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EFFECT OF SINTERING CONDITIONS ON THE PRODUCTION OF CERAMICS FROM LIGNITE FLY AND BOTTOM ASHES

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ABSTRACT

The current study aims at the extension of field application of lignite combustion by-products due to their considerable silica and alumina content. Fly/bottom ash mixtures were prepared and Powder Metallurgy processing techniques were applied, and then their microstructure and physico-mechanical properties were studied, in order to assess whether the chemical, mineralogical and morphological characteristics of these ashes render them suitable starting materials for ceramics development. The role of silica, with its different mineralogical structures, is highlighted here, while the absence of gehlenite in the sintered materials leads to promising results concerning their strength.

Key words: Siliceous fly ash, bottom ash, sintering, ceramics

1. INTRODUCTION

The valorization of solid industrial by-products as secondary raw materials in the manufacturing of value-added products can contribute to environmental protection, resources conservation as well as cost reduction. Besides, current advances in environmental legislation encourage manufacturers to optimize industrial by-products management and utilization. In particular, the valorization of fly ash and bottom ash, which are produced in massive quantities from lignite combustion for power generation, is nowadays of increasing importance [1-9].

In order to extend the utilization of ashes, one possible application can be the synthesis of ceramics by employing sintering procedures. The large amounts of ceramics that are annually manufactured support this endeavor. So far, combustion ashes from various origins have mainly been considered for incorporation in the clayey raw materials for the production of extruded ceramics (bricks), but a certain incompatibility of the ashes with the clay mixtures, especially regarding a reduced plasticity at high levels of ash, has lead to extrusion difficulties, and therefore to limited use of ashes. Recently, research has been undertaken on the development of compacted ceramics starting 100% from various Class-F coal ashes and using sintering processes. It should be noted that solid-state sintering is a generally established manufacturing technique for industrial ceramics, tiles etc. [10-16]. Lignite combustion ashes in particular, also appear attractive candidate secondary materials for the development of sintered ceramics, given their oxide composition. Indeed, highly-calcareous (Class-C) lignite ashes from Northern Greece (region of West Macedonia) have been successfully tested by the authors for the development of sintered ceramics in previous work [17].

The current research aims at the extension of field application by studying the effect of sintering conditions on the production of ceramics from siliceous fly and bottom ashes and mixtures of them derived from the lignite-fed power station of Southern Greece (region of Peloponissos, Megalopolis area), where lignite resources reach 240 million tones and considerable amounts of ashes are annually produced. The chemical, mineralogical and morphological characteristics of the ashes under investigation provide sufficient motivation to promote processing of these siliceous ashes towards sintered ceramics synthesis. Specifically, the rich-in-Si ash composition, associated with the different structures that silica undertakes, as well as

the different Al- and Ca-based compounds of the Megalopolis ashes, can be expected to yield an interesting mineralogy in the sintered microstructures. Moreover, the intense content of siliceous ingredients, along with the presence of a glassy phase in these ashes, is also known to contribute to better pozzolanic properties.

2. EXPERIMENTAL

2.1. Raw materials

Megalopolis power station is fed with a high ash and high moisture lignite from the open cast mine next to the power station.

Megalopolis fly ash (FA) [18-22], obtained from the electrostatic precipitators, is strongly siliceous since almost half of it (51.26 %) consists of SiO_2. Lesser amounts of Ca-bearing species are present (11.82 wt.% CaO content including only a 0.95 wt.% of free CaO), and therefore FA is barely a Class-C ash (CaO being barely over 10 wt.%). The Si/Al ratio is 2.64 for this FA. Besides, it has a specific gravity of 2.50 g/cm^3, a specific area of 3.87 m^2/g, a mean pore diameter of 165.1 (Å) and a pore volume of 0.016 cm^3/g. A SEM micrograph of Megalopolis FA is provided in Fig. 1.

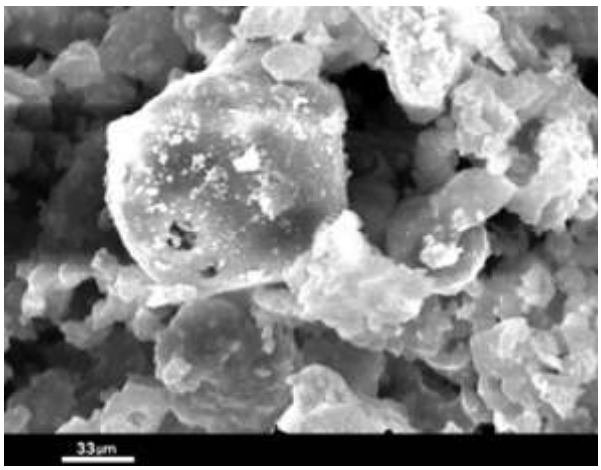

Fig. 1. SEM micrograph of Megalopolis FA.

