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Utilization of Industrial By-Products in Production of Ceramic Materials Focusing on CO_2 Emissions Reduction

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ABSTRACT

The current study focuses on potential utilization of glass cullet and emery in the field of ceramic industry. Both aforementioned materials may substitute the clay raw material of the brick industry, thus reducing the CO_2 emissions coming from carbonates decomposition. The experimental part of the current study included the production of bricks using 15 and 20 % w/w emery and 5% and 15% glass cullet substituting clay raw material. The final products were examined for their chemical composition, their mineralogical composition, their thermal behaviour, their morphology and they were subjected to specific quality tests: water absorption capacity, shrinkage percentage and compressive strength. Satisfactory results were obtained for the use of 15% glass cullet and 20% emery, especially with respect to water absorption capacity and compressive strength. Good results were also obtained with respect to the substitution of carbonates in the raw materials, with subsequent reduction of CO_2 emissions.

INTRODUCTION

The utilization of industrial minerals and byproducts is considered of great importance with respect to environmental protection and sustainable development. The current study focuses on three fundamental areas considering materials exploitation in the field of ceramic industry: (1) the potential utilization of an industrial byproduct such as glass cullet in brick industry. Glass cullet, even if is considered as relatively inert material, it is produced in huge quantities in Greece, derived from Glass Industry and the collection of glass bottles, posing problems related to waste management issues (2) the potential utilization of an industrial mineral such as emery in brick industry production. The particular mineral, found in large quantities in the island of Naxos Greece, is of the highest quality worldwide. Nevertheless, Greek emery is hardly disposed in the national and international market, due to the high competition of synthetic minerals, possessing similar attributes and lower production cost. An immediate consequence is the serious recession of the local economy, the accumulation of huge quantities of emery, the degradation of the landscape and the questionable safety and stability of the emery depositions (3) both aforementioned materials may substitute the clay raw material of the brick industry, thus reducing the CO_2 emissions coming from carbonates decomposition during the thermal processing of the raw material.

The brick industrial sector is considered one of the most important in Greece [Greek Ministry of Environment, 2008]. The raw material for brick production is clay and the industrial process includes mainly water addition, while the use of petroleum coke for aiding combustion is a common practice. Soil and water mixture is dried at 80 ºC and then heated up to 800 ºC so as to receive the final products. The latter are subjected to specific tests (shrinkage percentage, compressive strength etc) so as to reassure compliance of materials with international quality standards.

Many attempts are referred to the literature [Heystek et al, 1985, Shih et. al, 2004, Freidin & Erell 1995, Lin, 2006, Smith et al, 2005, Demir et al, 2005, Zhao et al, 2009], with respect to the substitution of some part of the brick raw material with several materials or wastes such as glass, slags and tailings, mud, fly ash etc. The critical difference of the raw material (clay) utilized in Greek Brick Industries is the high concentration of carbonates and specifically of $CaCO_3$. Chemical analyses prove the presence of calcium carbonate to concentrations up to 15%, mainly in the form of calcite. As a consequence, the substitution of the clay with alternative materials (free of carbonates) may lead to reducing CO_2 emissions, produced during heating process.

For the purposes of the current study, substitution of different percentage of clay soil with cullet and emery took place. More specifically, the addition of 15 and 20% emery, 5 and 15% of cullet in the raw material was conducted. The final products were examined for their chemical composition using X-Ray Fluoresence and analytical methods, their fundamental physicochemical attributes, their mineralogical composition using X-Ray Diffraction Analysis, their thermal behaviour using Thermogravimetric Analysis (TGA), their morphology using Scanning Electron Microscopy (SEM) and they were subjected to specific tests like water absorption capacity, shrinkage percentage and compressive strength. Results were compared with those obtained from laboratory brick production by the industrially used raw materials.

MATERIALS AND METHODS

A. Raw Materials

Chemical Analyses. The chemical composition of the raw materials was examined utilizing X-Ray Fluoresence (XRF analysis - PHILIPS 1606) and Atomic Absorption Spectrometry (AAS, Perkin Elmer 3300). Results are presented in Table 1.

