SINTEZĂ OPTIMIZATĂ A MATERIALELOR CERAMICE DE CONSTRUCȚIE UTILIZÂND CA ADAOS CENUŞĂ ZBURĂTOARE CU CONȚINUT MARE DE CALCIU
OPTIMIZED SYNTHESIS OF CONSTRUCTION CERAMIC MATERIALS USING HIGH-Ca FLY ASH AS ADMIXTURE

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The utilization of huge amounts of coal/lignite fly ash as efficient secondary resources for substituting standard clays in the manufacturing of value-added construction ceramic products is of increasing importance. Fly ash, composed of silica, alumina and other useful oxides, represents an attractive starting material for ceramics, and also the hollow spheres it contains can promote pore-forming for improving thermal insulation and facilitating thorough firing to attain energy savings. Use of ash will contribute to production cost alleviations and environmental protection with natural resources conservation, turning waste from one industry into useful feedstock for another one, which is strongly endorsed by current environmental policies. In the present work, the valorization of lignite high-Ca fly ash in the optimized synthesis of building bricks is investigated. Brick specimens were formed from various clay/ash mixtures by extrusion and firing (850, 950, 1050 and 1150^{o}C). The ceramic microstructures obtained were examined by XRD and SEM-EDAX, and also shrinkage, density, water absorption capacity, open porosity, thermal conductivity and strength before and after frost resistance testing were determined. According to the results, rich-in-Ca fly ash can efficiently be used as admixture into construction ceramics, as the mechanical performance does not significantly deteriorates by the embodiment of low ash percentages in the bulk of ceramics, whereas the thermal conductivity decreases indicating a potential significant gain in thermal insulation capability. Besides, the thermal conductivity also decreases with decreasing the sintering temperature from 1050^{o}C down to 850^{o}C, while the other properties remain practically unaffected, and therefore the optimum firing conditions could be lowered in a full scale operation of potential commercial interest to achieve energy savings.

Keywords: *High-Ca fly ash, admixture, construction ceramics, microstructure, thermal conductivity, physico-mechanical properties.*

1. Introduction

Only limited quantities of coal/lignite fly ashes, and especially of Class-C fly ash (rich-in-Ca), are currently recycled in cement industry as cement additive and for production of ready mixed concrete [1,2]. The development of alternative applications is therefore needed and several studies are reported in the last years concerning the beneficial utilization of this industrial solid by-product into value-added materials [3-7].

In particular, significant benefits from improved resource efficiency can be obtained by the substitution of clayey raw materials for fly ash in the production of traditional ceramics, such as construction bricks. Actually, fly ash contains useful oxides, mainly including silica and alumina, and therefore it can be considered as a material resource for ceramic manufacturing [8,9]. Cost savings could be attained due to the recycling of an industrial by-product as a secondary raw material, this also being helpful for solving problems associated with the environmental impact upon disposal of huge quantities of ash. The valorization of a solid waste should be emphasized, as the production of greener and sustainable building materials represents an increasingly urgent priority. Moreover, fly ash is mainly composed of hollow spheres that can promote pore-forming in the bulk of bricks both for facilitating thorough firing to attain energy savings and improving thermal insulation. Particularly in case of Class-C fly ash, pyritic S can also be captured from clays, thus reducing air pollution, but, on the other hand, Ca oxides and sulphates can form chalky deposits on the fired brick called as "scumming".

Especially, the use of fly ash in the bulk of insulating bricks or even in low thermal conductivity porous coatings is currently of increasing interest [10-12]. So far, the embodiment of many different industrial and agricultural waste by-products as pore formers has been investigated, including the partial replacement of clay with marble processing residue, bauxite, spent earth from biodiesel filtration and glycerine, recycled paper processing residues etc. [13-19]. Actually, thermal conductivity

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of construction materials is an increasingly important parameter that significantly influences the energy associated with heating and cooling in buildings [20], which is important especially in hot and cold countries. Particularly, use of ceramics as thermal insulating materials is one of their main applications. Consequently, recent trends in the brick manufacturing industry show an increase in the use of thermal insulation bricks [21-24].

In the current application, the incorporation of Class-C (high-Ca) lignite fly ash (from region of Western Macedonia, Northern Greece power units) into clay bricks is thoroughly investigated. Emphasis is placed on the improvement of the thermal insulating properties of clay bricks without significantly compromising their mechanical performance. Moreover, the firing conditions are optimized to achieve energy savings.

