

## II. ENVIRONMENTAL BIOTECHNOLOGY

### NOVEL TECHNICAL AND ECONOMICAL SUPERIOR APPROACH FOR SYNTHESIS OF ZEOLITES FROM COAL FLY ASH

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**Abstract.** The present paper is aimed on the preparation of zeolites from lignite coal fly ash using a superior synthesis approach that combines the advantages of different established technological schemes. The novel method is directed to improvement of the energy efficiency and the raw material economy, and at the same time resulting in better quality material. Fly ash zeolites of Na-X type were synthesized applying fusion stage of fly ash/NaOH mixtures followed by atmospheric self-crystallization. The obtained zeolite structure was investigated by X-ray diffraction for different periods of crystallization of the reaction mixtures under atmospheric conditions. Comparative studies of three different methods for synthesis of Na-X were performed taking into account the specific energy and the raw material consumption. It was considered that adsorbents of zeolite X type can be obtained by different ways of alkaline conversion of coal fly ash, and that is why the most important issues for the scale production of these materials are the economical aspects of the synthesis.

**Keywords:** synthesis of zeolites; adsorption; carbon emissions

#### INTRODUCTION

One of the most investigated issues of the modern world is the environment protection provoked by the continuously increasing consumption of technological resources. The global unsolved ecological problem is the enormous production of greenhouse gases, in the largest quantities from which carbon dioxide (CO<sub>2</sub>) is emitted into the atmosphere.

The thermal power plants are the major sources of CO<sub>2</sub> (approx. 40% of total generated CO<sub>2</sub> amount). In the last years, many technologies for carbon capture and storage are intensively studied directed to fuel combustion systems [1, 2]. Three main technological approaches have been outlined, such as pre-combustion capture, modified combustion and post-combustion capture. The post-combustion technology is based on the absorption of CO<sub>2</sub> from organic liquids (mostly amines) [3]. It is the most technical and economical compatible approach to the existing combustion plants, but is hindered by the high consumption of energy for desorption process, as well as the toxicity of these substances. Its negative aspects can be overcome by the development of appropriate solid adsorbents [4].

Zeolites are the most valuable natural and synthetic porous solids suitable for gas adsorption [5], which can be easily obtained from aluminosilicate by-products, such as coal fly ash [6,7]. The highest adsorption ability toward the polar CO<sub>2</sub> molecules has been established for zeolite types A and X due to their large pore size [8,9].

In our previous studies, the synthesis of zeolites type A and X by alkaline conversion of fly ash (FA) from incineration of Bulgarian lignite coals has been studied [10,11]. Sufficient results have been achieved in two different ways of treatment of fly ash mixed with sodium hydroxide as an alkaline activator: (1) hydrothermal activation with a prior stage of calcination at 550 °C; (2) atmospheric self-crystallization. The first method of synthesis gains an advantage with rapidly getting zeolite X for 24 hours, but has a major drawback because of the large energy consumption.

The second approach does not require any additional energy but a long period of 12 months is necessary to obtain zeolite X.

In this study, an alternative method for a hybrid synthesis is considered by the implementation of the scheme: fusion stage of fly ash/NaOH mixtures followed by atmospheric self-crystallization. This superior manner combines the advantages of the above approaches, while overcomes their main disadvantages.

#### MATERIALS AND METHODS

FA generated by combustion of lignite coals in the biggest power plant in Bulgaria "TPP Maritza East 2" has been previously studied with respect to its morphology, chemistry and structure. The composition of FA is reported in Table 1. The ratio of crystalline vs. amorphous phase has been found of 57/43.

Table 1. Chemical composition of raw fly ash

Component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	MnO	ZnO	Na <sub>2</sub> O	K <sub>2</sub> O
weight %	52.66	23.37	8.72	5.75	2.75	2.40	0.06	0.04	0.01	0.01

In our published investigations, FA zeolitization by a double stage fusion-hydrothermal syntheses and atmospheric crystallization has been thoroughly studied.

In this study, mixtures of FA and NaOH were prepared in two different ratios of 1/1 and 1.6/1.0 and were subjected in a double-stage treatment. The first stage of the synthesis was performed at temperature of 550 °C for 1 h in a muffle furnace. Thereafter, the sintered alloys were crushed, mixed with distilled water in a ratio of FA/H<sub>2</sub>O<sub>dist</sub>=1/10, and were filled into closed polypropylene containers. The second stage is so called “atmospheric self-crystallization”, which was realised at room temperature (approx. 20 °C). Small parts of the suspensions were taken off for analyses after 30, 60, 90, 120 and 180 days. The solid part was separated by filtration, thoroughly washed with distilled water and dried again at room temperature.