The Megalopolis bottom ash (BA) used, a granular material much coarser than FA, also formed during lignite firing, was removed from the bottom of dry boilers of the same power plant.

2.2.Ash compaction and sintering

Simple and economic powder metallurgy techniques were applied for the compacts preparation including ash compaction and sintering.

In order to form 13 mm diameter disc-shaped green specimens, FA, BA and 50-50 wt% FA/BA mixtures were uniaxially cold pressed in a stainless steel die using a hydraulic press (SPECAC, 15011). Two alternative series of specimens were prepared: one using as-received BA and the other using BA that had been previously heated at 550 ^{o}C for 12 h for the complete burnout of the residual carbon. The specimen green density and strength were evaluated and the compaction pressure was optimized, so that the pressed compacts had sufficient green density and strength to ensure safe handling and subsequent submission to sintering.

The ash compacts obtained were thermally treated in a laboratory chamber programmable furnace (THERMOCONCEPT, KL06/13) from room temperature up to 1050 ^{o}C at the relatively slow heating rate of 10 ^{o}C/min to reduce abrupt thermal gradient that could possibly lead to process-induced stresses. Particularly the series of specimens prepared from as-received (un-processed) BA were intermediately held at 550 ^{o}C for 2 h to facilitate residual carbon burnout during sintering. Finally, all specimens were held at the maximum sintering temperature (1050 ^{o}C) for 2 h and then gradually cooled to ambient temperature. The sintering conditions applied were optimized on the basis of preliminary experimental trials. In particular, a tendency for superficial melting and shape distortion for all specimens that were sintered at 1150 ^{o}C for 2 h should be recorded.

3.3. Characterization of sintered ash compacts

Phase characterization of green and sintered specimens was realized by X-Ray Diffraction (XRD - Siemens, Diffractometer D-5000). The microstructures produced were studied using Scanning Electron Microscopy (SEM - Jeol, JSM-6400). Shrinkage of the samples was evaluated as the volume change (%) upon sintering.

3. RESULTS AND DISCUSSION

Photographs of representative sintered specimens of all compositions considered are presented in Figure 2.

