CHARACTERIZATION OF A NEW LABORATORY CERAMIC PRODUCT FROM INDUSTRIAL BY-PRODUCTS AS RAW MATERIALS AND CAUSTIC MAGNESIA AS ADDITIVE

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Abstract

A new ceramic product is introduced by mixing caustic magnesia, produced in the laboratory from pure, high quality magnesite, and natural silt. Bottom ash and red mud, two well known environmentally hazardous industrial by-products, were also added in the mixture. After testing various recipes we concluded that addition of 5% caustic magnesia in the ceramic product greatly enhances its performance. Increase bonding of the ceramic microstructure is attributed to the formation of periclase necks, the concurrent formation of small quantities of amorphous material and the homogeneously distributed pores during the experimental firing of the mixture. Combined X-ray Diffractometry and Scanning Electron Microscopy of the ceramic product revealed the occurrence of unreactive phases, inherited by the raw materials, as well as newly-formed albite and magnesioferrite. Our results show that utilization of by-products may be important and environmental friendly materials in producing low cost ceramic building materials.
Keywords: *ceramics, caustic magnesia, by-products, red mud, bottom ash.*

Περίληψη

Στην εργασία αυτή παρουσιάζεται ένα νέο κεραμικό προϊόν που παράχθηκε από μίξη καυστικής μαγνησίας, που παρασκευάστηκε εργαστηριακά από υψηλής καθαρότητας μαγνησίτη, φυσικού πηλού καθώς και τέφρας πυθμένα και ερυθράς ιλύος, προϊόντα γνωστά για τις δυσμενείς περιβαλλοντικές επιπτώσεις τους. Έπειτα από δοκιμή ποικίλων συνταγών, συμπεράναμε ότι προσθήκη 5% καυστικής μαγνησίας στο κεραμικό προϊόν βελτιώνει τις μηχανικές επιδόσεις του. Αυτό αποδίδεται στο γεγονός ότι το περίκλαστο της καυστικής μαγνησίας σχηματίζει «λαιμούς», οι οποίοι ισχυροποιούν τους δεσμούς στη μικροδομή του κεραμικού, σε συνδυασμό με τον ταυτόχρονο σχηματισμό μικρών ποσοτήτων άμορφου υλικού και την ομοιογενή κατανομή των πόρων, που δημιουργούνται κατά την όπτηση. Με συνδυαστική μελέτη Περιθλασιμετρίας Ακτίνων Χ και Σαρωτικού Ηλεκτρονικού Μικροσκοπίου του

κεραμικού υποδείχτηκε η παρουσία αναλλοίωτων φάσεων, προερχόμενων από τις πρώτες ύλες, καθώς και νεοσχηματισμένων κρυστάλλων αλβίτη και μαγνησιοφερρίτη. Τα αποτελέσματα της παρούσας μελέτης δείχνουν ότι η χρήση παραπροϊόντων μπορεί να είναι σημαντική και περιβαλλοντικά φιλική στην παραγωγή φτηνών δομικών κεραμικών.

Λέξεις κλειδιά: κεραμικά, καυστική μαγνησία, παραπροϊόντα, ερυθρά ιλύς, τέφρα πυθμένα.

1. Introduction

Pure magnesite has restricted industrial applications, mainly used as fertilizer, filler in rubber materials or plastics, paints and colour industries, comprising also a cheap source of MgO (Harben, 2002; Sikalidis *et al.*, 2003). Its basic features are its white colour and its relatively low hardness. Caustic magnesia and dead burned magnesia are produced from pure magnesite after heating at 1000°C and $1800 - 2000^{o}$C, respectively. Caustic magnesia has plenty of industrial applications, such as catalyst and pharmaceutical products (Harben, 2002) whereas dead burned magnesia is used as raw material in the production of basic refractories.

This study aims in synthesizing and characterizing a new, low-cost, ceramic material, using natural silt, bottom ash and red mud, as well as caustic magnesia, produced from pure Greek magnesite, as additive. Adopting usage of such materials will contribute to reduction of waste products, as they can be used in environmental-friendly, large-scale production of ceramic products.