Structural analysis of the obtained solid powders was performed by X-ray diffraction (XRD) technique on a Bruker D2 Phaser diffractometer with CuK<sub>α</sub>-radiation and a Ni filter.

For the evaluation of the economical parameters of the different synthesis approaches, the electricity consumption of the considered processes was estimated with an energy measurement device, Brennenstuhl PM231 E. The obtained results are attributed to the specific consumption per mass unit of FA zeolite (FAZ) in kWh/kg FAZ. The quantities of NaOH and water spent for activation, as well as the energy consumption for drying were also considered in the economical evaluation.

## RESULTS AND DISCUSSIONS

XRD patterns of the samples obtained by calcination at 550 °C of FA/NaOH mixtures at a ratio of 1.6/1 are shown on Figure 1. The kinetics of the zeolitization process under self-crystallization in water media was investigated in three stages during the period of 190 days. First analysis of the extracted solid material was performed after 30 days of its incubation. The XRD pattern indicates absence of any crystalline phases excepting the hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). After 100 days of room temperature synthesis, well-expressed peaks are observed which correspond to the Na-X zeolite phase.

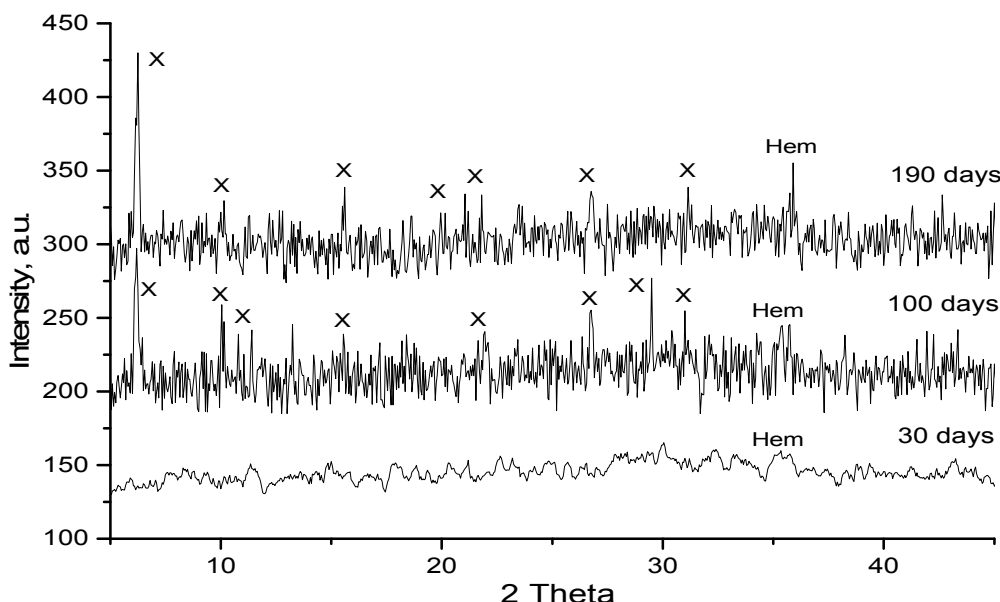
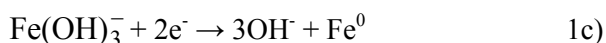
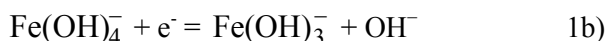
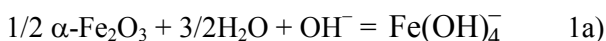


Fig. 1. XRD patterns of samples obtained by calcination at 550 °C of FA/NaOH mixtures at a ratio of 1.6/1.0 for different self-crystallization times, where: X is Na-X zeolite; Hem is  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

Third analysis is performed after 190 days, and it can be seen that the intensity of the main peak on the XRD pattern of the Na-X zeolite phase is increased, which indicates an improved yield of FAZ. Other specific peaks of Na-X, such as that at  $2\theta = 30.85^\circ$  is disappeared due to the changes in the crystal growth directions. Further prolongation in the synthesis duration may result in crystallization of more stable zeolitic phases such as chabazite or sodalite.

