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VALORISATION OF GREEK LIGNITE FLY ASH FOR THE SYNTHESIS OF DIFFERENT LOW COST ZEOLITES, SUITABLE FOR ENVIRONMENTAL AND AGRICULTURAL APPLICATIONS

C. Vasilatos[1*] , I. Mitsis[1] , M. Andreadi[1] , S. Giannatou[1] , V. Karayannis[2], N. Koukouzas[3] and M. Stamatakis[2]

[1] Department of Economic Geology and Geochemistry, Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens, Panepistiomiopolis, 15784, Athens, Greece.

[2] Department of Chemical Engineering, Faculty of Engineering, University of Western Macedonia, Kila, 50100, Kozani, Greece.

[3] Chemical Process and Energy Resources Institute, The Centre for Research and Technology, Hellas, 15125, Maroussi, Athens, Greece.

*Corresponding author: Email: vasilatos@geol.uoa.gr, Tel: +302107274664

Abstract

The aim of this study is to examine the effectiveness of low temperature alkaline hydrothermal treatment methods of Greek lignite fly ashes for the synthesis of specific zeolites suitable for environmental and agricultural applications. Relatively high silica fly ash samples from Meliti and Megalopoli Electric Power Stations, were tested as raw materials that underwent alkaline hydrothermal treatments by NaOH and KOH solutions, at about 100°C, with a constant ratio of raw material/alkaline solution 100gr/L. The applied techniques mainly aimed at the dissolution of Al-Si bearing phases of the fly ash and the subsequent precipitation of the zeolitic minerals. Both the initial materials and the final solid products were subjected to XRD and SEM study along with EPMA for the identification of their mineral phases. XRF was used for the determination of the materials' chemical changes after the thermal alkali digestion. Furthermore, the CEC values of the original and the treated materials were determined. An 1M NaOH activation solution was used to produce Na-P1 zeolite, a synthetic mineral with high ion exchange capacity, due to the substitution of Si(IV) by Al(III) in its structure, which results in an overall negative charge, leading to applications as ion exchange or molecular sieve. This zeolite has an affinity with some metal ions, generally found in acid mine drainage effluents, and may be used for remediation. As KOH solutions present lower conversion efficiency than the respective NaOH under the same temperature, the experimental conditions were modified and a 6N KOH solution as activation agent was used and the treatment period was extending to 72h and the K-bearing zeolite-F was synthesized. The Zeolite-F rich has a potential in soil

amendments and slow release fertilizers. Moreover, those treated fly ashes exhibit more than ten times higher CEC values than the initial materials due to the presence of the zeolites.
Keywords: Synthetic zeolites; fly ash; soil amendments; remediation

1 INTRODUCTION

The synthesis of zeolites is one of the potential applications of fly ash production to obtain high value industrial products with environmental technology utilization (Querol *et al.*, 2001). The synthesis of zeolite products from fly ash is analogous to the formation of natural zeolites from volcanic deposits or other high-Si-Al rocks, rich in amorphous phases, by the interaction of hot alkaline water on the glass fraction of the rocks. That zeolite development process may take thousands of years in order to form natural zeolites. In the laboratory, the process can be speeded up (to days or hours) for both volcanic and fly ash.

The application of zeolites as natural amendments for the remediation of polluted soils has been studied extensively during last years. Furthermore, zeolite applications in agriculture have been studied by many researchers Savvas *et al.* (e.g 2004) and Stamatakis *et al.* (2001, 2017). It has been referred that zeolites may be more suitable for rehabilitation of heavy metal-contaminated soils than other amendments, because they regulate soil pH value modestly and do not import any new pollutants (Castaldi and Santona, 2005). Many patents and technical articles have proposed different methods to synthesize different types of zeolites from fly ash. Most of these methodologies are based on the alkaline hydrothermal activation. Shigemato *et al.* (1993) optimized the direct conversion method by the introduction of a fusion step prior to synthesis. This fact permitted to obtain different types of zeolites with potential industrial application (such as Na-X zeolite). The direct conversion method was also applied by the use of dry conversion systems (Park *et al.*, 2000). Other studies on direct conversion allowed reducing the synthesis time (from hours to few minutes) by microwave assisted method (Querol *et al.*, 1997). However, the zeolitic products obtained by direct conversion have relatively low CEC values due mainly to incomplete conversion of the fly ash in zeolite. Hollman *et al.* (1999) had tested zeolite synthesis using SiO_2 extracts from FAs and obtained high purity zeolites ($> 95\%$ of A and X zeolite), and Moreno *et al.* (2002) optimized this method and synthesized minerals equivalent to zeolites obtained by direct conversion method. Alkaline fusion process was also tested and improved to obtain high porous size and CEC zeolitic material (Moreno *et al.*, 2001).

