Original Research

Characterization of X-type Zeolite Prepared from Coal Fly Ash

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Abstract

This study presents experimental results dealing with the possibility of transforming F-class fly ash into a zeolitic material. Two types of synthesis methods were used in the research: hydrothermal and low-temperature synthesis. As a result of alkaline reaction of fly ash with NaOH, all experimental cases yielded zeolitic material that are rich in a Na-X phase. The mineralogical composition (determined by SEM and XRD analysis) as well as the physio-chemical (chemical composition, CEC, textural parameters – BET surface area and PSD) properties of a Na-X phase were determined. The ratio Si/Al in the case of Na-X obtained by hydrothermal reactions was 1.2, but low-temperature reaction resulted in 1.04. CEC values for hydrothermal synthesis (average 240 meq/100g) are higher than low-temperature synthesis (average 200 meq/100 g). The BET surface area of hydrothermal Na-X is almost five times higher (332.5 m^2/g) than low-temperature Na-X (73 m^2/g). Hydrothermal reaction gave the zeolitic phase rich in Na-X that amount in total reaction products was from 55 to 60%, whereas in low-temperature reactions the Na-X phase in zeolitic material ranged from 42 to 55%. This work showed the potential of fly ash to be zeolitic materials through the proposed synthesis methods. An effective reaction turned out to be hydrothermal synthesis, which could form about 60% zeolite phase during a 24-hour reaction.

Keywords: fly ash, Na-X zeolite, hydrothermal and low-temperature synthesis

Introduction

Slag and fly ash are produced in heat and power generating plants as well as boiler plants. They pose a great threat to the environment as well as to human health, mostly due to the leaching of heavy metals into soils and releasing light fraction to the atmosphere [1-3].

Storage of CCP (Circumstantial Combustion Products) on heaps or in containment ponds is particularly burdensome and costly, mainly because of the need for additional protection required in order to avoid ash fly off and for soil isolation.

The majority of these particular wastes are comprised of fly ash [4], making their management an increasingly sig-
nificant problem and requiring a new and sophisticated approach to their utilization.

During the search for new practical uses of fly ash, a similarity between their chemical and mineralogical composition to some naturally occurring materials was found. On the basis of this observation, many research studies regarding synthesis of zeolites and other aluminosilicates from fly ash were initiated [5-9].

Zeolites are mostly hydrated aluminosilicates of alkaline elements, alkaline soils elements, or on rare occasions other cations. The very useful properties of zeolites (sorption, catalytic, molecular-sieve, ion exchange, and other properties) are the results of the specific structure of its aluminosilicate skeleton. This zeolitic structure comprises a system of channels and cavities, which are a result of

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sequential combining of alumino-silico-oxygen tetrahedra rings. These tetrahedra rings form so-called secondary building units (SBU), which are the most often used criteria for zeolite separation into different structural types.

One of the most distinguished types of natural structural zeolites is fajausite (FAU), for which the synthetic analogue is Na-X zeolites (its commercial names: X and 13X) [10]. A large channel diameter 0.74 nm and high content of sodium is characteristic of this type of structure. That makes zeolites an attractive material used in industrial purposes as molecular sieves and ion exchangers.

Zeolitic material (rich in Na-X phase), because of the presence of micropores and their large volume as well as high thermostability, may be useful in purification of water, wastewater, soil remediation [11, 12] purposes, entrapment of ^{137}Cs [13], and for adsorption of industrial gases. Previous studies have confirmed the high adsorption of SO_2, CO_2, and NH_3 on 4A-X zeolites synthetisized from fly ash [13-15].

A broad range of industrial applications has led to an attempt to synthesize zeolite material from fly ash using a process conducted in hydrothermal conditions under atmospheric pressure and low-temperature (atmospheric pressure and room temperature).

Experimental

Materials

Samples of fly ash used for synthesis were delivered from the Department of Technical Services and Recycling at the ZUTER Company. The fly ash is a result of energetic combustion of hard coal in the Kozienice Power Plant. The fly ash that was subjected to transformation into zeolitic material came from a unit of about 500MW power. The initial product was constituted using hard coal from KWK Bogdanka – Lubelski Węgiel Bogdanka S.A (in eastern Poland).