2. Experimental

2.1. Materials

Representative clay mixtures used by the ceramic industry were selected as raw materials base. The fly ash utilized was derived from a lignite power unit situated in Northern Greece, Western Macedonia region, Ptolemais site.

The chemical composition (Spectro X-Lab 2000 Energy Dispersive X-ray Fluorescence spectrometer) of the clays as well as of the fly ash, is shown in Table 1. This ash is highly-calcareous (26.02% CaO), categorized as class-C fly ash, while the clay samples contain lower amounts of CaO (3.50-11.82%). Additionally, clay samples do not contain any S, while fly ash contains significant amounts of S (7.30%).

Table 1

Chemical composition (wt.%) of the clayey raw materials (Clay 1-3 & Fly Ash) (XRF-analysis)

Oxides	Clay 1	Clay 2	Clay 3	FA
SiO_2	46.88	52.64	47.67	36.62
Fe_2O_3	5.61	5.22	3.82	5.55
Al_2O_3	17.98	19.05	9.55	17.38
TiO_2	0.72	0.68	0.43	0.29
CaO	7.53	3.51	11.82	26.02
MgO	8.15	5.91	8.39	3.92
SO_3	0.01	0.00	0.00	7.30
P_2O_5	0,14	0.18	0.98	0.22
Na_2O	1.75	2.45	2.03	0.77
K_2O	3.15	3.65	1.36	1.19
LOI	7.5	6.4	12.8	0.5

The main mineralogical phases (Figure 1) identified (Siemens D-500 X-Ray Diffraction spectrometer) in the ash are quartz (SiO_2), gehlenite ($Ca_2Al_2SiO_7$), anhydrite ($CaSO_4$) and lime. Albite ($NaAlSi_3O_8$), enstantite ($(Mg,Fe)SiO_3$) and illite are found in the clays.

2.2. Brick specimen fabrication

Various clay/0-9 wt.% fly ash mixtures were prepared, kneaded with water in appropriate proportions to form a proper plastic mass and shaped into 80X43,5X18 mm rectangular specimens by plastic extrusion employing a pilot-plant simulation of industrial brick manufacturing processes (Figure 2), involving a vacuum extruder provided with manual cutter [25,26].

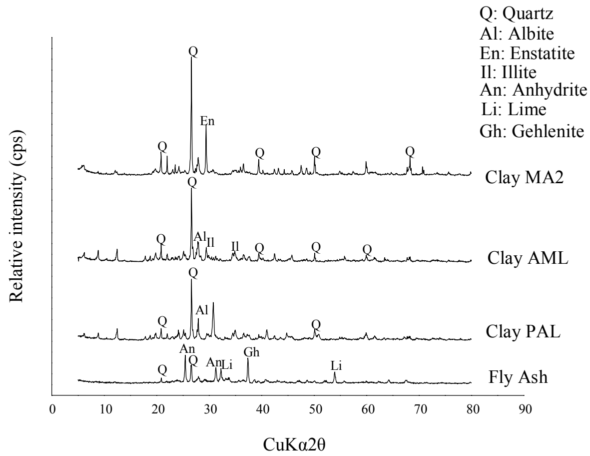


Fig. 1 - XRD patterns of the raw materials.

The extruded green specimens (Figure 3) were weighed for moisture determination and then exposed to natural drying for 12 h and then to forced drying (at 110^{o}C) until reaching a constant weight.

The dried test pieces were fired following a protocol of gradual temperature increase up to a peak temperature in a programmable electric chamber furnace for only 15 min in order to minimize the energy consumption. The maximum sintering temperatures considered were of 850, 950, 1050 and 1150^{o}C.

2.3. Brick specimen characterization

The *microstructure* of the fired specimens was characterized by X-ray Fluorescence, X-ray Diffraction and Scanning Electron Microscopy.

The determination of *physico-mechanical properties*, including water absorption capacity, flexural strength and also freeze/thaw resistance, was conducted on fired specimens according to the ASTM C67: Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile. Mean values are reported in the results.