Mineralogical Analyses. The mineralogical composition of raw materials (with the exception of glass cullet which is amorphous) was examined utilizing X-Ray Diffraction (XRD, Siemens 500 D-500 Diffractionmeter). The main phases that have been detected are illustrated in Table 2.

Table 1: Chemical Composition of Raw Materials

Clay (% w/w)		**Emery (% w/w)**		**Glass Cullet (% w/w)**	
SiO_2	48.8	**SiO_2**	3.5	**SiO_2**	70.6
Fe_2O_3	19.2	**Fe_2O_3**	46.4	**Fe_2O_3**	0.5
Al_2O_3	24.6	**Al_2O_3**	46.8	**Al_2O_3**	1.8
CaO	5.5	**CaO**	0.8	**CaO**	10.7
MgO	1.0	**TiO_2**	2.3	**MgO**	2.5
K_2O	0.8			**K_2O**	0.5
Na_2O	0.9			**Na_2O**	13.2

Table 2: Mineralogical Composition of Raw Materials

Chemical Form	Clay	Emery
SiO_2	+	+
$CaCO_3$	+	
$Ca(OH)_2$	+	
Fe_2O_3	+	+
Fe_3O_4		+
FeO(OH)	+	+
Al_2O_3	+	+

Granulometry. After grinding the raw materials were examined with respect to their granulometric composition using Mastersizer micro-Malvern (MAF 5000). For glass cullet, 10% of its mass is finer than 12.94μm, 50% finer than 103.40μm and 90% finer than 212 μm. For emery 10% is finer than 8,93μm, 50% finer than 73.54μm and 90% finer than 163.26 μm. Finally, considering clay soil, 10% of its mass is finer than 2.86μm, 50% finer than 22.88μm and 90% finer than 81.12 μm.

Thermal Behavior. For purposes of examination of the raw materials thermal behavior, Thermogravimetric Analysis (up to 1000°C) was conducted using Mettler TGA/STDA 851^{C}. Results are presented in Table 3.

Table 3: Results of Thermogravimetric Analysis for raw materials

Emery (mass loss - % w/w)				
170-350ºC	**360-600ºC**	**600-710ºC**	**710-900ºC**	**25-900ºC**
1,37	1,55	0,43	0,0026	3,35
Clay (mass loss - % w/w)				
25-100ºC	**100-330ºC**	**330-450ºC**	**600-1000ºC**	**25-900ºC**
0,59	1,55	2,83	3,06	8,03

B. Mixture process – Preparation of bricks – Final products

Five series of bricks were prepared as illustrated in Table 4.

Table 4: Proportion of raw materials in final products

Product Number	Clay Soil (% w/w)	Emery (% w/w)	Glass Cullet (% w/w)
1 (Reference)	100	-	-
2	85	15	-
3	80	20	-
4	95	-	5
5	85	-	15

In all mixtures, 20% of water was added as it occurs in industrial process. Products (5 X 5 X 5 cm patterns) were left for 24 h at room temperature. Seven specimens from each type were formed, i.e. 35 in total. The next step included drying at 80 °C and measurement of weight loss and dimensions. The respective results are presented in Table 5.

Table 5: Bricks shrinkage after drying at 80 °C

Product Number	Shrinkage (%)
1 (Reference)	0,99
2	3,51
3	0,66
4	2,08
5	4,52

All specimens were heated at 800 °C for 24 h, in order to receive the final products. The latter, after cooling at room temperature, were examined with respect to their weight loss, dimensions, water absorption (ASTM, C 109) and compressive strength (EN 711 - 1:2003). Results are presented in Table 6. It should be mentioned that simulation of the industrial process was attempted.