Synthesis Conditions

In previous laboratory works [16] concerning transformation of fly ash into zeolites, the synthesis conditions were analyzed. For the conducted processes they depended on the following parameters: concentrations of reagents (NaOH), and time and temperature of reactions. Concentrations of NaOH were changed within the range 2M to 4M, time of reaction was from 6 to 36 hours, and temperature ranged from 50ºC to 100ºC for hydrothermal reactions; for low-temperature synthesis, concentrations of NaOH were from 2M to 7M, and time of reaction was from 1 to 6 months. For all reactions room temperature (about 21-22ºC) was assumed.

After such experiments the most effective reactions with regard to percent of NaX in obtained in both reactions material were established. Therefore, for hydrothermal synthesis of zeolitic material the following methodological conditions of the process were applied: 20 g of fly ash was immersed in 500 ml 3M NaOH solution; the synthesis process was conducted for 24h at 75ºC. Furthermore, after such a cycle of reactions, the zeolitic material was rinsed a few times with distilled water in order to remove excess NaOH [16].

A low-temperature synthesis process was conducted under the following conditions: 20 g of fly ash was immersed in 800 ml 3M NaOH solution, the synthesis process was conducted for 12 months (from time to time the substrates of the reaction were mixed) at atmospheric pressure and room temperature [17].

Analytical Methods

The mineral composition of reaction products was determined *via* powder X-ray diffraction (XRD) using a Philips X'pert APD diffractometer (with the PW 3020 goniometer), Cu lamp, and graphite monochromator. The analysis was performed within the angle range of 5-65 2θ. Philips X'Pert and the ClayLab ver. 1.0 software were used to process diffraction data. The identification of mineral phases was based on the PCPDFWIN ver. 1.30 database formalized by the JCPDS-ICDD.

The morphology and the chemical composition of the main mineral components of the examined materials in the micro area domain were determined using the electron scanning microscope (SEM). The equipment used was a FEI Qanta 250 FEG scanning microscope, which was additionally equipped with a chemical composition analysis system based on energy dispersion scattering – the EDS EDAX.

Chemical composition of fly ash was determined by the XRF method. The Philips spectrometer PW 1404 was applied. Induction source was constituted by an XRD lamp with double anode (Cr-Au) with maximum power of about 3 kW.

Cation exchange capacity (CEC) of the zeolitic material was determined on the basis of the amount of Ba^{2+} ions saturated in the sample and desorbed by 1M $MgCl_2$. At firs the samples were divided into portions (from 33 to 500 mg) that were mixed with 10 ml of 0.1M solutions of $BaCl_2$ and shaken 30 min. This procedure was repeated 5 times. Next, by atomic absorption spectroscopy (AAS) the concentrations of Na, K, Mg, and Ca ions in the solution were determined. On the basis of obtained values, the values of mean CEC were calculated. In order to desorb Ba cations, washed and dried samples were treated with 1M $MgCl_2$ solution, and its contents were measured by AAS. The CEC values were calculated per weight of the dehydrated samples. This method is recommended by the international association AIPEA [16, 18].

Specific surface area as well as pore size and radius dependent on distribution were determined on the basis of the shape of nitrogen pairs in an adsorption/desorption isotherm at -196.15ºC temperature. The previously mentioned parameters of zeolitic material texture were determined after previous degassing of the sample under strictly controlled conditions at temperature (250ºC, during 24 h) and reduced pressure (10^{-3} hPa).

Previous experiments concerning determination of the specific surface area and pore size for these materials were carried out in temperatures ranged from 200 to 350ºC. The results have shown that the values of the specific surface area and pore size increased together with an increase of temperature [16]. Nevertheless, to this study only 250ºC was chosen because this values is standard for each material tested by means of an ASAP analyzer.

