them on plaster boards, then kneaded and plastic mud was obtained. Afterwards, the samples with the dimensions of 200×20×15 mm were formed in a plaster mold for the shrinkage and water absorption tests. After having been dried at 75 °C for 1 day, the samples were fired at 1160 °C for 7 h in a laboratory type electrical furnace (soak time 10 min). Linear shrinkage and water absorption values are directly related with open porosity, are properties easy to measure. The linear shrinkage, LS (%), of fired samples has been determined by means of the following equation [24]:

$$LS = \frac{L_s - L_c}{L_s} \times 100 \quad (1)$$

All samples of each composition have passed through the water

absorption test after firing. The weight of the test samples has been measured in both condition of air and water for dry weight (Dw) and wet weight (Ww). Then the water absorption has been calculated (2) after the excessive water had been wiped off [25].

$$W(\%) = [(Ww - Dw)/Dw] \times 100 \quad (2)$$

After firing, color changes and surface texture of bodies were visually investigated. Then some experimental tests have been carried out with the ceramic clay bodies. Optical parameters of the samples were investigated by Minolta 3600-d spectrophotometer. Crystal phases developed during firing were determined with X-ray diffraction (XRD- Rigaku Rint 2000 Series) and scanning electron microscopy (SEM- Zeiss EVO 50) techniques. In order to determine thermal expansion coefficient values samples were heated in a dilatometer (Netzsch DIL 402 PC) at a rate of 10 °C/min up to 600 °C.

After characterization tests, artistic applications were done by using these standard and waste added stoneware clay compositions. In the first application, tiles pressed in 15×15 cm dimensions. After drying, alkali-boron-zinc glaze containing 3% CuCO₃ was applied on to tiles which were conducted to biscuit firing at 1000 °C oven. Then they fired at 1160 °C. In the second application, standard clay and marble waste added clay compositions were mixed with electrolyte additive to obtain casting slurry. Andesite plates were selected for the application. Andesite is a silica-containing (53–63%), fine-grained volcanic rock, with a color between grey and black [26]. Andesite plates were gathered from the mine and cut in the factory to desired dimensions (1,5×15×30 cm). After cleaning their surfaces, andesite plates were surrounded by the tapes which have different thicknesses on all sides in order to obtain a reservoir for casting. A prepared slurries poured into the reservoir in andesite plates and set aside until the slurry becomes as hard as skin. Benefiting from the porosity of andesite stone, some cracks were allowed during the drying process. The cracks were partly oriented by changing the direction of the drier. In order to obtain small cracks, thin slips and faster drying are used; thick slips are used for larger cracks. After the cracking and drying processes were completed, some of the cracked pieces were removed from the andesite tablet surface as a part of the designing project. Glaze was not applied between andesite muds and andesite plates. Andesite melts in 1160 °C when it is in powder form and andesite created semi-vitreous surface when it is in the form of plates. Because of these properties, an interface was formed between stone and applied slurry [27,28].

3. Results and discussion

Chemical analysis of the raw materials and marble wastes used in the study are presented in Table 2. As it seen from the Table 2, the waste is high in calcium oxide content, followed by magnesium oxide. Basically, the source of each waste material is recognized from the waste composition with regard to the rate of contamination in

Table 2

Chemical analysis of the raw materials and marble waste used in the bodies (wt%).

Raw Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	^a L.O.I
Sodium feldspar	69,37	18,90	0,20	0,54	0,45	9,16	0,24	0,30	0,84
Potassium feldspar	70,08	15,37	0,20	0,55	0,05	2,51	10,65	–	0,59
Quartz	99,50	–	–	–	–	–	–	0,07	0,43
Kaolin	57,58	26,75	1,38	0,37	0,52	0,82	0,33	0,67	11,58
Fire Clay	47,44	32,45	2,76	0,54	0,82	0,46	1,00	0,85	13,68
Clay	53,02	28,28	1,92	0,39	0,88	0,2	1,71	0,84	12,76
Marble Waste	0,52	–	0,10	53,51	1,66	0,09	–	–	44,12

^a Loss on ignition.

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