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Synthetic zeolites from lignite fly ash and biomass ash for agricultural applications

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The production 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.

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 mine-water treatment (Itskos *et al.*, 2015) and as soil amendments in acid mining soils (Giannatou *et al.,* 2017, 2018). Since K is considered as a nutritient in agriculture (e.g. Stamatakis *et al*., 2016), in the present study KOH was selected as an activation solution, in order to develop a K-rich synthetic zeolite suitable for utilization in agriculture.

In the current study we are evaluating the results of the hydrothermal activation of lignite fly ash and biomass asses from Greece, by KOH in order to produce synthetic zeolites, for agricultural applications.

As KOH solutions present lower conversion efficiency than the respective NaOH under the same temperature (Itskos *et al*., 2015) the experimental conditions were modified from those proposed by Koukouzas *et al*. (2010) Itskos *et al.* (2015) and Giannatou *et al.* (2017, 2018), by using a 6N KOH as activation solution and extending the treatment period to 72h. Lignite fly ash samples from Meliti (MEL-FA) and Megalopoli (MEG-FA) Electric Power Stations and biomass ash from sawdust (SAWD-ASH), reed (REED-ASH) and olive kernel (OL-ASH) were used as raw materials that underwent the alkaline hydrothermal treatment at 100ºC. The applied techniques mainly aimed at the dissolution of Al-Si bearing phases of the ashes and the subsequent precipitation of the zeolitic minerals.

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 thermalalkali digestion, has been carried out at the R&D Department of the Titan Cement Company.

Table 1: Effect of hydrothermal treatment (HT-) in the mineralogical composition of the biomass and lignite fly- ashes

Mineral phase	REED-ASH	HT-REED-ASH	SAWD-ASH	HT-SAWD-ASH	OL-ASH	HT-OL-ASH	MEG-FA	HT-MEG-FA	MEL-FA	HT-MEL-FA
Zeolite-F($KAlSiO_4 1,5H_2O$)								✓		✓
Anhydrite	✓	✓					✓	✓	✓	✓
Arcanite (K_2SO_4)	✓	✓			✓	✓				
Calcite	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Gehlenite	✓	✓								
Hematite	✓	✓	✓	✓			✓	✓	✓	✓
Periclase	✓		✓							
Portlandite	✓						✓	✓	✓	✓
Feldspars	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Sylvite (KCl)	✓		✓		✓					
Bassanite			✓		✓	✓				
Fairchildite ($K_2Ca(CO_3)_2$)					✓					
Cristobalite			✓				✓			
Diopside			✓							
Gismondine			✓				✓	✓	✓	✓
Muscovite			✓							
Ankerite					✓	✓				
Quartz	✓	✓		✓	✓	✓	✓	✓	✓	✓
Maghemite									✓	✓
Magnetite							✓	✓		
Gypsum		✓					✓	✓	✓	✓
Amorphous phase	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

Amorphous phases were present in all initial biomass and lignite fly ash samples. The synthetic zeolite produced from both lignite fly ashes was the K-bearing Zeolite-F [$KAlSiO_4 1,5H_2O$] (Table 1). The formation of the synthetic zeolite from lignite fly ashes was also confirmed by the SEM investigation. The effect of hydrothermal treatment in the mineralogical composition of the biomass and lignite fly- ashes is abstracted in Table 1.

Table 2 presents the impact of the alkaline activation in the chemical composition of the initial fly ashes. Biomass ashes failed to develop any zeolitic material after the low temperature hydrothermal alkaline treatment due to their primary shortage of Al_2O_3

The cation exchange capacity of the initial and the hydrothermally treated (HT-) ashes is 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 Zeolite-F presence.

No major phase conversion has been identified in the treated biomass ash samples probably due to their initial low Al_2O_3 content (Table 2) as a result of the minorpresence of aluminum bearing mineral phases in the initial ashes.

Table 2: Effect of hydrothermal treatment (HT-) in the major chemical compounds of the treated fly- and biomass ashes

Sample	MEG-FA	HT-MEG-FA	MEL-FA	HT-MEL-FA	REED-ASH	HT-REED-
SiO_2	41.15	32.10	51.82	37.58	49.42	37.71
Al_2O_3	15.67	13.07	17.98	16.09	1.62	2.76
Fe_2O_3	11.09	10.11	7.12	7.27	1.24	2.77
MgO	2.52	2.28	2.36	3.10	4.11	7.60
CaO	16.12	14.53	9.94	9.66	10.14	7.73
Na_2O	0.60	0.23	1.54	0.66	0.54	0.23
K_2O	1.66	10.72	1.98	11.95	14.14	18.75
TiO_2	0.72	0.66	0.79	0.85	0.10	0.19
P_2O_5	0.32	0.13	0.11	0.12	1.66	1.70
MnO	0.09	0.08	0.10	0.09	0.06	0.12
Cr_2O_3	-	-	0.02	-	-	-
TOT/C	-	-	0.95	-	-	-
TOT/S	7.28	0.30	0.44	0.25	3.72	0.36
LOI	4.21	14.65	2.10	11.52	12.63	19.76
Sum	101.43	98.86	99.96	99.14	99.38	99.68

Table 3: Cation exchange capacity of raw and hydrothermally treated (HT-) materials

Sample	CEC meq/100g
MEG-FA	11.02
MEL-FA	15.61
OL-ASH	24.79
REED-ASH	17.45
SAWD-ASH	11.02
HT-MEG-FA	145.10
HT-MEL-FA	152.45
HT-OL-ASH	32.14
HT-REED-ASH	17.45
HT-SAWD-ASH	92.75

Concluding, the synthetic zeolite produced by both lignite fly ashes was Zeolite-F. The cation exchange capacity of those synthetic materials is improved with respect to the initial ashes.Chemical and mineralogical properties of those lignite fly ashes treated, make them a suitable raw material for the synthesis of hybrid zeolitic products with upgraded potential for agricultural applications.On the contrary, biomass ashes failed to develop zeolitic material after the low temperature hydrothermal alkaline treatment due to their primary shortage of Al_2O_3.

The synthesized Zeolite-F rich materials will be tested in the near future for their performance as soil amendments and slow release fertilizers.

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