The *flexural strength* was assessed by three-point bend testing using an automated Galdabini CTM/5 tester, and the modulus of rupture (M.O.R.) of the solid specimens was calculated from the following equation. Tests were performed on 30 specimens of each firing program.

$$\text{M.O.R.} = \frac{3Pl}{bd^2}$$

where P = the fracture load (MN),

l = half of the span between the supports of the bend ring (m),

b = the specimen width (m) and

d = the height (thickness) of the specimen (m).

For the *water absorption capacity* measurement, the fired samples were weighed before and after immersion in water for 24 h.

One of the criteria of ceramics quality is their low temperature stability. The *frost resistance* of the brick specimens produced was examined by freezing/thawing procedure (25 cycles) with the following steps:

a. water immersion at room temperature for 72 h.
b. cooling to 0^oC in about 110 min.
c. stay at 0^oC for 1 h.
d. further cooling down to -15^oC and stay at that temperature for 1 h.
e. quick heating to room temperature and stay for 1 h at 25°C.

The *thermal conductivity coefficient (k)* of sintered specimens was determined at 25^oC (Anter Unitherm Model 2022) by applying the "guarded heat flow meter" method. The tests are in accordance with the ASTM E1530 Standard: Test Method for Evaluating the Resistance to Thermal Transmission of Thin Specimens of Materials by the Guarded Heat Flow Meter Technique. A sample of the material to be tested is held under a reproducible compressive load between two polished metal surfaces, each controlled at a different temperature. The lower contact surface is part of a calibrated heat flux transducer. As heat flows from the upper surface through the sample to the lower surface, an axial temperature gradient is established in the stack. By measuring the temperature difference across the sample (Tu-Tm) along with the output from the heat flux transducer (Q), thermal conductivity (k) of the sample can be determined when the thickness (d) is known.

3. Results and discussion

3.1. The effect of fly ash incorporation (wt.%)

The 100% clay bricks (0% ash) present a red-brown color after firing due to their iron oxides content. The increasing % addition of fly ash in the raw materials mixture leads to a gradual shift to more pale coloring. Usually, pale yellow or light brown color is obtained in the ceramic body when metakaolinite, mullite, melilites or pyroxenes are formed, especially in Ca-rich ceramic bodies such as these ones incorporating high-Ca fly ash in the raw materials.

The chemical composition of three brick specimen series, from clay mixtures containing 0, 6 or 9 wt.% fly ash respectively, fired at a typical sintering temperature of 1050^oC is given in Table 2. Apparently, all bricks compared have a generally similar chemical composition. Naturally, the % CaO content slightly increases with increasing the % incorporation of the calcareous fly ash, but values remain comparable.

Fortunately, no free lime - which could adversely affect the mechanical behavior and even cause cracks and fissures - was detected in bricks of all compositions examined, and brick surface was practically free of any chalky deposits of CaO.

Table 2

Chemical composition (wt.%) of the bricks as determined by XRF-analysis.

Oxides	Clay Brick 1 (0% fly ash)	Clay Brick 2 (5% fly ash)	Clay Brick 3 (9% fly ash)
SiO_2	46.88	52.64	47.67
Fe_2O_3	5.61	5.22	3.82
Al_2O_3	17.98	19.05	9.55
TiO_2	0.72	0.68	0.43
CaO	7.53	3.51	11.82
MgO	8.15	5.91	8.39
SO_3	0.01	0.00	0.00
P_2O_5	0,14	0.18	0.98
Na_2O	1.75	2.45	2.03
K_2O	3.15	3.65	1.36
LOI	7.5	6.4	12.8

Phase composition of clay bricks, presented in Figure 2, is not significantly modified when incorporating up to 5 wt.% fly ash. In fact, the same main mineralogical phases, namely quartz (SiO_2), albite ($NaAlSi_3O_8$), diopside ($Ca(Mg,Al)(Si,Al)_2O_6$), were revealed in the samples prepared without fly ash addition as well as in those with 5% fly ash. In the 9% fly ash content specimen in particular, additional mineralogical phases were identified, such as gehlenite ($Ca_2Al_2SiO_7$) and anorthoclase ($(Na,K)(Si_3Al)O_8$).