The effective and low cost products for soil amendments remains a challenging task for scientists. It is noted that the production and the transportation cost of ash-based zeolites is the main barrier to their industrial-scale synthesis and utilization for environmental and agricultural applications as vast quantities of fly ash have to be transported from the thermal power plant to the zeolitization plant. Furthermore, thermal power stations are not always ideally located to introduce a market-oriented product focusing on small-medium applications). Previous studies have demonstrated the utilization of lignite fly ash Na- bearing synthetic zeolitic materials for the removal of heavy metals from wastewater (e.g. Koukouzas *et al.*, 2010), for environmental applications Itskos *et al.* (2015) and as soil amendments in acid mining soils (Giannatou *et al.*, 2018, 2017). Since K is considered as a nutrient in agriculture (e.g. Stamatakis *et al.*, 2017), in the present study KOH was also used as an activation solution, in order to develop a K-rich synthetic zeolite suitable for utilization in agriculture.

The aim of this study is to examine the effectiveness of low temperature alkaline hydrothermal treatment methods of Greek lignite fly ashes for the synthesis of specific zeolites suitable for environmental and agricultural applications.

2 MATERIALS AND METHODS

The experimental work included zeolite synthesis from fly ash collected by two Hellenic thermal power stations, i.e. Megalopolis (850 MW) and Meliti (330 MW), in Southern and Northern Greece, respectively under maximum electricity load. Both plants are normally fed by the nearby lignite mines. For this scope, relatively high silica representative fly ash samples from Meliti (MEL-FA) and Megalopoli (MEG-FA) Electric Power Stations, were sampled and tested as raw materials for zeolite synthesis.

The applied techniques mainly aimed at the dissolution of Al-Si bearing phases of the fly ash and the subsequent precipitation of the zeolitic minerals. An 1M NaOH activation solution was used to produce synthetic zeolite The alkaline hydrothermal treatment, proposed by Koukouzas *et al.* (2010) and Itskos *et al.* (2015) took place at 90-100°C. In the present study, two interventions took place in the above method of zeolite synthesis: a) refilling with NaOH solution throughout the heating-stirring, so that the NaOH /fly ash ratio remained constant and b) increasing the heating-stirring period from 24 hours to 36 hours.

As KOH solutions present lower conversion efficiency than the respective NaOH under the same temperature, the experimental conditions were modified and a 6N KOH solution as activation agent was used and the treatment period was extending to 72h and the K-bearing zeolite-F was synthesized.

Both the initial materials and the final solid products, were subjected to X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) study along with electron microbe microanalysis [Energy Dispersive System (EDS)] for the identification of their mineral phases at the Laboratory of Economic Geology and Geochemistry, National and Kapodistrian University of Athens. The cation exchange capacity (CEC) of the original and the hydrothermally treated materials had been determined in the same Laboratory. Furthermore, X-ray fluorescence analysis for the determination of the materials' chemical changes after the thermal alkali digestion, has been carried out at the R& D Department of the Titan Cement Company.

3 RESULTS AND DISCUSSION

By the alkali hydrothermal treatment, the glass phase and the Al-Si bearing phases of fly ash are digested, giving rise to a porous, zeolitic structure in both fly ash samples. The effect of the treatment in the mineralogical composition of lignite fly ashes is abstracted in Table 1. Amorphous phases were present in lignite fly ash samples. The synthetic zeolite produced by NaOH treatment, from lignite fly ashes, was the Na-bearing Na-P1 ($Na_6Al_6Si_{10}O_{32}\cdot 12H_2O$), while the initial coal fly ashes consisted mainly of glass and quartz. Both the quantity and quality of the synthetic zeolitic material produced by the above process were high. This is probably due to two interventions made in the method of Koukouzas *et al.* (2010) and Itskos *et al.* (2015). Na-P1 zeolite is a synthetic mineral with high ion exchange capacity, due to the substitution of Si(IV) by Al(III) in its structure, which results in an overall negative charge, leading to applications as ion exchange or molecular sieve. This zeolite has an affinity with some metal ions, generally found in acid mine drainage effluents, and may be used for remediation (e.g. Itskos *et al.*, 2015; Koukouzas *et al.*, 2010).

The synthetic zeolite produced by KOH treatment, from both lignite fly ashes, was the K-bearing Zeolite-F [$KAlSiO_4 1{,}5H_2O$] (Table 1). The formation of the synthetic zeolites was also confirmed by the SEM investigation.

Table 2 presents the impact of the alkaline activation in the chemical composition of the initial fly ashes. The Si, Al, Fe, Mg, Ca, Ti, P and Mn values were reduced in the synthetic zeolitic material, while alkalies (Na and K) was the only major element that increased according to the alkali treatment respectively (Table 2). This is due to the treatment with the alkali

Table 1: Mineralogical composition of the materials used for the experimental procedure (MEG-FA: Megalopoli lignite fly ash, MEL-FA: Meliti lignite fly ash)and the effect of hydrothermal alkali treatment in the mineralogical composition of the and lignite fly ashes (Na-MEG-FA: NaOH treated Megalopoli fly ash, Na-MEL-FA: NaOH treated Meliti fly ash, K-MEG-FA: KOH treated Megalopoli fly ash, K-MEL-FA: KOH treated Meliti fly ash).