Specific surface area was determined on the basis of Braunauer-Emmett-Teller's multilayer adsorption theory (BET) at p/p_0 between 0.06 and 0.3 (p, p_0 – equilibrium pressure and saturation pressure of nitrogen). The volume of pores V_p was determined from the volume of adsorbed nitrogen at pressure $p/p_0 = 0.98$.

Diameters of pores D_p were calculated according to the equation $D_p = 4V_p/S_{BET}$. Distribution of pore volumes R_p was calculated using a general isotherm equation based on the combination of a modified Kelvin equation and a statistical thickness of adsorbed film. The texture of the zeolitic materials was examined on an ASAP 2405 Micromeritics analyzer.

Results

Mineralogical and Chemical Characteristics of Fly Ash

The chemical composition of the tested fly ash was determined by XRF method in Ancaster Laboratories, Canada. Those analysis revealed that the dominant components are SiO_2 52.12, Al_2O_3 32.19, Fe_2O_3 5.17, trace components: MgO 1.29, CaO 1.16, Na_2O 0.49, K_2O 2.87, TiO_2 1.38, P_2O_5 0.43, LOI = 2.60%. The ratio SiO_2/Al_2O_3 wt.% in the examined fly ash is 1.62, and the sum of main oxides indicates that the tested fly ash is an F-class fly ash (alumino-silicated) according to ASTM C618-08 [19].

Weight percentages of other components were determined following EU specifications (EN 450, EN 451) [20, 21]: chlorides – 0.001-0.01wt %; free CaO - 0.02-0.10 wt.%, pH 10.7.

Mineral composition of the tested fly ash is presented in Fig. 1. The main component is an aluminosilicated glass (Fig. 1A), which varies from 50 to 60% content range, with a very characteristic spherical form (Fig. 1B), mullite
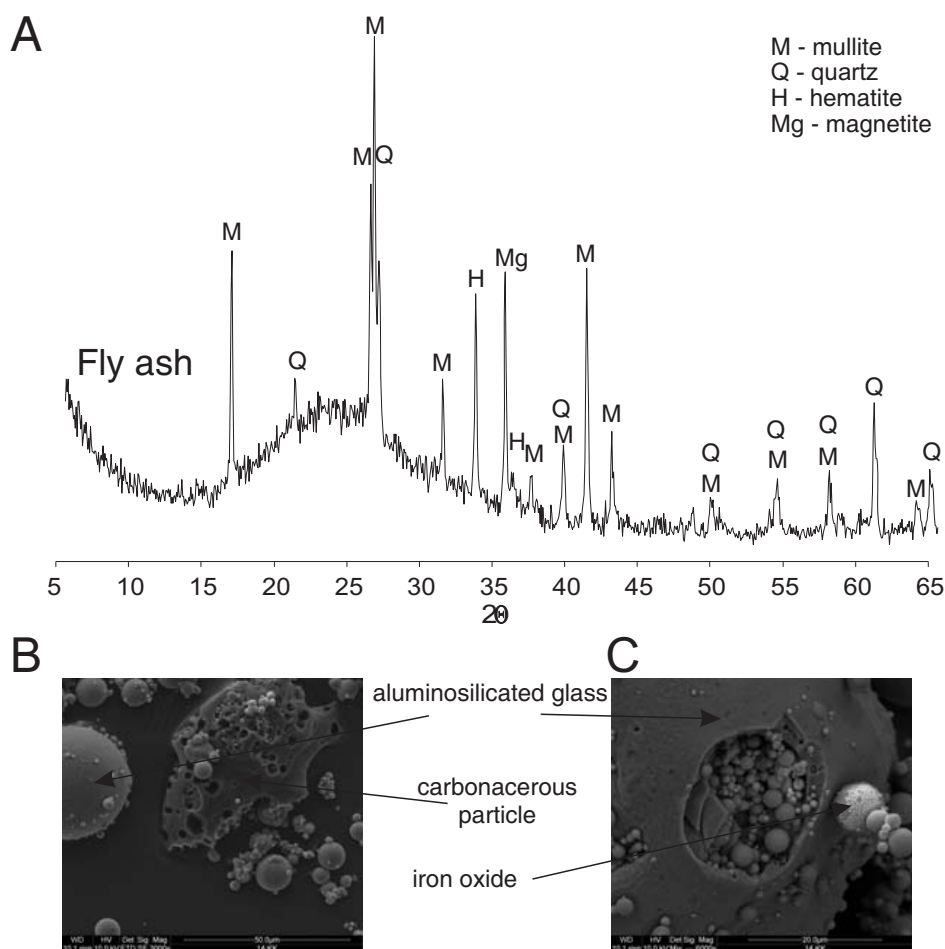