In Fig.2, the XRD patterns of samples obtained at a FA/NaOH ratio of 1/1 are shown. Increasing NaOH molarities from 1.5 to 2.5 M, the crystallization of zeolite from the reaction mixture is accelerated. The conversion process of FA into X type zeolite is finished just for 30 days, as the intensity of the reflections of Na-X phase for the sample after a month is almost equal to that after longer self-crystallization periods for 90 and 130 days. At these synthesis conditions, the characteristic peaks of  $\alpha\text{-Fe}_2\text{O}_3$  on the XRD patterns are diminished. This probably due to the higher concentration of the NaOH solution which causes an electrochemical reduction of  $\alpha\text{-Fe}_2\text{O}_3$  to  $\text{Fe}(\text{OH})_3$  and Fe, according to the scheme [12]:



Thus, the obtained  $\text{Fe}(\text{OH})_3$  co-precipitate with sodium silicate and sodium aluminate hydrogel and  $\text{Fe}^{3+}$ -ions incorporates into aluminosilicate zeolite framework or play a role as a charge compensator of  $\text{AlO}_{4/2}$ -anions.

In our previous studies, preliminary experimental results on  $\text{CO}_2$  adsorption onto FAZ with Na-X structure have been reported [13,14].  $\text{CO}_2$  adsorption tests were performed on FAZ synthesized by a two stage fusion-hydrothermal synthesis at FA/NaOH=1/2, FA/ $\text{H}_2\text{O}$ =1/20, calcination for 1 h at  $550^\circ\text{C}$ , 16 hours magnetic stirring, hydrothermal activation for 4 h at  $90^\circ\text{C}$ , and drying for 1 h at  $105^\circ\text{C}$ . FAZ obtained by atmospheric self-crystallization of mixtures of FA/NaOH=1/1 and FA/ $\text{H}_2\text{O}$ =1/10 during 12 months (approx. 360 days) of zeolitization. Promising adsorption capacity was obtained for zeolite samples, prepared by different techniques. Thus, the most important point for application of FAZ for adsorption of  $\text{CO}_2$  in large scale systems is the economical superiority of their synthesis approach. The sequences of the different technological schemes of syntheses are presented in Fig. 3.

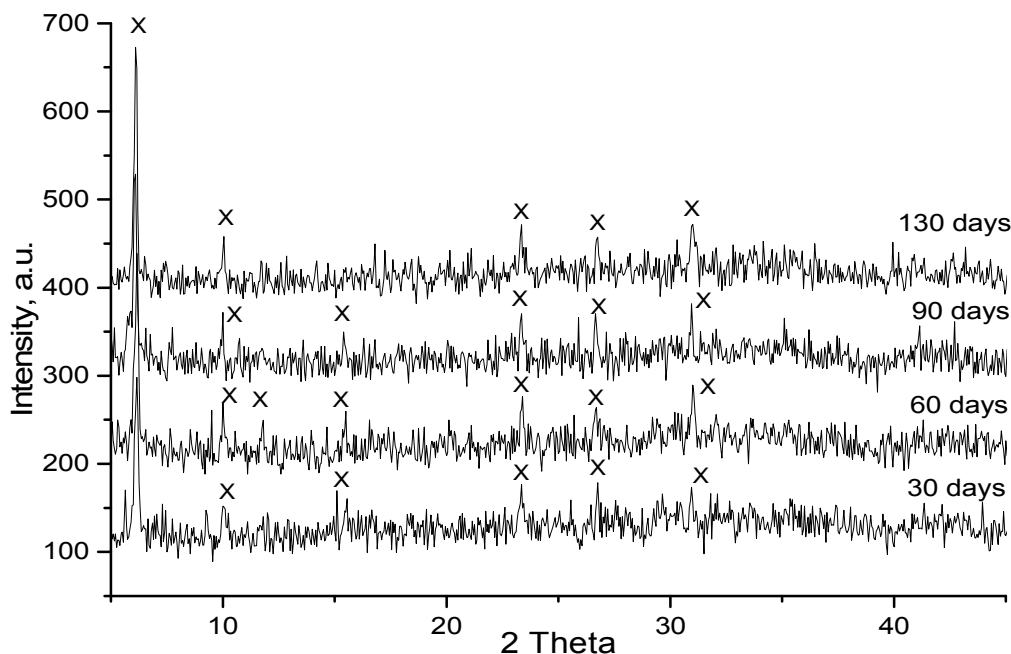
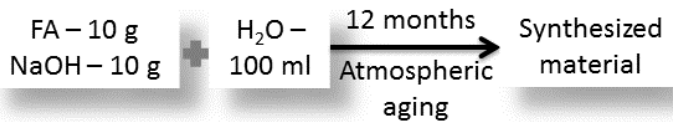
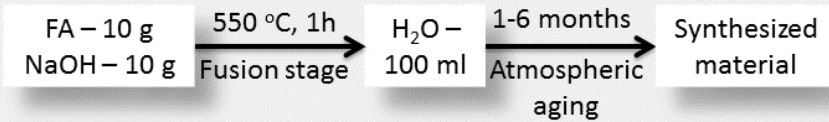


