ZEOLITES FROM POWER PLANT ASH FOR WASTE WATER TREATMENT

Maria HARJA[1], Ana Andreea GURITA [2], Marinela BARBUTA[3], Ramona Carla CIOCINTA[2]
E-mail: maria_harja06@yahoo.com

Abstract

The capitalisation of ash from power plant for obtaining zeolites is very interesting, because obtained products have high environmental applications. Zeolites may be easily obtained from ash by direct alkaline conversion processes, diffusion process and microwave. The zeolites have been researched for a variety of environmental applications in agricultural, they have remarkable properties: cation-exchange, adsorption, and molecular sieving properties.
From the types of zeolites which may be obtained, in this study are presented different zeolitic products for wastewater with high CEC. The zeolitic products which were obtained were analyzed as composition and properties. The synthesized products provide a significant increase of CEC and a high ability to adsorb heavy metal ions.
The aim of this study is establish the experimental conditions f or power plant ash zeolitization. On the base of their cation-exchange properties, zeolites can be use for cation-exchange in wastewater.

Key words: power plant ash, characterization, synthesis, zeolitization

The ash produced from the burning of coal is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected from the flue gas by means of electrostatic precipitators (Kumar K. A., Kumar P., Teng T. T., Chand S., Wasewar K. L., 2011).

Approximately 75% from ash (fly ash and bottom ash) generated is still disposed or storage lagoons. Much of this ash, however, is possible of being recovered and used. Examples of these applications are (Harja M., Barbuta M., Gavrilescu M., 2009; Cline, J.A., Bijl M., Torrenueva A., 2000; Criado M., Fernandez-Jimenez A., Palomo A., 2007): Immobilization of heavy metals from wastewater; Land stabilization in mining areas; Sorbents for flue gas desulfurization; Fireproof materials; Material for soil amendment; Filter material for the production of different products; Geopolymerization; Zeolitization.

The compositional similarity of ash to volcanic material, precursor of natural zeolites, was the main reason to experiment with the synthesis of zeolites from this by-product.

The zeolites have a wide range of industrial applications, mainly based on:

- Ion exchange, especially heavy metal.
- Gas adsorption: selective absorption of specific gas molecules.
- Water adsorption: reversible adsorption of water without any desorption chemical or physical change in the zeolite matrix.

Many researches (Barbuta M., Harja M., Baran I., 2010; Ippolito J. A., Tarkalson D., Lehrsch G., 2011; Kalra N., Harit R. C., Sharma S. K., 2000, Yoo J. G., Jo Y.M., 2003) have proposed different hydrothermal activation methods to synthesize different zeolites from ash. All the methodologies developed are based on the dissolution of Al-Si bond from ash phases with alkaline solutions (NaOH or KOH) and the subsequent precipitation of zeolitic material. In most studies, the fly ash activation is carried at temperature 70 - 200 ºC, conversion time 4 - 48 h, alkali concentration 0.5 - 5 M and liquid/solid ratio 1 - 20 mL g^{-1} (Querol X., Moreno N., Umaña J. C., Alastuey A., Hernández .,López-Soler A., Plana F., 2002). The zeolite than can be obtained are presented in *table 1*.

In the wastewater can exist singular heavy metals in or association of the four metals or more: Pb, Cu, Zn, Cd. Heavy metals contaminated water have been treated with zeolites.

[1] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Iaşi
[2] University of Agricultural Sciences and Veterinary Medicine, Iaşi
[3] "Gheorghe Asachi" Technical University of Iasi, Faculty of Civil Engineering and Building Services, Iaşi

Table 1

Zeolites and other neomorphic phases synthesized from fly ash and Joint Committee of Powder Diffraction Standard (JCPDS) codes for XRD identification (Querol X., Moreno N., Umaña J. C., Alastuey A., Hernández .,López-Soler A., Plana F., 2002)