Mineral phase	MEG-FA	MEL-FA	Na-MEG-FA	Na-MEL-FA	K-MEG-FA	K-MEL-FA
Zeolite Na-P1 (Na6Al6Si10O32·12H2O)			✓	✓		
Zeolite-F (KAlSiO41,5H2O)					✓	✓
Calcite	✓	✓	✓	✓	✓	✓
Hematite	✓	✓	✓	✓	✓	✓
Portlandite	✓	✓	✓		✓	✓
Feldspars	✓	✓	✓	✓	✓	✓
Cristobalite	✓					
Gismondine	✓	✓			✓	✓
Quartz	✓	✓	✓	✓	✓	✓
Maghemite		✓		✓		✓
Magnetite	✓		✓		✓	
Gypsum	✓	✓	✓	✓	✓	✓
Amorphous phase	✓	✓	✓	✓	✓	✓

Table 2: Chemical composition of the materials used for the experimental procedure (MEG-FA: Megalopoli lignite fly ash, MEL-FA: Meliti lignite fly ash)and the effect of hydrothermal alkali treatment in the mineralogical composition of the and lignite fly ashes (Na-MEG-FA: NaOH treated Megalopoli fly ash, Na-MEL-FA: NaOH treated Meliti fly ash, K-MEG-FA: KOH treated Megalopoli fly ash, K-MEL-FA: KOH treated Meliti fly ash).

Sample	MEG-FA	MEL-FA	Na-MEG-FA	Na-MEL-FA	K-MEG--FA	K-MEL--FA
SiO2	52.12	51.82	48.23	47.44	32.10	37.58
Al2O3	16.11	17.98	15.45	15.94	13.07	16.09
Fe2O3	6.84	7.12	6.52	6.65	10.11	7.27
MgO	3.01	2.36	2.35	2.05	2.28	3.10
CaO	11.24	9.94	11.38	6.77	14.53	9.66
Na2O	0.70	1.54	3.52	6.62	0.23	0.66
K2O	1.86	1.98	1.83	1.15	10.72	11.95
TiO2	0.56	0.79	0.74	0.75	0.66	0.85
P2O5	0.23	0.11	0.24	0.06	0.13	0.12
MnO	0.09	0.10	0.08	0.10	0.08	0.09
LOI	4.30	2.10	8.16	11.90	14.65	11.52
Sum	100.09	99.96	99.02	100.82	98.86	99.14

Table 3: Cation exchange capacity of raw and hydrothermally treated lignite fly ashes.

Sample	CEC meq.100gr^{-1}
MEG-FA	11.02
MEL-FA	15.61
Na-MEG-FA	147.45
Na-MEL-FA	151.02
K-MEG-FA	145.10
K-MEL-FA	152.45

solution and, subsequently, the addition of the relevant element in the solid to produce the synthetic zeolite.

The synthetic zeolites formed differ from the natural ones, being less siliceous than the naturally occurring zeolite tuff, having Si/Al ratio of 40/12 and 60/12 respectively.

The newly formed phases may accommodate nutrients or metal pollutants either as major constituents (Chen *et al.*, 2000) or as minor components co-precipitated in hydroxides (Boisson *et al.*, 1999; Chlopecka and Adriano, 1997).

The cation exchange capacity of the initial and the hydrothermally treated ashes are presented in Table 3. The hydrothermally treated lignite fly ashes exhibit more than ten times higher CEC values than the initial materials due to the presence of the synthesized zeolites.

Some authors have claimed that the remediation of polluted soils by zeolitic amendments may be mainly attributed to the cation exchange capacity (e.g. Castaldi and Santona, 2005). As suggested by Ross (1995), the cation exchange capacity of a soil is a measure of the quantity of negatively charged sites on soil surfaces that can retain positively charged cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^{+}), by electrostatic forces. Cations retained electrostatically are easily exchangeable with cations in the soil solution so a soil with a higher CEC values is predicted to have a greater capacity to maintain adequate quantities of the above mentioned cations than a soil with a lower CEC.

The synthetic zeolites produced seem to be effective, exhibiting good quality and low cost due to the low activation temperature and subsequently low energy consumption.

4 CONCLUSIONS

The synthetic zeolites produced by a low cost alkali hydrothermal treatment Na-P1 and Zeolite-F have potential applications as soil amendments and slow release fertilizers. Moreover, those treated fly ashes exhibit more than ten times higher CEC values than the initial materials due to the presence of the zeolites. The synthetic zeolites produced seem to be effective, exhibiting good quality and low cost due to the low activation temperature and subsequently low energy consumption.

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