2. Materials and Methods

2.1. Analytical Methods

Whole-rock geochemical analyses of magnesite were performed at Acme Analytical Laboratories LTD., Vancouver, Canada, by ICP-emission spectrometry following a Lithium metaborate/tetraborate fusion and dilute nitric digestion. Loss on ignition (LOI) was calculated by weight difference after ignition at 1000°C. The detection limit for major elements was 0.01%. The analytical precision calculated from replicate analyses was better than 5% for most elements. Scanning Electron Microscopy (SEM) was carried out at the Laboratory of Electron Microscopy and Microanalysis, University of Patras, using a JEOL JSM-6300 SEM equipped with EDS and WDS. Operating conditions were accelerating voltage 15 kV and beam current 3.3 nA with 4 μm diameter beam. EDS and WDS spectrum information with the ZAF correction software information was used. X-ray diffractometry (XRD), performed at the Research Laboratory of Minerals and Rocks, Department of Geology, University of Patras, using a BRUKER D8 ADVANCE diffractometer. Diffraction patterns were measured in 2θ range of $2 - 70^{o}$, using CuKα radiation of 40 kV and 40 mA, with 0.3 s step time/0.015^{o} step. Qualitative analysis was performed by the DIFFRACplus EVA® software (Bruker-AXS) based on the ICDD Powder Diffraction File. Differential Scanning Calorimetry (Netzsch STA 449 F3) was employed in order to obtain the transition temperature of magnesite to periclase. DSC was performed at the Department of Chemical Engineering, University of Patras, using a Du Pond 910 calorimeter equipped with a 99 thermal analyzer. The instrument was calibrated with a sapphire (Al_2O_3) standard. The sample was heated up to 1400°C, at a heating range of 10°C/min.

2.2. Raw Materials

2.2.1. Magnesite

Magnesite samples were collected from a mining industry quarry in the Gerakini area, Chalkidiki peninsula, north Greece. The magnesite has a cryptocrystalline structure (crystal size below 10 μm), hence no particles are discernible even under a microscope. Whole-rock geochemical

analysis revealed that the samples are highly pure magnesites, containing only low amounts of SiO_2 and CaO impurities (Table 1). The predominance of magnesite in the collected samples is also indicated in XRD patterns (Figure 1).

Table 1 - Chemical composition of the magnesite used in the laboratory production of caustic magnesia and of raw materials used as additives in the production of ceramic tiles (-: below detection limit; nd: not determined).

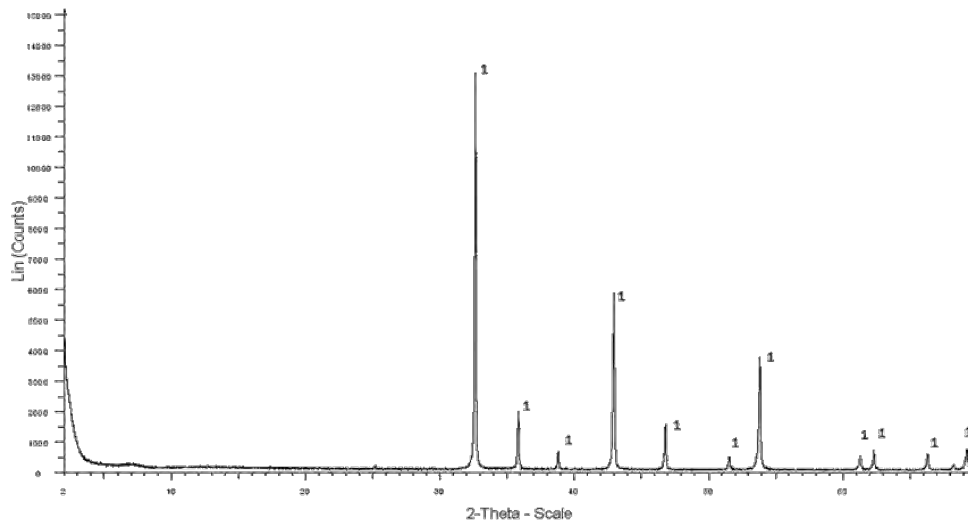|	*Magnesite*	*Natural silt*	*Bottom ash*	*Red mud*
Major oxides wt.%				
SiO_2	1.64	48.29	44.60	7.79
TiO_2	-	-	-	5.17
Al_2O_3		13.61	19.93	17.04
Fe_2O_3		5.30	6.28	44.34
MnO	-	-	-	-
MgO	43.13	3.11	1.43	0.57
CaO	0.46	12.72	7.51	11.64
Na_2O	-	0.59	-	3.17
K_2O	-	2.49	0.75	0.07
Cr_2O_3	-	-	-	-
SO_3	nd	nd	1.22	nd
C	nd	nd	10.10	nd
L.O.I	50.80	13.64	nd	9.77
Total	96.03	99.75	91.82	99.56

Figure 1 - XRD pattern of a highly pure cryptocrystalline magnesite (1) sample.