Zeolitic product		JCPDS
NaP1 zeolite	$Na_6Al_6Si_{10}O_{32}$ $12H_2O$	39-0219
phillipsite	$K_2Al_2Si_3O_{10}$ H_2O	30-0902
K-chabazite	$K_2Al_2SiO_6$ H_2O	12-0194
zeolite F linde	$KAlSiO_4$ $1.5H_2O$	25-0619
herschelite	$Na_{1.08}Al_2Si_{1.68}O_{7.44}$ $1.8H_2O$	31-1271
faujasite	$Na_2Al_2Si_{3.3}O_{8.8}$ $6.7H_2O$	12-0228
zeolite A	$NaAlSi_{1.1}O_{4.2}$ $2.25H_2O$	43-0142
zeolite X	$NaAlSi_{1.23}O_{4.46}$ $3.07H_2O$	39-0218
zeolite Y	$NaAlSi_{2.43}O_{6.86}$ $4.46H_2O$	38-0239
perlialite	$K_9NaCaAl_{12}Si_{24}O_{72}$ $15H_2O$	38-0395
analcime	$NaAlSi_2O_6$ H_2O	19-1180
hydroxy-sodalite	$Na_{1.08}Al_2Si_{1.68}O_{7.44}$ $1.8H_2O$	31-1271
hydroxy-cancrinite	$Na_{14}Al_{12}Si_{13}O_{51}$ $6H_2O$	28-1036
kalsilite	$KAlSiO_4$	33-0988
tobermorite	$Ca_5(OH)_2Si_6O_{16}$ $4H_2O$	19-1364

For wastewater treatment although of natural zeolite can be used and zeolite synthesized from ash, especially ash from power plats (Harja M., Barbuta M., Gavrilescu M., 2009; Criado M., Fernandez-Jimenez A., Palomo A., 2007; Ippolito J. A., Tarkalson D., Lehrsch G., 2011; Harja M., Barbuta M., Rusu L., Munteanu C., Buema G., Doniga E., 2011).

MATERIAL AND METHOD

Materials. The studied material was zeolite - synthesized from ash. This is based on the combination of different activation solution/ash ratios, with temperature and reaction time to obtain different zeolite types. Potassium hydroxide solutions with different molarity, at atmospheric and water vapour pressures at 80°C and 2 to 16 h have been combined to synthesise up to 16 different zeolites from the same ash. The concentration of the KOH solution is between 1 - 5 M. In this interval we decide to 2 am 4 M and s/L ration of 1/2-1/5.

The zeolite material was obtained by direct alkaline conversion processes in bath with magnetic stirrer using KOH 2 M solution, at different treatment interval, Table 2. In the same condition was synthesized zeolite but at 4 M KOH solution. The zeolites obtained were filtered, washed (until pH 7) and dried for 4 hours at 353 K in oven.

Table 2

Experimental conditions

Sample	s/L ratios	Temperature	Curing time
Z1	1/2	70°C	4 hour
Z2	1/2	70°C	8 hour
Z3	1/3	70°C	4 hour
Z4	1/3	70°C	8 hour
Z5	1/2	90°C	4 hour
Z6	1/2	90°C	8 hour
Z7	1/3	90°C	4 hour
Z8	1/3	90°C	8 hour

Method. In order to use the ash for the synthesis of zeolites, the ash has to undergo a process of characterization from a morphological, chemical, mineralogical and technological point of view. For this we used following equipments: SEM/EDX for morphology and elementary analysis of the ashes samples, QUANTA 3D - AL99/D8229; diffractometer X'PERT PRO MRD; multi-Parameter Consort C831, pH 0 - 14.00, conductivity 0 - 200 mS, temperature 0 - 100 °C. For heavy metal analysis it was used the atomic absorption spectroscopy with Buck Scientific AAS equipment. The chemical characterization of the ash and zeolites has been performed in accordance with the SR EN standard - 450-1:2006.

RESULTS AND DISCUSSIONS

Capitalize of ash in order to obtain new materials for heavy metal adsorption depends on their properties. The chemical composition is influenced by those of the coal burned and the condition of storage.

The analysis demonstrated that the used ash has as principal elements: Si, O, Al, Ca, Fe, K, Mg, that are in oxidic form (*tab. 3*), in accordance with the data reported in literature (Harja M., Barbuta M., Gavrilescu M., 2009, Barbuta M., Harja M., Babor D., 2010).

Table 3

The characterisation of coal ash

Composition, %	1	2
SiO_2	51.2	51.3
Al_2O_3	26.93	25.08
Fe_2O_3	6.98	6.28
CaO	7.31	5.21
MgO	2.075	1.7596
Ignition loss 1200°C - total loss, %	2.42	2.3
Density (kg m^{-3})	2340	2518
Ration SiO_2/Al_2O_3	1.9	2

From the SEM analysis can be observe that the ash particles have spherical shapes and irregular- due to the presence of a relative high amount of unburned carbon (*fig. 1*).