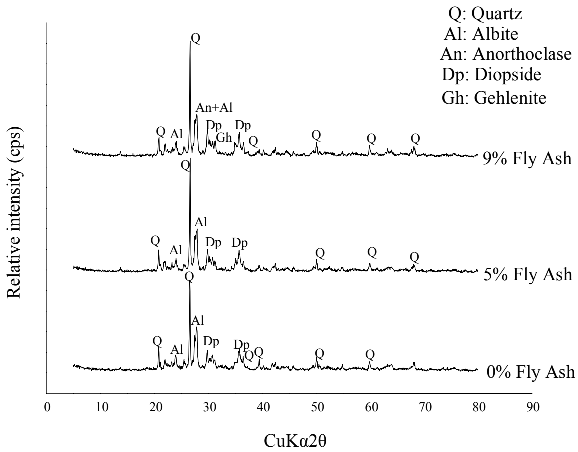


Fig 2 - XRD patterns of sintered bricks.

In following Figure 3, the experimental results for (a) thermal conductivity coefficient (k) at 25^oC, (b) water absorption (%) and (c) modulus of rupture of bricks sintered at 1050^oC are presented as a function of % fly ash addition in the clayey mixture.

Figure 3a shows that the thermal conductivity of clay bricks, and consequently the heat flow through the material, decreases almost linearly to the % fly ash content increase, specifically by approx. 20% for 6% fly ash addition and even by approx. 30% for 9% ash incorporation. To understand this behaviour, the