2.2.2. Production of Caustic Magnesia

Experimental thermal treatment of magnesite revealed that its decomposition to periclase and CO_2 starts at around 500°C and completes at 700°C, as it is indicated in a DSC thermogram (Figure 2).

There is a considerable mass loss of about 52%, plausibly due to escape of CO_2, and the decomposition of magnesite is a strongly endothermic event, which may be described by the reaction: $MgCO_3 \rightarrow MgO + CO_{2(g)}$. During this experiment, the sample was heated up to $1400^{o}C$ but no other alteration was observed beyond $700^{o}C$.

The production of the caustic magnesia took place in the laboratory, after heating treatment of the magnesite at $1000^{o}C$ for 4 hours, in an electric furnace. Crystalline periclase has been detected in the produced caustic magnesia by X-ray diffraction analysis (Figure 3). Magnesite was fully decomposed to periclase and CO_2, as it is suggested from the geochemical analysis of the caustic magnesia product that yielded MgO content above 94% wt. % (not shown). Traces of forsterite appear as a new phase in the caustic magnesia, as it is indicated by a small peak in the XRD pattern (Figure 3). It is interpreted that the forsterite was formed, during thermal treatment, from the reaction of magnesite or/and of magnesia with the impurities of silica.
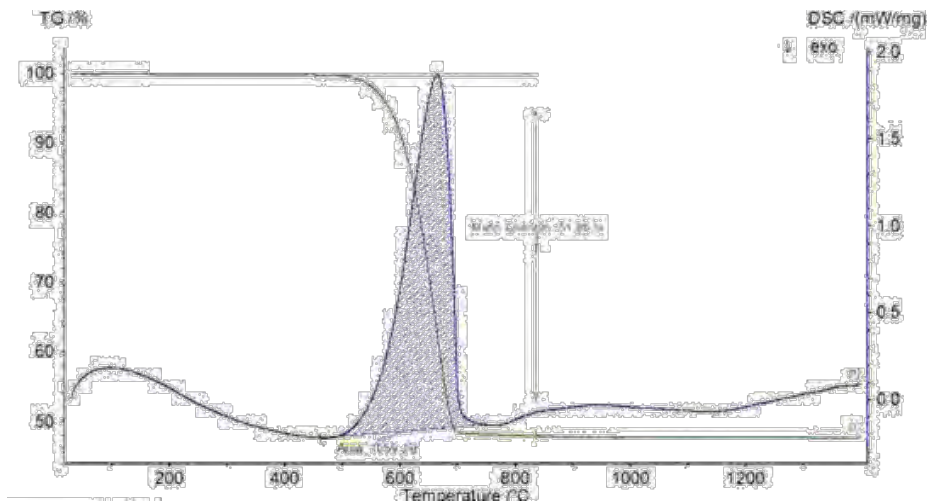