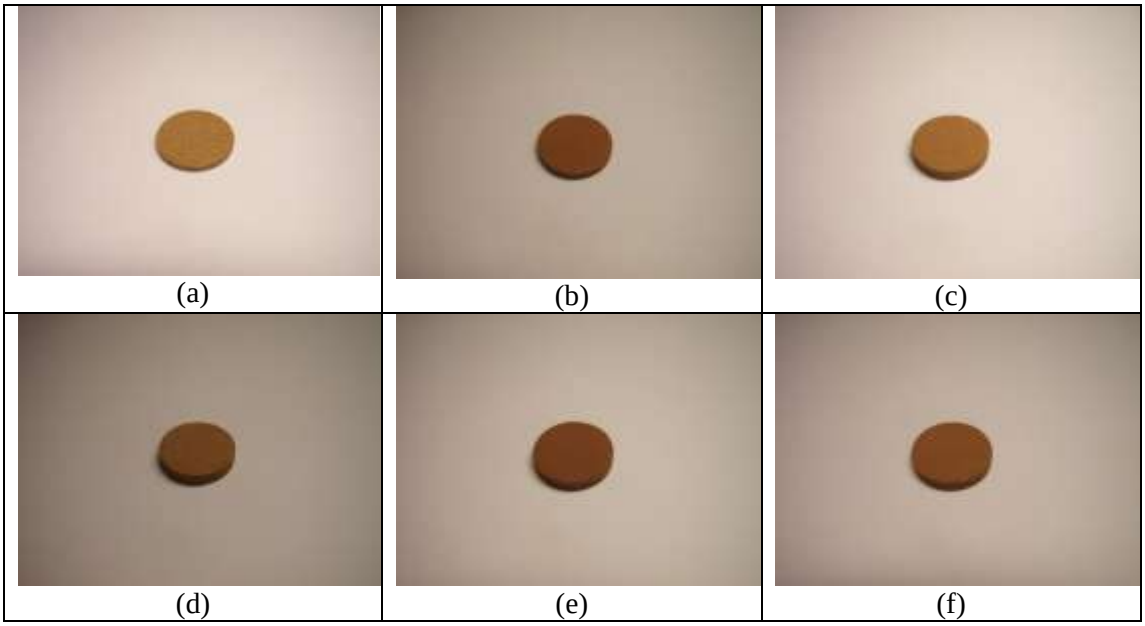

Fig. 2. Photographs of sintered specimens (diameter: 13 mm) made of: FA (a,d), BA (b) and 50-50 wt.% FA/BA mixture (c), from as-received BA, and BA (e) and 50-50 wt.% FA/BA mixture (f) from pre-processed (550 ^{o}C, 12 h) BA.

It can be seen from Figure 2 that the specimens of both series, of this one prepared from as-received BA and of that made from previously thermally treated BA (550 ^{o}C, 12 h, for the residual carbon burnout), are integral and yellowish brown. The color of the specimens made of BA and even of FA/BA mixture is slightly darker than that of the FA specimens. Apparently, successfully consolidated materials are obtained for all compositions at the sintering conditions selected. It results that the moderate heating rates that were employed should contribute to avoiding significant temperature gradients between the surface and the interior that could otherwise lead to process-induced stresses thus endangering the integrity of the sintered materials. This can be of importance especially for the production of large-size workpieces from low thermal conductivity raw materials such as fly ash, which is mainly consisted of hollow sphere-shaped particles.

Typical XRD spectra of green and sintered (1050 ^{o}C, 2 h) ash specimens are shown in Figure 3.

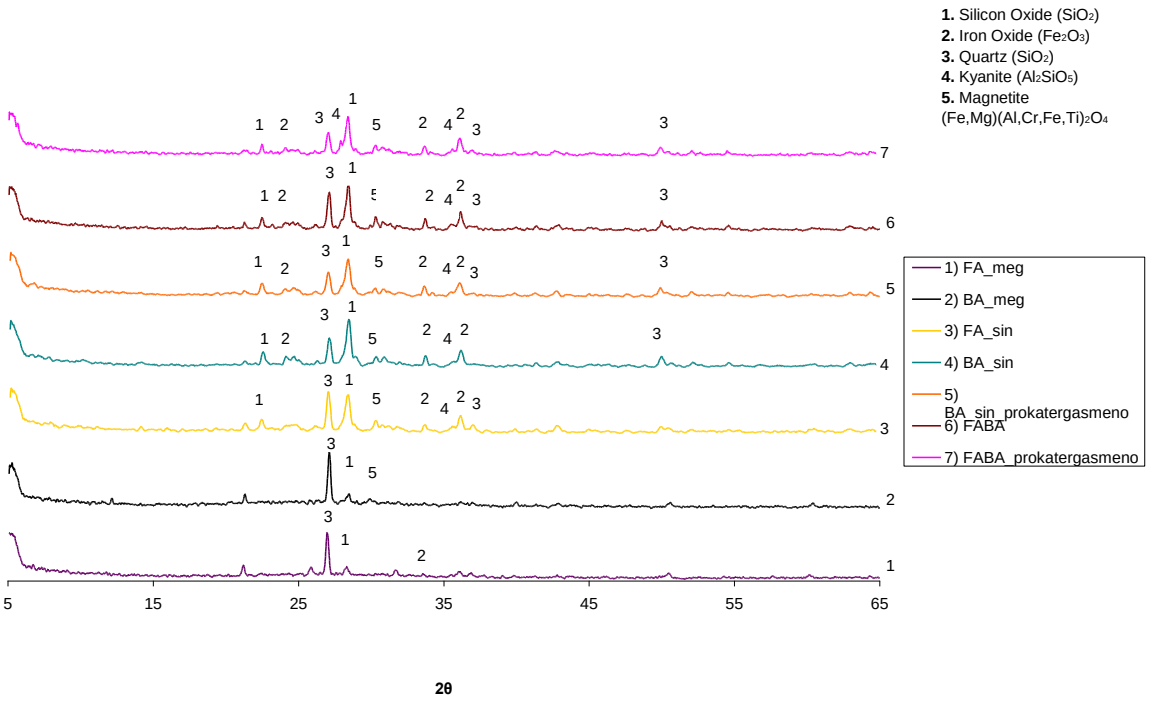

Fig. 3. Typical XRD spectra of green (1,2) and sintered (3,4,5,6,7) ash specimens.