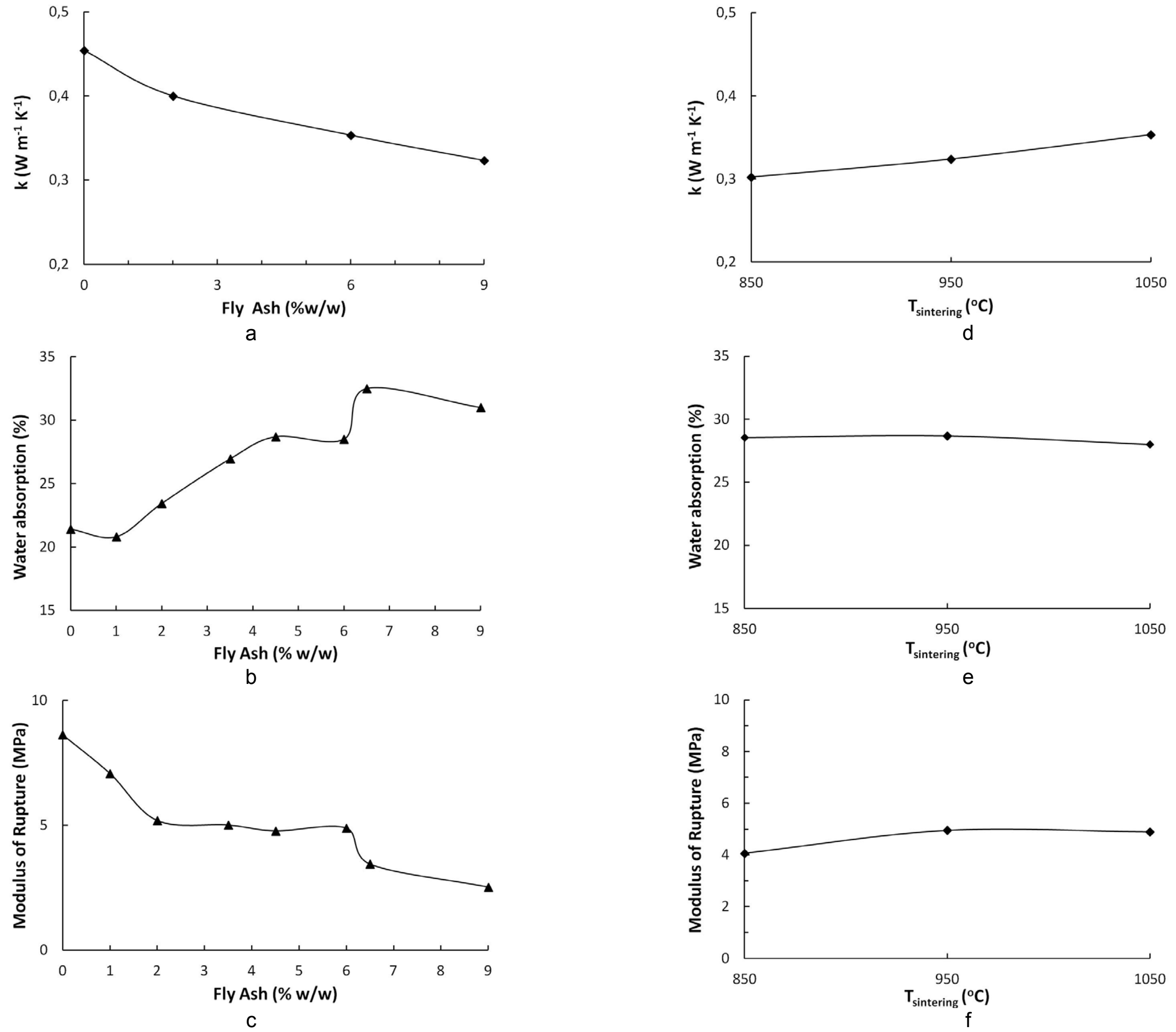


Fig. 3 - Thermal conductivity, water absorption and modulus of rupture: as a function of % fly ash content for clay bricks sintered at 1050°C (a, b & c, respectively), and as a function of sintering temperature for 6 % fly ash content bricks (d,e & f, respectively).

experimental results for water absorption capacity should be taken into consideration. Actually, water absorptivity is directly related to open porosity, an important factor influencing the thermal conductivity of a solid material. The pores tend to act as useful insulators, this decreasing the overall thermal conductivity of the bulk of the material. The results presented in Figure 3b for water absorption (%) versus % fly ash addition indicate an almost linear relationship between these two parameters, especially up to about 6% fly ash content, which can be attributed to an increasing formation of open pores. Further ash addition in the mixture (>6%) surprisingly leads to a slight drop in water absorption capacity, which may indicate that a more pronounced closed instead of open porosity would be created. It should be noticed here that thermal conductivity bricks does not only depend on open porosity, but also mineralogical composition and specific microstructural features may count. In particular, thermal conductivity of the crystalline phases identified in the sintered ceramic bodies can be different. Moreover, the type of porosity (open or closed), pore size distribution, pore interconnection are important, as closed and small pores are reported to contribute to a higher extent to increase brick thermal insulating properties.

The M.O.R. of bricks (Figure 3c) decreases, with the fly ash content increase up to 2%. The open pores and other microscopic imperfections probably act as stress concentrator notches resulting in strength reductions. Actually, materials strength strongly depends on porosity of the sintered body, although several other factors including grain size, inter-particle bonding necks, pore size distribution, pore shapes and flaws should be taken into consideration. For further fly ash addition up to 6%, almost constant strength values are obtained. Taking into account the finding that even higher % ash content strongly deteriorates the bending strength, it is concluded that mechanical behavior drawbacks can be tolerable for low ash addition up to about 6%. Hence, it is proved that fly ash acts as a pore-forming agent producing lighter materials with enhanced thermal insulation and acceptable strength up to an optimum 6% fly ash content in the clayey raw materials.

3.2. The effect of sintering temperature

The influence of firing temperature on (d) thermal conductivity, (e) water absorption capacity and (f) modulus of rupture of clay-based bricks incorporating 6% fly ash is shown in Figure 3d, 3e and 3f, respectively.

Figure 3d shows that the thermal conductivity increases by almost 17% as the sintering temperature is raised from 850°C up to 1050°C, reflecting a better densification degree and porosity reductions. Unfortunately, no measurement was taken for specimens fired at 1150°C, as it was not possible to machine the sintered materials to shape appropriate cylindrical samples for measurement, due to the elevated hardness (≈ 500 Hv) of the bricks produced at this temperature compared to that (≈ 25 Hv) of specimens fired at lower temperatures. Apparently, even higher thermal conductivities should be attended for these bricks sintered at 1150°C, given their superior densification and an elimination of porosity.

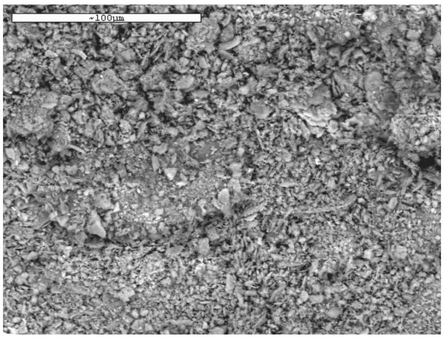
On the other hand, water absorptivity and bending strength (Figures 3e and 3f respectively) appear less influenced by the firing temperature variation. Consequently, lowering the sintering temperature at 850°C to achieve energy savings would be sufficient enough for the consolidation of clay-based bricks with enhanced thermal insulating behavior using fly ash as pore-forming agent, without compromising other critical properties of the materials.