Figure 2 - DSC thermogram of the decomposition of natural magnesite from Gerakini to periclase and CO_2; the green line indicates mass change whereas the blue line shows the endothermic breakdown of magnesite at a temperature range between 500 and 700°C.
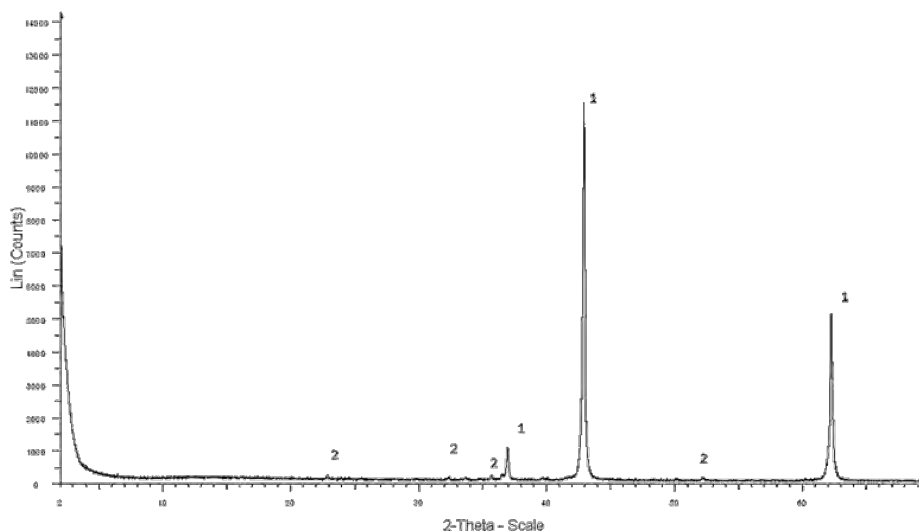

Figure 3 - XRD pattern of caustic magnesia produced after thermal treatment (1000 ^{o}C) of pure natural magnesite (1: periclase, 2: forsterite).

2.2.3. Other Raw Materials

Raw materials that were additionally used in order to synthesize various ceramic tiles include natural silt, used for industrial purposes, bottom ash by-product, derived from a lignite Power Plant, Megalopolis, N. Greece, as well as red mud, derived from waste deposits of aluminium production in central Greece. Chemical analyses of these materials were performed by Pontikes (2007) and Anagnostopoulos (2009) and their average compositions are listed in Table 1. Both bottom ash and red mud are generally thought to cause severe environmental problems (Georgakopoulos *et al.*, 1992, 2002; Varnavas and Achilleopoulos, 1995; Liu *et al.*, 2007, 2011; Izquierdo *et al.*, 2011).

2.2.4. Synthesis of the Ceramic Material

After testing several mixtures of the aforementioned raw materials, we found that the best performance was obtained by the ceramic recipe which included 70% silt (grain diameter < 30μm), 20% bottom ash (grain diameter < 30μm), 5% red mud (grain diameter < 40μm) and 5% caustic magnesia (grain diameter < 30μm). All materials were pulverized in a laboratory mill and subsequently the various mixtures were shaped under a load of 220 MPa. The pressed samples were dried initially at room temperature for 24 h and then in a drying oven at $110^{o}C$ till constant weight. Sintering was performed in a laboratory muffle furnace at $1000^{o}C$ following the industrial thermal cycle of ceramic products. The whole heating and cooling procedure lasted 36 h and conducted in the Department of Chemical Engineering, University of Patras.

3. Chemical Characterization of the new Ceramic Material

The geochemical composition of the ceramic product was calculated according to the percentage of its constituent raw materials. Plot of the calculated composition on a SiO_2-Al_2O_3-$(TiO_2+Fe_2O_3+MgO+CaO+Na_2O+K_2O)$ diagram shows that this new product can be classified, according to its chemical affinities, as a high porosity ceramic material similar to majolica or cottoforte type (Figure 4).
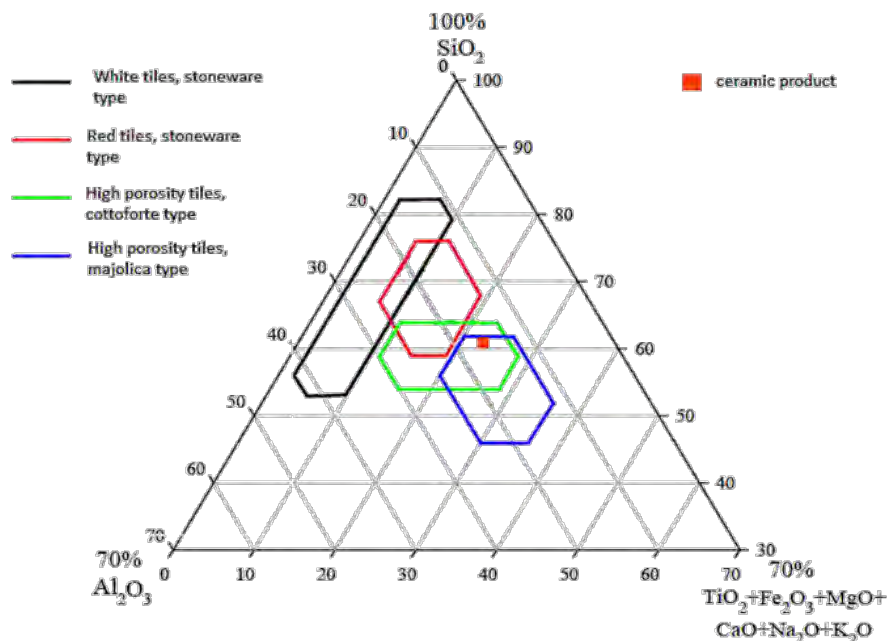