From Figure 3, the ceramic crystalline phases that obviously predominate in all sintered materials are quartz and silicon oxide (SiO_2) due to the strongly siliceous character of the Megalopolis ashes used. These hard and crumble resistant minerals should contribute to the consolidation and quality of the obtained products. The iron oxide (Fe_2O_3) and magnetite that are also identified both in the ashes and in the sintered materials are attributed to a noticeable Fe content occurring in the lignite of this origin. No particular difference can be recorded between the specimens made of as-received BA and those of pre-processed BA. It should be emphasized that the absence of gehlenite that can be stated for all sintered materials leads to promising results concerning their strength.

SEM micrographs that are provided in Figure 4 reveal effectively densified and uniform microstructures, where a continuous network of characteristic solid-state sintering necks can be clearly seen. The surface of the sintered FA/BA mixtures prepared using as-received BA appears slightly more porous compared to this of the FA/BA specimens made of pre-processed BA, which should be due to carbon burnout during sintering in the first case. Residual porosity may also, to a certain degree, be

attributed to another form of pores, since fly ash contains not only solid but also hollow particles (cenosheres).

Certainly, porosity may be desirable to attain weight reduction of the final products as well as for specific applications. On the other hand, when better densification is demanded, the use of BA previously treated for the residual carbon burnout should be preferred. Moreover, Ca-bearing phases are mainly identified in some small white spots according to EDX analysis results (Figure 5).