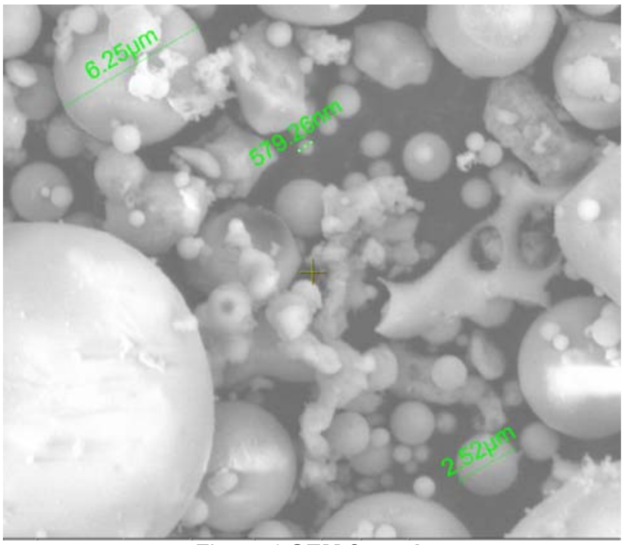


Figure 1 **SEM for ash**

XRD as seen in *figure 2* show that the ash contain crystalline phases: illite (I), kaolinite (K), mullite (Mu), hematite (He), magnetite (M), muscovite (Ms), rutile (R) and glassy phase (Mishra A., Choudhary D., Jain N., Kumar M., Sharda N., Dutt D., 2008).

The zeolites synthesized have morphological form presented in *figure 3*.

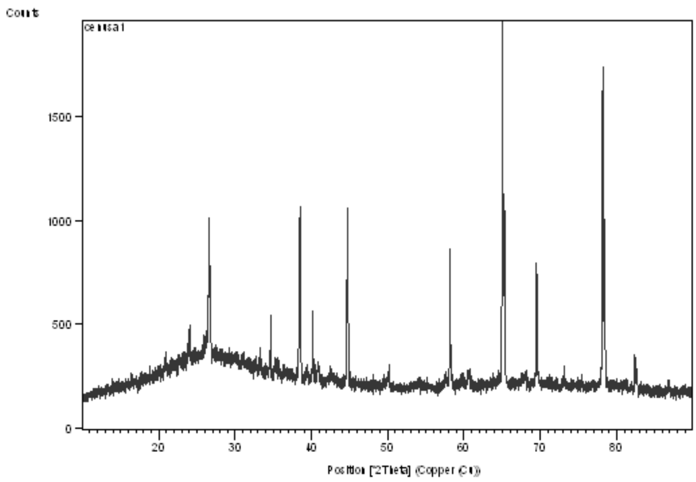
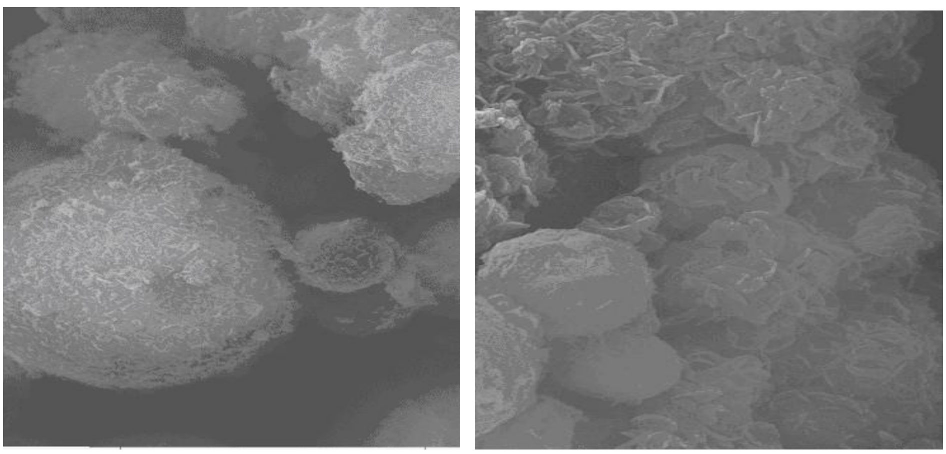


Figure 2 **XRD diffractogram for ash**



Z2 Z6

Figure 3 **SEM for Z2 and Z6**

In *table 4* is presented and the elementary composition of the zeolite Z2 compared with raw ash.