Fig. 1. Mineral composition of fly ash used for synthesis. A – XRD diffraction pattern, B – spherical forms of aluminosilicated glass and a fragment of carbonacerous particle, SEM, zoom 3000X, C – spherical form of glass, iron oxides on the glass surface, SEM, zoom 6000X.

(<30%), quartz (5-8%), and small amounts of uncombusted carbonacerous substances, Fe oxides – hematite, and magnetite (Fig. 1C).

Mineralogical Properties of Zeolitic Materials

The proposed methodology for conducting the reaction process of the fly ash with NaOH produced a zeolitic material that was predominantly Na-X in the case of low-temperature reaction and low-level amounts of sodalite in the case of a hydrothermal reaction. Moreover, quartz, mullite and remains of unreacted amorphic matter (see on X-ray diffraction patterns, Fig. 2A) were found to be the residuum in both conducted reactions.

The main identification method of the zeolitic phase was XRD analysis. Each crystal phase is characterized by a group of interlayers d-spacing. In the case of mineral mixtures it is important that in case of small amounts of mineral in the XRD diffraction pattern only the most intensive peaks are observed. The Na-X phase was identified on the basis of a group of characteristics for their reflections (d=14.47, 3.81, 5.73, 8.85, 4.42, 7.54, 4.81, 3.94), whereas

sodalite, because of a small amount in tested materials was recognized only on the basis of the most intensive reflections, d=3.63, 6.28, 2.81.

XRD analysis showed that residuum in both reaction constituted mullite that was recognized by the most intensive reflection (d=3.39, 3.42, 5.38) and quartz recognized by d=3.34 and 4.25. In XRD diffraction patterns of the zeolitic materials, background is lower within the range 15 to 30 (2 theta) than fly ash. This phenomenon is related to crystallization of zeolitic phase (mainly from aluminosilicated glass).