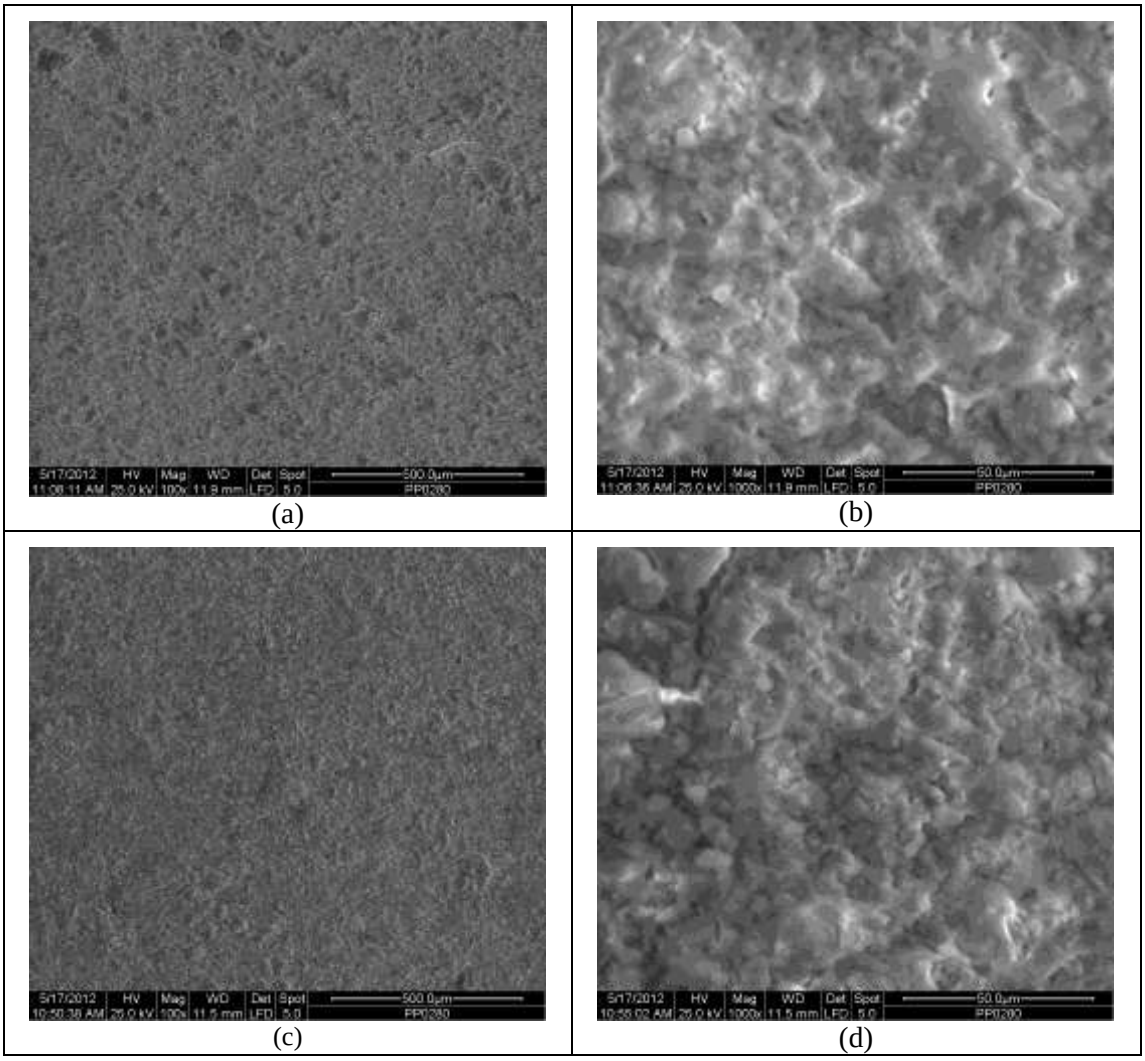

Fig. 4. SEM micrographs (at two magnifications) of sintered FA/BA specimens prepared using as- received BA (a,b) or pre-processed (550 ^{o}C, 12 h) BA (c,d).

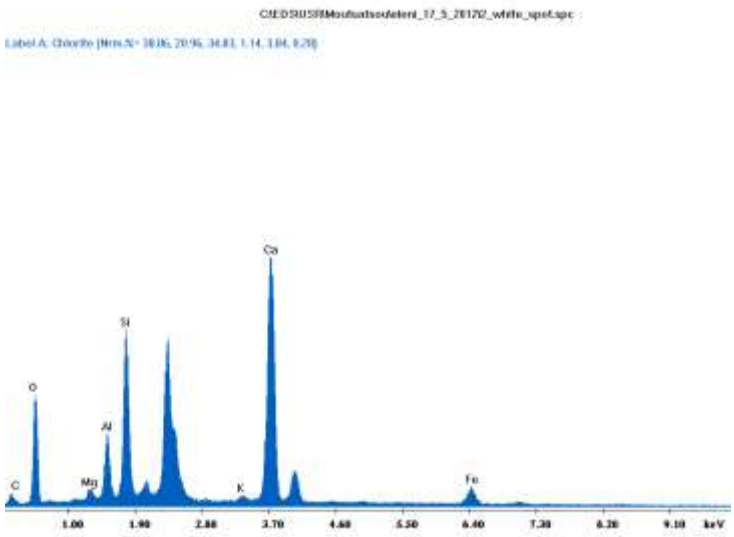

Fig. 5. EDX analysis particularly located on white spots.

4. CONCLUSIONS

Production of successfully solidified and uniform microstructures, mainly composed of siliceous ceramic phases, is achieved upon sintering FA, BA and FA/BA mixtures originated from Megalopolis power station. When higher densification is demanded, the use of BA previously treated for the residual carbon burnout should be preferred. The absence of gehlenite in the sintered materials leads to promising results concerning their strength.

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REFERENCES

[1] M. Ahmaruzzaman, A review on the utilization of fly ash, *Progress in Energy and Combustion Science*, 36, 2010, 327–363.

[2] E. Marin, M. Lekka, F. Andreatta, L. Fedrizzi, G. Itskos, A. Moutsatsou, N. Koukouzas and N. Kouloumbi, Electrochemical study of Aluminum-Fly Ash composites obtained by powder metallurgy, *Materials Characterization*, 69, 2012, 16-30.

[3] S.C. Kou and F. Xing, The effect of recycled glass powder and reject fly ash on the mechanical properties of fibre-reinforced ultrahigh performance concrete, *Advances in Materials Science and Engineering*, Article ID 263243, 2012, 8 pages.

[4] N. Koukouzas, C. Ketikidis, G. Itskos, X. Spiliotis, V. Karayannis and G. Papapolymerou, Synthesis of CFB-coal fly ash clay bricks and their characterization, *Waste and Biomass Valorization*, 2, 2011, 87–94.