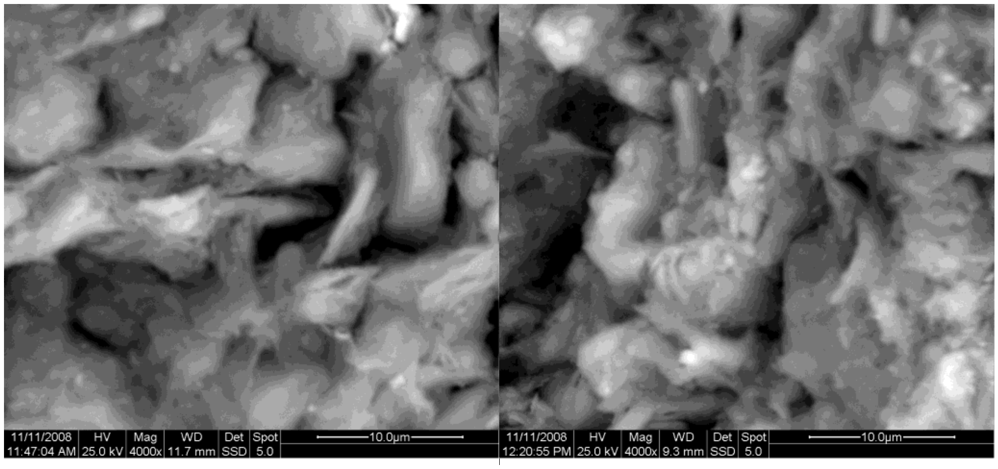
Table 6: Attributes of the final products (negative shrinkage = increase of dimensions)

Product Number	% Weight loss	Firing Shrinkage (80 -800°C) (%)	Water absorption (%)	Compressive strength (N/mm^2)
1	22,10	-0,92	13,93	18,7
2	21,81	+0,96	13,45	17,2
3	23,10	+0,46	14,22	19,4
4	21,19	-0,87	13,54	22,3
5	19,10	-1,02	12,78	25,4

Additionally, all final products were examined for their mineralogical composition using XRD and their morphology using Scanning Electron Microscopy (SEM, JSM-6300 JEOL). The mineralogical phases detected are presented in Table 7, while representative photos from SEM investigation are illustrated in Photos 1 and 2.

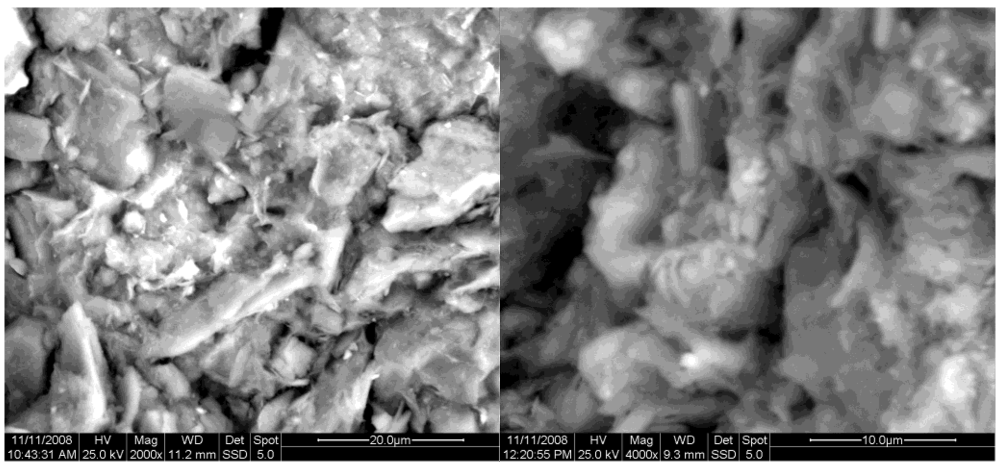
Table 7: Mineralogical analysis of the final products

Chemical Form	Product 1 (Reference)	Product 2	Product 3	Product 4	Product 5
SiO_2	+	+	+	+	+
CaO	+	+	+	+	+
Fe_2O_3	+	+	+	+	+
Fe_3O_4		+	+		
Al_2O_3	+	+	+	+	+



(a) (b)

Photo 1: SEM photographs for (a) brick with addition of 15% glass cullet, (b) brick with 100% clay soil



(a) (b)

Photo 2: SEM photographs for (a) brick with addition of 20% emery, (b) brick with 100% clay