The morphological forms represented by Na-X zeolite in hydrothermal synthesis are often needle-like crystals about a few µm in size, creating a pattern resembling that like "skein of wool." It is worth noting that the occurrence of tile-shaped crystals was clearly much rarer (Fig. 2B). In the case of zeolite material obtained through low-temperature synthesis, the Na-X crystals that occur are predominantly of the needle like form, along with mineral aggregates, which are irregular in shape and at times observed to be somewhat tile/scale in their form (Fig. 2C).
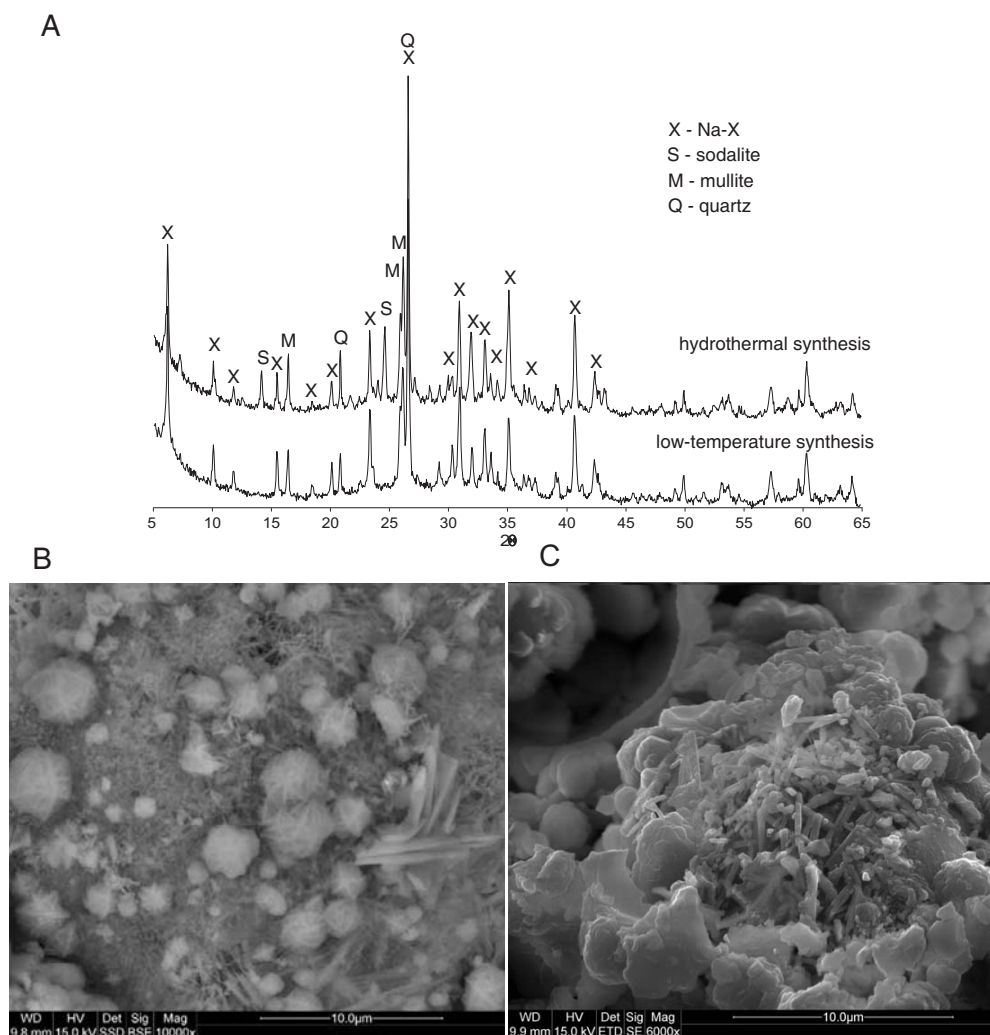

Fig. 2. Mineral composition of synythesis products. A – XRD diffraction patterns: X – main reflections are characteristic for Na-X zeolite, S – main reflections are characteristic for sodalite; B – SEM micropohotograph of zeolitic material obtained through hydrothermal synthesis, zoom 10000X; C – SEM micropohotograph of material obtained through low-temperature synthesis, zoom 6000X.

Table 1. Textural properties and CEC of fly ash and zeolitic material.

Materials	S_{BET} [1]	V_{mic} [2]	S_{mic} [3]	V_{mes} [4]	S_{mes} [5]	CEC avarage values
	[$m^2 \cdot g^{-1}$]	[$cm^3 \cdot g^{-1}$]	[$m^2 \cdot g^{-1}$]	[$cm^3 \cdot g^{-1}$]	[$m^2 \cdot g^{-1}$]	[meq/100g]
Fly ash	16.2	0.0005	2.04	0.0301	19.8	11
Hydrothermal Na-X	332.5	0.1426	238.04	0.1382	62.0	240
Low-temperature Na-X	259.9	0.1123	176.60	0.2201	66.2	200

[1] S_{BET} – BET equations based surface area, [2] V_{mic} – micropore volume, [3] S_{mic} – micropore area, [4] V_{mes} – mesopore volume, [5] S_{mes} – mesopore area

Chemical Characteristics of Zeolitic Materials

The synthesized zeolitic materials obtained from both methods are characterized by a similar chemical composition. Sodium is the main exchangeable cation in the structure balancing the charge of the aluminosilicate lattice. Average ratios of individual cations received as a result of sample microchemical EDS analysis are the following: Na+K/Si=0.55, Na+K+Ca+Mg/Si=0.60, Na+K/Si=0.65, Na+K+Ca+Mg/Si=0.79, Si/Al=1.12 for hydrothermal reaction, and Na+K/Si=0.52, Na+K+Ca+Mg/Si=0.68, Na+K/Si =0.56, Na+K+Ca+Mg/Si = 0.70, Si/Al=1.04 for low-temperature reaction.