Figure 4 - Ternary SiO_2-Al_2O_3-$(TiO_2+Fe_2O_3+MgO+CaO+Na_2O+K_2O)$ diagram for high porosity ceramics based on industrial uses (fields after Sandrolini and Palmonari, 1974).

4. Mineral Composition and Microstructure of the New Ceramic Product

The mineralogical composition of the new ceramic product was obtained using combined XRD and SEM/EDS analyses. Microstructure observations, with particular emphasis on the impact of the caustic magnesia as additive, were also undertaken by means of SEM. The observed mineral phases in the ceramic matrix include quartz, hematite, gypsum, periclase, albite and magnesioferrite surrounded mostly by a pelitic matrix (Figure 5, 6a). In places, amorphous (glassy) material of Ca-Al-Si, Fe-Al-Si and Ca-Si compositions surrounds the grains filling their interstices (Figure 6b, c). Numerous pores, up to 0.5 mm, are rather homogeneously distributed both in the pelitic groundmass, as intergranular porosity, and in the glassy matrix (Figure 6d, e). Notably, periclase crystals show characteristic "neck" formations around its rims (Figure 6f).
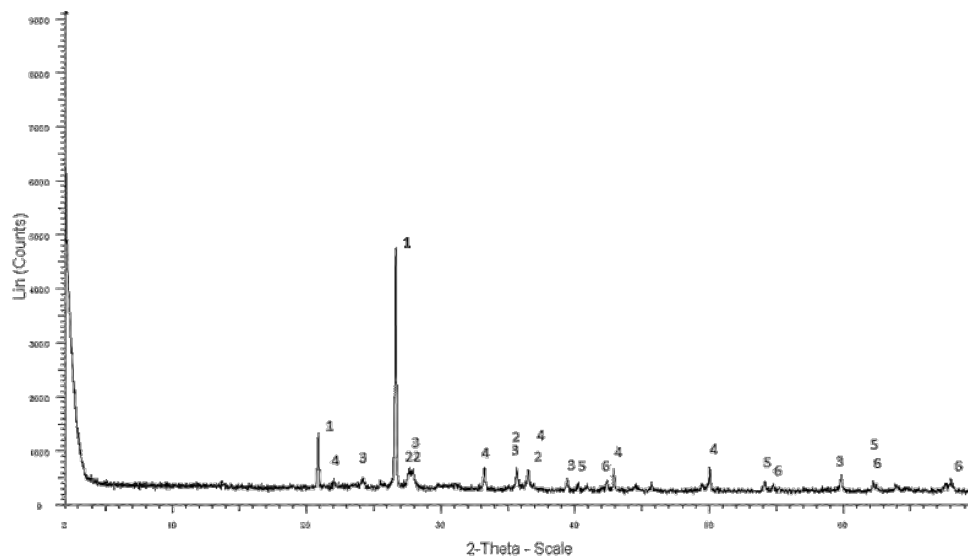

Figure 5 - XRD pattern of the new ceramic sample (1: quartz, 2: albite, 3: periclase, 4: hematite, 5: gypsum, 6: magnesioferrite).

5. Physicomechanical Properties

Psysicomechanical properties of the ceramic product were conducted according to ASTM C373-88 directions. Shrinkage and mass loss during firing, as well as density, open porosity, water absorption and bending strength of the ceramic were measured for its characterization (Table 2). The obtained values are in the range of similar products, which have been created in laboratory or in industry (e.g. Anagnostopoulos, 2009).