Microstructural examination using SEM micrographs (Figure 4a, b, c and d) of clay bricks at the optimum 6 wt.% fly ash content, sintered at 850, 950, 1050 and 1150°C, respectively, confirms above stated densification improvements with firing temperature increase. Viscous flow, indicative of liquid phase sintering phenomena, is revealed particularly at 1150°C.

4. Conclusions

High-Ca fly ash from lignite combustion power station can be efficiently embodied in clayey raw materials for bricks manufacturing.

The thermal conductivity decreases with increasing the % ash content, indicating a potential significant gain in thermal insulation capability. Moreover, the thermal conductivity decreases with decreasing the sintering temperature from 1050°C down to 850°C, while the other properties remain



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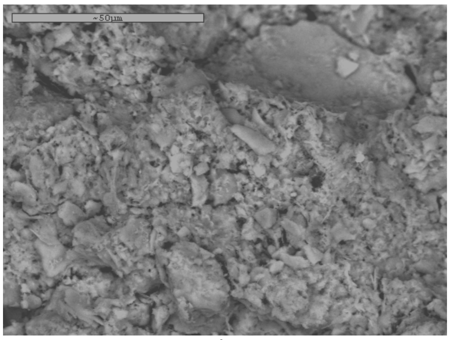

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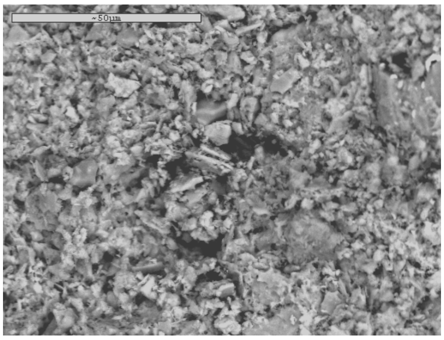

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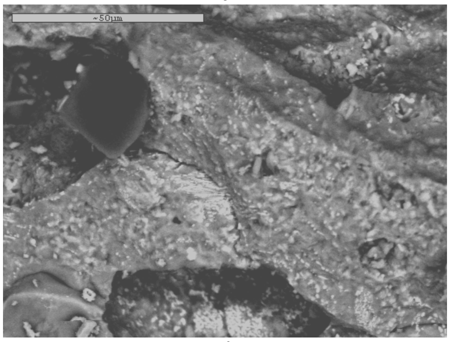

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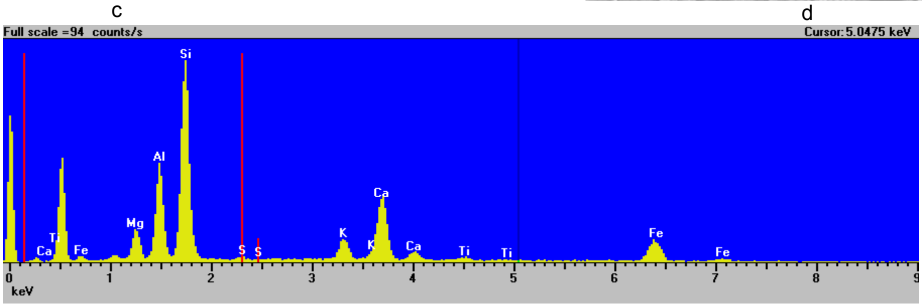

Fig. 4 - SEM micrographs of 6% fly ash content bricks sintered at 850 (a), 950 (b), 1050 (c) & 1150°C (d) and a representative EDAX spectrum (e).

practically unaffected, and therefore the optimum firing conditions could be lowered in a full scale operation of potential commercial interest to achieve energy savings.

The mechanical performance does not noticeably deteriorate by the incorporation of low ash percentages, up to an optimum of 6% ash, in the bulk of bricks.

Significant microstructural changes take place particularly at 1150^{o}C, suggesting further investigation in the 1050-1150^{o}C heating range, which would broaden the understanding of the sintering process of the clay/fly ash mixtures.

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