Fig. 2. XRD pattern of samples obtained by calcination at  $550^\circ\text{C}$  of FA/NaOH mixture at a ratio of 1/1 and different self-crystallization times, where X is Na-X zeolite structure.

**Self crystallization**



**Self crystallization with prior fusion**



**Hydrothermal activation with prior fusion**

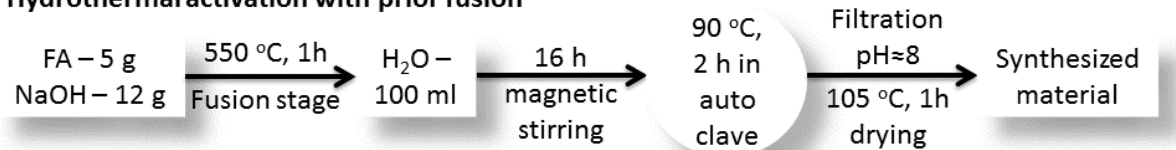


Fig. 3. Principle schemes of the three different methods of synthesis.

The economical and technical parameters of production of 1kg FAZ in Table 2 and the different synthesis manners were evaluated comparing their specific consumption for the corresponding costs in Table 3.

Table 2. Technical and economical comparison of different approaches for synthesis of zeolite X from 1 kg fly ash.

Method of FAZ synthesis	Calcination at 550 °C for 1 h	Magnetic stirring	Hydrothermal activation at 90 °C	Drying at 105 °C	Distilled water	NaOH	Time of synthesis
	kWh/kg FAZ	kWh/kg FAZ	kWh/kg FAZ	kWh/kg FAZ	l/kg FAZ	kg/kg FA	
Two stage fusion-hydrothermal	1.759	0.820	1.742	0.230	20	2	22 hours
Atmospheric self-crystallization	N/A	N/A	N/A	N/A	10	1	365 days
Two stage fusion-atmospheric	1.759	N/A	N/A	N/A	10	0.6	190 days
Two stage fusion-atmospheric	1.759	N/A	N/A	N/A	10	1	90 days

Table 3. Comparative cost analysis of different approaches for synthesis of zeolite X from 1 kg fly ash.

Method of FAZ synthesis	Cost per unit electric power	Value	Cost per unit NaOH	Value	Cost per unit water	Value (incl. washing)	Total cost
	Euro/kWh	Euro/kg FAZ	Euro/kg	Euro/kg FAZ	Euro/m <sup>3</sup>	Euro/kg FAZ	Euro/kg FAZ
Two stage fusion-hydrothermal	0.1012	0.4607	2.5560	5.1129	1.0635	1.0656	<b>6.6392</b>
Atmospheric self-crystallization	N/A	N/A		2.5560		1.0646	<b>3.6206</b>
Two stage fusion-atmospheric	0.1012	0.1780		1.5336		1.0646	<b>2.7762</b>
Two stage fusion-atmospheric	0.1012	0.1780		2.5560		1.0646	<b>3.7986</b>

The obtained cost values in Table 3 are calculated for a laboratory scale experiments including industrial costs for electrical energy without distribution and water with purification. It could be expected a serious price discount for FAZ produced in large-scale systems supposing that energy efficient processes will be installed in the frame of a Thermal Power Plant by utilization of residual thermal energy, and by concentration and multiple utilization of the exhausted alkaline solution. In addition, cost reduction will be also realized estimating the expenses for fly ash transportation and disposal. Furthermore, carbon capture by solid adsorbents is the most economically efficient and environmentally friendly approach in comparison to the other existing low-carbon technologies.