Table 2 - Physicomechanical properties of the new ceramic product.

Shrinkage (%)	Mass loss (%)	Density (g/cm^3)	Water absorption (%)	Open porosity (%)	Bending strength MPa
7.20	9.12	1.83	16.20	30.64	8.01

6. Discussion

He *et al*. (2012) and Zhao *et al*. (2010) have suggested the usage of red mud for high porosity ceramics due to the fact that it results in the increase of density of the ceramic products. Additionally, bottom ash is considered as a perfect raw material for ceramics due to its high carbon content (Porreca *et al*., 2007, Hu *et al*., 2008), and because it increases the bending strength between the particles (Schabbach *et al*., 2012).
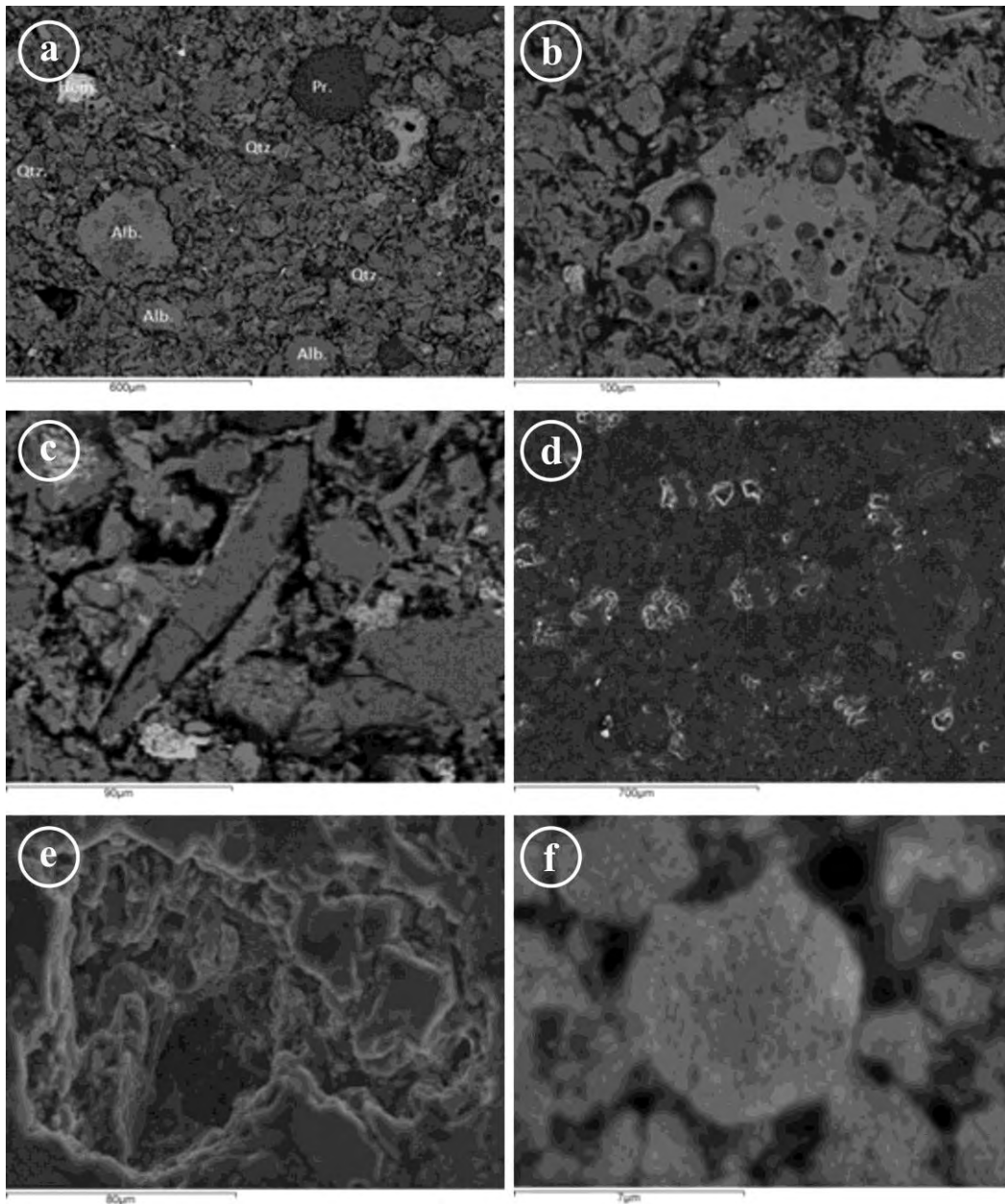
Figure 6 - Backscattered (BSE) and secondary electron (SE) images illustrating the main textural characteristics of the produced ceramic material: (a) coexisting unreactive and new phases (BSE); (b) development of Ca-Al-Si-rich amorphous phase (centre of the image) due to melting and vesicles formation possibly due to gas escape (BSE); (c) elongated quartz grain surrounded by a Ca-Al-Si-rich amorphous phase (BSE); (d) open porosity of the ceramic product (SE); (e) pore walls details (SE); (f) neck development among periclase crystals after firing of the ceramic (BSE) (Qtz.: quartz, Pr.: periclase, Alb.: Albite, Hem.: Hematite).