[5] Ö.Ç. Sola, M. Yayla, B. Sayın and C. D. Atiş, The effects of different types of fly ash on the compressive strength properties of briquettes, *Advances in Materials Science and Engineering*, Article ID 430604, 2011, 6 pages.

[6] G. Itskos, N. Koukouzas, Ch. Vasilatos, I. Megremi and A. Moutsatsou, Comparative uptake study of toxic elements from aqueous media by the different particle-size-fractions of fly ash, *Journal of Hazardous Materials*, 183, 2010, 787–792.

[7] A. Karamberi, K. Orkopoulos, A. Moutsatsou, Synthesis of glass-ceramics using glass cullet and vitrified industrial by-products, *Journal of the European Ceramic Society*, 27 (2-3), 2007, 629–636.

[8] P. Asokana, M. Saxena, S.R. Asolekar, Coal combustion residues – environmental implications and recycling potentials, *Resources, Conservation and Recycling*, 43, 2005, 239–262.

[9] S. Tsimas and A. Moutsatsou-Tsima, High-calcium fly ash as the fourth constituent in concrete: problems, solutions and perspectives, *Cement and Concrete Composites*, 27 (2), 2005, 231–237.

[10] B. Kim and M. Prezzi M., Compaction characteristics and corrosivity of Indiana class-F fly and bottom ash mixtures, *Construction and Building Materials*, 22, 2008, 694–702.

[11] M. Erol, S. Küçükbayrak and A. Ersoy-Meriçboyu, Characterization of sintered coal fly ashes, *Fuel*, 87 (7), 2008, 1334–1340.

[12] N. Chandra, P. Sharma, G.L. Pashkov, E.N. Voskresenskaya, S.S. Amritphale and N.S. Baghel, Coal fly ash utilization: Low temperature sintering of wall tiles, *Waste Management*, 28 (10), 2008, 1993–2002.

[13] V. Adell, C.R. Cheeseman, M. Ferraris, M. Salvo, F. Smeacetto, A.R. Boccaccini, Characterising the sintering behaviour of pulverised fuel ash using heating stage microscopy, *Materials Characterization*, 58, 2007, 980–988.

[14] X.-J. Ren, X.-B. Zhang, G.-Y. Meng and X.-Q. Liu, Preparation and characterization of the porous ceramics from fly ash, *Journal of Coal Science and Engineering*, 13 (1), 2007, 95–98.

[15] X. Lingling, G. Wei, W. Tao and Y. Nanru, Study on fired bricks with replacing clay by fly ash in high volume ratio, *Construction and Building Materials*, 19, 2005, 243–247.

[16] E. Benavidez, C. Grasselli and N. Quaranta, Densification of ashes from a thermal power plant, *Ceramics International*, 29, 2003, 61–68.

[17] A. Moutsatsou, V. Karayannis, D. Matsas, E. Katsika and S. Tsipoura, Microstructure analysis of sintered lignite combustion ashes, in Proceedings of the 2nd International Congress on Ceramics – ICC2, Verona, Italy, 2008, 9 pages.

[18] G. Itskos, P.K. Rohatgi, A. Moutsatsou, J.D. DeFouw, N Koukouzas, Ch. Vasilatos and B.F. Schultz, Synthesis of A356 Al–high-Ca fly ash composites by pressure infiltration technique and their characterization, *Materials Characterization*, 47 (9), 2012, 4042-4052.

[19] M. Izquierdo, N. Koukouzas, S. Touliou, K. Panopoulos, X. Querol, and G. Itskos, Geochemical controls on leaching of lignite-fired combustion by-products from Greece, *Applied Geochemistry*, 26 (9-10), 2011, 1599–1606.

[20] A. Moutsatsou, G. Itskos, P. Vounatsos, N. Koukouzas and Ch. Vasilatos, Microstructural characterization of PM-Al and PM-Al/Si composites reinforced with lignite fly ash, *Materials Science and Engineering: A*, 527 (18-19), 2010, 4788–4795.

[21] O.K. Karakasi and A. Moutsatsou, Surface modification of high calcium fly ash for its application in oil spill clean up, Fuel, 89, 2010, 3966–3970.

[22] A. Moutsatsou, E. Stamatakis, K. Hatzitzotzia and V. Protonotarios, The utilization of Ca-rich and Ca–Si-rich fly ashes in zeolites production, *Fuel*, 85, 2006, 657–663.