Evaluation of CEC

The possibility for practical use of zeolitic material is mainly determined by cation exchange capacity and the textural parameters of the obtained material – which is indirectly related to the content of zeolite in the test material.

Ion exchange capacities CEC of zeolitic material obtained through hydrothermal synthesis are slightly higher, reaching amounts from 210 to 240 meq/100g, while for low-temperature synthesis they vary from 180 to 220 meq/100g. This parameter is about 20 times higher than CEC of fly ash, which in this case varies from 10 to 12 meq/100g. Despite the satisfactory potential in ion exchange capacity of the fly ash by itself, products of their zeolitization ensure much better ion exchange possibility, which in turn allows for the use of the obtained materials in different types of wastewater and industrial waste material treatment processes.

Textural Parameters

The textural properties of the obtained zeolitic materials are shown in Table 1. Adsorption/desorption isotherm of N_2
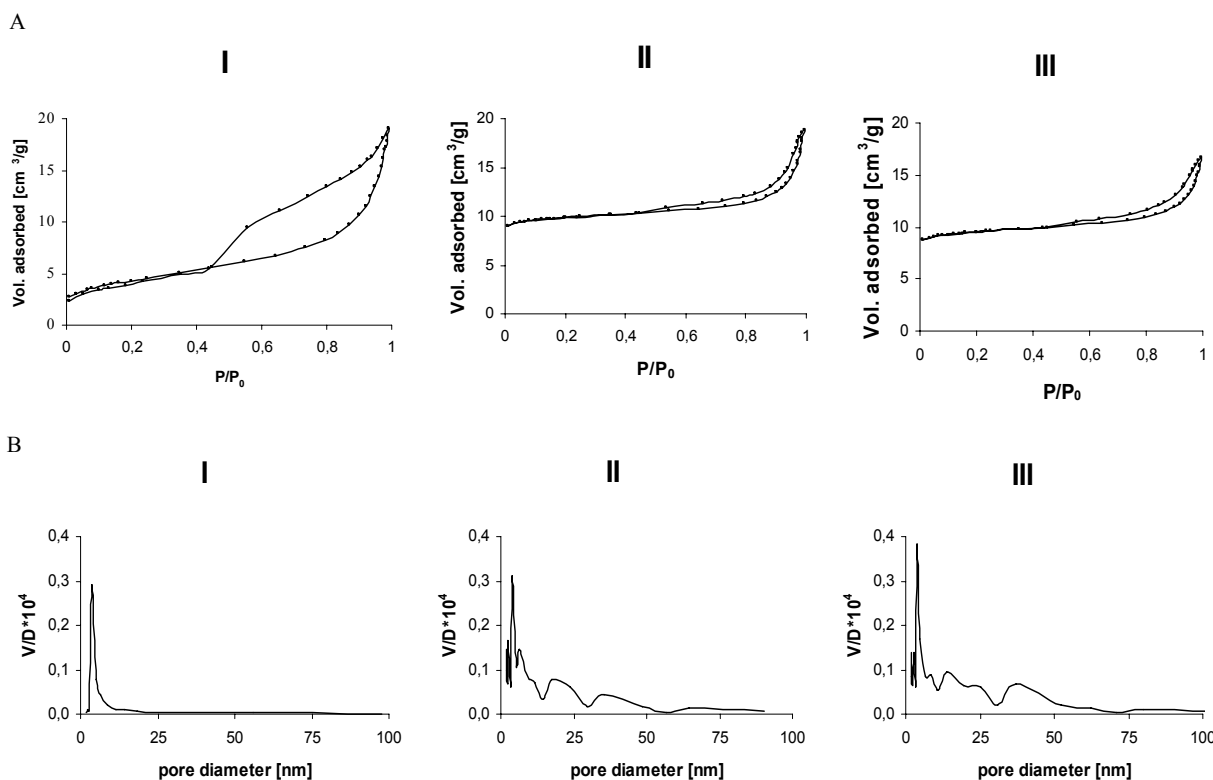