RESULTS AND DISCUSSION

Considering chemical and mineralogical analyses of the raw materials (Tables 1 and 2), it is confirmed that carbonates concentrations are significantly low in emery, implying subsequent reduction of CO_2 emissions produced during the bricks production process. On the other hand, glass cullet is a by-product coming from high temperature processing, thus does not contain any carbonates that may lead to CO_2 emissions. The thermal behaviour of emery and clay, as presented in Table 3, illustrates a strong resistance of the industrial mineral to temperature increase, since they are no crystalline phases that decompose below 1000 °C, except from crystalline water trapped within the matrix of emery. On the other hand, the presence of carbonates in clay, lead to significant weight loss after 600 °C, which unavoidable leads to CO_2 emissions.

After bricks production, no macroscopic differentiation was noticed (e.g. colour) comparing specimens with 100% clay and those with the addition of emery and glass cullet.

In literature [Zhao et al, 2009, Lin, 2006, Freidin & Erell, 1995)], the average loss of ignition after brick production process is almost 15%. Nevertheless, Greek clay raw material is significantly different with respect to calcium and magnesium carbonates, thus leading to higher loss of ignition percentages. As it is shown in Table 5, for all specimens loss of ignition fluctuates between 20.7% (100% clay) and 23.10% (15% emery). For the latter material, the high loss of ignition is probably attributable to the loss of crystalline water molecules, up to 80°C.

All specimens with additives have presented higher % shrinkage during the drying process, with respect to reference product (Table 5). The only exception was the brick with 20% emery that was proved very resistant to shrinkage. Considering the firing shrinkage values (80 -800°C), specimens containing glass cullet and 100% clay, have illustrated an increase in their dimensions (Table 6), while bricks containing emery slightly decrease their dimensions during the firing process. As far as it concerns clay, the dimension increase is probably attributable to the gases produced during the firing process. On the other hand, glass cullet under the firing temperature, peripherally covers the granules of the clay and traps both decomposition gases and steams coming from the crystalline water.

Considering the water absorption results (Table 5), the specimen with 15% glass cullet presents the lower value, including the specimen with 100% clay. All specimens illustrated satisfactory water absorption, which is a very important attribute affecting the stability of the final product with respect to environmental conditions.

Compressive strength results were also satisfactory, while the specimen with 15% glass has presented the best results. The only specimen with lower compressive strength than the reference specimen is the one with 15% emery, however, its compressive strength is satisfactory. It should be mentioned that compressive strength is perhaps the most important mechanical attribute of the final product [Shih et al, 2005, Smith et al, 2006], since it is the most representative expression of the mechanical quality of the brick. It is obvious that the addition of glass cullet and emery (20%) ameliorates mechanical behavior of the final products.

The main differentiation of the mineralogical composition of the final products compared to the raw materials is the exclusion of calcite due to its decomposition to CaO and CO_2. The quantitative interpretation of calcite decomposition, with respect to CO_2 emissions, is much more encouraging in case of specimens with the additives (especially those with 15 and 20% substitution of clay), since the initial concentration of calcite is significantly lower. Moreover, for specimens with the addition of emery, magnetite appears as a new phase, probably after transformation of aimatite and goethtite at high temperatures. On the other hand, specimens with the addition of glass cullet do not lead to any new mineralogical phase, due to the fact that glass cullet is amorphous. Nevertheless, after the thermal process at 800 °C, glass cullet can act as welding connection between granules, thus increasing the compressive strength. SEM photos, presenting the morphology of the final product, confirm the above statement.

CONCLUSIONS

Conducting an examination of the possibility of adding emery (15, 20%) and glass cullet (5, 15%) to the raw material of the brick industry, the mechanical attributes, the mineralogical composition, the thermal behavior and the morphological characteristics of the raw materials and the final products were investigated. Satisfactory results were obtained for the use of

15% glass cullet and 20% emery in the raw materials, especially with respect to water absorption capacity and compressive strength. Lower quality results were obtained for 5% glass and 15% emery in the raw materials, nevertheless were not prohibitive for their use in industrial process. Good results were also obtained with respect to the substitution of carbonates in the clay raw material, with subsequent reduction of CO_2 emissions produced during the bricks production process.

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