On the base of the performed economical analysis and considering the balance between the specific cost and the time consumption for FAZ production, the best results are obtained for the double stage fusion-atmospheric synthesis with the higher NaOH concentration, but depending on the specific necessities, the lower alkaline process could also be effective.

## CONCLUSIONS

Lignite coal fly ash was converted into zeolite of Na-X type applying a novel hybrid approach, which consists of a double stage fusion-atmospheric self-crystallization, combining the advantages of the existed manners for preparation of zeolites from aluminosilicate by-products. A comparative

economical evaluation was performed for three different methods for obtaining of zeolite Na-X by alkaline treatment of coal fly ash in laboratory scales. The best results are obtained for the hybrid fusion-atmospheric synthesis at a concentration of the alkaline activator corresponding to 1.5-2.5 M NaOH, considering the balance between the specific cost and the time consumption for the production of mass unit of the zeolite. Furthermore, the simultaneous resolving of two global ecological problems, such as fly ash deposition and carbon dioxide capture has an inestimable environment protection benefit.

***Acknowledgements.** The authors are thankful to the Technical University of Sofia for the financial support under contract No. 152PD0020-02/2015; D. Zgureva thanks to Karoll Financial Group for the PhD Fellowship.*

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## ПОДОБРЯВАНЕ ТЕХНИКО-ИКОНОМИЧЕСКИТЕ ПОКАЗАТЕЛИ НА МЕТОДИТЕ ЗА СИНТЕЗ НА ЗЕОЛИТИ ОТ ЛЕЛЯЩА ПЕПЕЛ

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**Резюме.** Опазването на околната среда е най-актуалният въпрос на съвременния свят, породен от непрестанно нарастващата консумация на технологични ресурси. Един от нерешените в глобален мащаб екологични проблеми е свръхпроизводството на парникови газове, от които в най-големи количества се емитира въглероден диоксид (CO<sub>2</sub>).

Основен дял в генерирането на CO<sub>2</sub> заемат инсталациите за производство на електроенергия (около 40 % от общогенерираните въглеродни емисии). През последните години се разработват интензивно технологии за улавяне и подземно депониране на CO<sub>2</sub> от продуктите на горене. Към момента се развиват три основни подхода за улавяне на CO<sub>2</sub> при горивни процеси: чрез модифициране на горивния процес, преди и след изгаряне на горивата. За съществуващи горивни инсталации, технически и икономически най-целесъобразна е следгоривната технология, която се основава на абсорбцията на CO<sub>2</sub> от органични съединения (най-често амини), свързано с високи енергийни разходи за десорбционния процес и токсичните характеристики на тези вещества. Разработването на подходящи твърдофазни адсорбенти ще реши тези два негативни аспекта.

В предишни изследвания сме разгледали възможността за синтез на zeoliti от леляща пепел, получена при изгарянето на български лигнитни въглища и последващото им приложение като адсорбенти на въглеродни емисии. От изследваните методи за получаване на високопорьозни zeoliti от тип А и Х, най-добри резултати са постигнати при два подхода: хидротермална активация с етап на предварително стапяне при 550 °С и атмосферна самокристализация. При всички експерименти, като алкален реагент е използван натриев хидроксид (NaOH). Предимство на първия метод на синтез е бързото получаване на крайна zeolitna структура-24 часа, а основен негов недостатък е разхода на големи количества енергия. При втория подход не се влага никаква допълнителна енергия, но изисква продължителен период до достигане на богата на zeolit Х крайна фаза - 12 месеца.

Настоящото изследване предлага алтернативен хибриден метод на синтез, който обединява предимствата на описаните по-горе подходи, като елиминира основните им недостатъци чрез реализиране на схемата: атмосферна самокристализация с прилагане на етап на предварително стапяне. По този начин се спестява енергията, необходима за хидротермалната активация, а с етапа на предварително стапяне при 550 °C се съкращава четирикратно времето, необходимо за атмосферна самокристализация. Постигнатите резултати подобряват технико-икономическите показатели на процеса на зеолитизация на летящата пепел, с което се намалява себестойността на технологията за следгоривно улавяне на единица маса CO<sub>2</sub>.

**Ключови думи:** синтез на зеолити, адсорбция, въглеродни емисии

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