Table 4

The characterization of samples

Composition, %	Ash	Zeolite Z2
O	34.38	35.24
K	1.38	4.97
Mg	2.83	1.86
Al	17.93	16.88
Si	33.30	32.58
Na	0.39	1.40
Ca	5.42	2.13
Ti	0.63	0.74
Fe	5.10	4.14

The analysis demonstrated that in the zeolite principal elements the followings: Si, O, Al, Ca, Fe, Na, K, and small quantities of Ti and Mg. In zeolite structure appear K ions, because the synthesis was performed with potassium hydroxides and calcium content decreases. EDAX for zeolite Z2 are presented in *figure 4*.

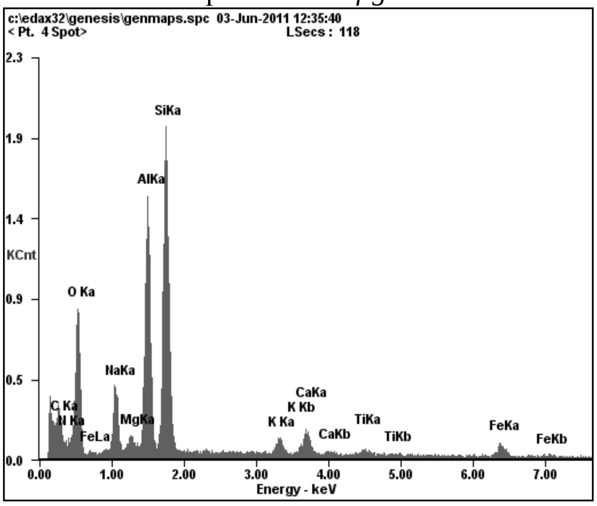


Figure 4 **Chemical composition for zeolite Z2**

Other information about the mineralogical component is presented in XRD diffractogram, *figure 5*.

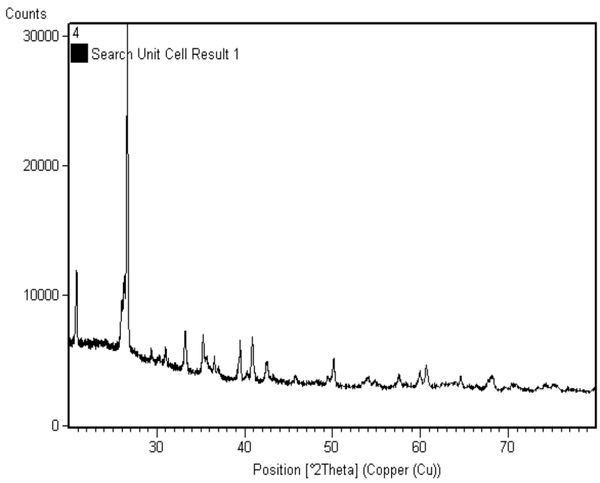


Figure 5 **XRD for zeolite**

Compared with diffractogram from *figure 2* it can observe that the zeolitic material was obtained, in this case K-chabazite $K_2Al_2SiO_6$ H_2O.

In function of curing treatment the following zeolitic materials can be obtained K-F at low temperature, K-Cabazite at low temperature but at time curing of over 12 h. At temperature over 150°C was obtained K-Philipsite and Kalsilite.

These materials have the cation exchange capacity between 0.15 to 0.99 meq/g.

CONCLUSIONS

Based on the experimental results, we found that the analyzed ash as it results after the combustion of coal, belongs to the F class. This type of ash can be used to obtain zeolitic materials for up taking heavy metals from wastewater.

For zeolitization of ash the activation time is 12-24 h, the concentration of the activation agents 2.0 M and the ash/solution ratio is of 1/2-1/3. The temperature may be smaller than < 90 °C for synthesis zeolites with a high CEC.

Analyzing the obtained data it can observe the destruction of ash network and crystallization of the new phase and by increasing the time of hydrothermal attack it obtains a structure nearer to the zeolite ones.

It is evidently that this alkaline attack procedure can convert ash into a beneficial product, which would prove effective in improvement of water quality.

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