Fig. 3. Textural result curves. A – Adsorption/desorption isotherm of N_2 (-196.15ºC): I – fly ash, II – hydrothermal Na-X, II – low-temperature Na-X; B – BJH desorption pore size distributions (nm), in V/D×10^4: I – fly ash, II – hydrothermal Na-X, III – low-temperature Na-X.

for fly ash represents II type (according to IUPAC [22]). This type of isotherm is characteristic of macroporous materials and corresponds to a situation when at low compressibility relative to the adsorbate on the surface of the adsorbent (fly ash), a monomolecular layer (N_2) is formed. Furthermore, at higher pressure the multimolecular layer could be formed. Low surface area and low volume of pores at its relatively large diameter (Fig. 3A-I) indicate that the fly ash used for synthesis possesses a microporous structure.

Adsorption isotherms obtained for tested zeolitic material could be classified as type I (so-called Langmuir isotherm), adsorption increases within the range of low relative pressures rather than in the case of fly ash. This is an indication of a definite growth in the number of micropores, which is one of the defining features of zeolitic material (Figs. 3A-I, 3A-II).

Specific surface area calculated by the BET method increases significantly after the zeolitization process because of the texture of micropores of zeolite structure. Specific surface area for the hydrothermal material equals 332.5 m^2/g and it is slightly larger than with respect to the low-temperature variant by 73 m^2/g. The methodology of quantitative determination of Na-X content in the obtained material on the basis of surface area, micropore volume, and micropore surface [17] indicates that the amount of Na-X phase in the material obtained through hydrothermal synthesis ranges from 55 to 60% and 42 to 55% for low-temperature synthesis.

Pore size distribution PSD determined on the basis of BJH calculation (Barrett-Joyner-Halenda method) is correct for those mesopores that fall within the range from 1.7 to 300 nm and indicate an increase of pore volume (Table 1). Pore size distribution in tested samples of zeolitic material and fly ash is shown in Fig. 3B (I-III). It can be observed from the PSD that the dominant part of pores have a 4 nm diameter. Desorption BHJ curves show significant capillary condensation in the mesopore range.

Conclusions and Potential Applications

Literature describes the many methods for transforming fly ash into zeolitic material. Depending on fly ash (different content of SiO_2), reagent type (NaOH, KOH), and methods of transformation (selection of suitable parameters, e.g. temperature and reaction time); the different obtained zeolites include: X [13, 23], P [6, 24], and Na-P1 [25], etc. Synthesis of zeolites on a laboratory scale (hydrothermal and low-temperature synthesis) allows to optimize in detail the reaction conditions. Concentrations of reagents oscillate from 0.1 M to 8 M, times of reaction are from 0.5h to a few months, and temperature spans from room temperature to 350ºC. Sometimes such experiments are conducted in higher pressure [26]. Nevertheless, the main aim of each method is to obtain the most optimal (economical and effective) conditions of reaction, where final products contain as many zeolites as possible and as little as possible residuum.

Both of the proposed methods of fly ash zeolitization result in a material that is rich in Na-X phase. The hydrothermal method requires only 24 hours of the reaction time in order to produce sorbent containing about 60% zeolite phase. On the other hand, material obtained by low-temperature reaction method (12 months) is characterized by a lower Na-X phase content (max. 55%). But when the production of zeolites on an industrial scale is planned, this method seems be better. Room temperature of reaction could lower energy costs. Also, when lower temperature is applied, the reactor systems does not need a system of heating that can add costs.

Therefore, the next step should be to conduct low-temperature experiment using seawater, especially how that the first experiments are in progress.

Due to high CEC of zeolites, adsorption of heavy metals may be feasible. Zeolitic material rich in Na-X phase synthesized from fly ash does not have a quality and effectiveness comparable to commercial 13X zeolite, which is produced from pure reagents. However, it could be employed as a cheaper substitute in technologies that do not require adsorbents with high purity.

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