The desirable cohesiveness of the new ceramic product was achieved using as eutectic phases the red mud, bottom ash and natural silt. The research of the new ceramic took place among several mixtures and as a result we observed that 5% of caustic magnesia in the initial mixture improved

the properties of the ceramics, while adding more than 10% resulted in failure of the final product. The quality of the magnesite is crucial in producing high quality caustic magnesia, free of impurities. The Gerakini magnesite is an excellent raw material for this purpose.

The mineral chemistry of the new ceramic product includes unreactive phases that have been retained in the new product from the raw materials, as well as newly formed phases (Figures 5 and 6a). Albite and magnesioferrite comprise the newly-formed minerals, whereas very fine-grained quartz, hematite and gyspum are dispersed throughout the ceramic matrix or form aggregates in it and are considered as unaltered phases that were contained in the bottom ash and the red mud; periclase derived from the caustic magnesia additive. The improvement of the ceramic performance by addition of small amounts of caustic magnesia is attributed to the formation of "necks" around the rims of the unreactive periclase after further thermal treatment. This textural formation results in an interconnecting crystal framework, likely enhancing the cohesiveness of the product (Figure 6f). In addition to this, the occurrence of the amorphous phases contributed to bonding and partial cementation of the ceramic matrix (Figure 6b, c). Their chemical composition strongly suggests their derivation from partial melting of the eutectic phases occurring in the raw materials (silt, red mud and bottom ash).

Overall the obtained values of the physicomechanical properties of the ceramic that produced in our Laboratory indicate its good mechanical performance, suggesting also its effective in-service behaviour. Its high open porosity value (Table 2) is attributed to gas volatilization and to incomplete solid reactions and melting during the heating treatment. The observed homogeneous pore distribution, rather than an irregular segregation of pores that would result in localized areas of weakness, is another factor for the enhancement of the ceramic properties (Figure 6d, e). This, along with its rather high water absorption value do not negatively affect the mechanical properties of the material as it also yielded high bending strength value.

7. Conclusions

A new, low-cost, in-house, high porosity ceramic material was produced by mixing pure caustic magnesia and natural silt with bottom ash and red mud, which are commonly considered as environmentally hazardous industrial by-products. Caustic magnesia of high purity was synthesized after thermal treatment of a Greek magnesite. Testing various mixtures with caustic magnesia, we found that addition of 5% caustic magnesia positively affected the physicomechanical properties of the final product, while other mixtures gave products of inferior quality or unsuccessful. Necks developed on periclase during its formation after thermal treatment for producing caustic magnesia seem to promote significantly bonding of the ceramic microstructure. The mechanical performance of the final product is further enhanced by the sporadic presence of amorphous material and the homogeneous distribution of pores, developed during thermal treatment. Quartz, hematite and periclase remained as unreactive minerals inside the new ceramic microstructure, while albite and magnesioferite are formed during firing.

Utilization of environmental hazardous by-products and limitation of energy consumption during production of the final product are suggested for ceramics production. The recommended recipe for the ceramic produced in this study, at a laboratory scale, is suggested to be tested in an industrial scale production, in order its benefits to the environment, as well as to the building materials industry to be evaluated.

8. Acknowledgements

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