

The conversion technology of fly ash into zeolites

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Abstract This paper presents a sub-pilot scale process of synthesis of Na-P1 zeolite from the coal fly ash. After establishing the appropriate synthesis conditions (20 kg of fly ash, 12 kg of NaOH, 90 dm³ of water, the reaction temperature: 80 °C and reaction time: 36 h), the high-purity (81 wt%) Na-P1 zeolite product was obtained. Its chemical, mineralogical, and textural properties were determined (by means of XRD, XRF, SEM–EDS and ASAP 2020). The synthesized material has a specific BET surface area (88 m²/g) c.a. six times higher than the fly ash from which it has been derived (15 m²/g). The pore-size distribution indicates a mesoporous character of the obtained zeolite, with the following pores size contents: micropores (2.76 %), mesopores (61.81 %), and macropores (35.43 %). The presented technological/production line is fully automated and allows to regulate the conditions of the synthesis process, therefore different types of zeolite materials (including: Na-X, Linde-A, and Na-P1) can be obtained using the same equipment.

Keywords Technological line · Fly ash · Na-P1 · Synthesis reaction

Introduction

Zeolites are micro and mesoporous hydrated aluminosilicates of alkali elements, alkaline earth metals, or other cations. Their structure is built up with a framework of tetrahedral molecules, linked with shared oxygen atoms (Merrikhpour and Jalali 2013). Their crystal structure contains numerous channels and chambers of different sizes (in the order of several angstroms) giving them a range of unique ion-exchange, sorption, molecular-sieve, and catalytic properties (Derkowski et al. 2006, 2007). Due to their unique properties, zeolites have found application in many branches of industry: in agriculture (e.g. Polat et al. 2004), medicine (Andronikashvili et al. 2009), chemical technology [i.e. desulfurization of fuel (Muzic et al. 2012) or oil refining (Zhu et al. 2013)], and environment engineering [i.e. to remove of ammonium ions (Franus and Wdowin 2010; Liu et al. 2012) or heavy metals from waters and waste water (Merrikhpour and Jalali 2013; Wang et al. 2009) or separation/adsorption of gases such as CO₂ (Walton et al. 2006; Wdowin et al. 2012), SO₂ (Yi et al. 2012) or mercury (Morency et al. 2002), and removal of radionuclides from the mine waters (Chalupnik et al. 2013)].

Natural zeolites are represented by more than 100 mineral forms. They are formed in different geological environments (magmatic, sedimentary, and metamorphic). However, only some of them (among others clinoptilolite, mordenite, philipsite, or chabazite) occur in a formation that can be viable for extraction and processing.

At the end of the last century, the technologies of manufacturing synthetic zeolites started to develop with great intensity. They allow us to obtain zeolites with specific structure parameters, which qualify them for particular industrial applications (including as selective molecular

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sieves). Synthetic zeolites can be produced from numerous resources such as:

- Clay minerals: bentonite (Faghihian and Godazandeha 2009), kaolin (Ismael 2010), illite–smectite (Baccouche et al. 1998),
- Minerals from the group of silica: perlite (Christidis and Papantoni 2008; Pichór et al. 2014), diatomite (Höllén et al. 2012),
- Waste materials such as coal fly ash (Derkowski et al. 2006, 2007; Izidoro et al. 2013; Querol et al. 2002; Steenbruggen and Hollman 1998; Yadav and Manyar 2005).

As natural zeolites generally require costly modifications in order to be applied in industry, the synthetic zeolites are considered to be more desirable mineral resource for industrial applications. However, as the process of zeolite synthesis is also associated with substantial costs inexpensive mineral or waste materials, such as fly ash, should be used as a substrate for the synthesis reaction (Franus and Wdowin 2011).

The possibility of using hard coal fly ash (conventional and fluidised bed combustion), as well as brown coal for the synthesis of zeolite materials has been intensively investigated in the recent years. Depending on synthesis condition, it is possible to obtain various types of zeolitic materials.

Literature and data show that by using appropriate synthesis conditions, coal fly ash can be converted into different zeolite structures such as analcime (Adamczyk and Bialecka 2005; Querol et al. 1997; Wang et al. 2003), chabazite (Wang et al. 2003), cancrinite, gmelinite, Na-P1 (Adamczyk and Bialecka 2005; Hollman et al. 1999; Wang et al. 2003), ZSM-5 (Mohamed et al. 2008), ZSM-28 (Wang et al. 1998), Na-X (Derkowski et al. 2006, 2007; Franus 2012; Querol et al. 1997; Tanaka et al. 2002), Na-Y (Ojha et al. 2004), philipsite (Querol et al. 1997), and sodalite (Musyoka et al. 2011).

Though many laboratory researches have been devoted to the conversion of fly ash into zeolites, there is little research concerning the implementation of this process at a pilot-plant or industrial scale (Kikuchi 1999; Mainganye et al. 2013; Moutsatsou et al. 2008; Querol et al. 2001). However, those scaled up processes were either very simplified (Mainganye et al. 2013; Moutsatsou et al. 2008) or over complicated (Kikuchi 1999). In addition, the weight percent of pure-zeolite phase in the synthesized materials was relatively low (30–40 wt%) (Querol et al. 2001).

Following successful conversion of class F coal fly ash into synthetic zeolites (on the laboratory scale), a prototype of a technological line for this kind of process has been constructed. After numerous tests, the process line has been optimized and its current state is described in this paper.

Material

F-class fly ash from the combustion of coal at the Rybnik power plant in Poland was used as a substrate for the synthesis reaction of the zeolite material. The chemical composition of this fly ash consists predominately of SiO₂ (52 %), Al₂O₃ (32 %), and Fe₂O₃ (5 %), respectively. The rest of the chemical components occurs in insignificant amounts (Franus 2012).

The mineral composition is dominated by spherical forms of aluminosilicate glass (68 %) and mullite (22 %). In addition, quartz and iron oxides (in the form of magnetite and hematite) have been observed on the surface of the aluminosilicate spheres (Fig. 1).

Methods

The chemical and mineral composition of substrates and products were determined by using a scanning electron microscope SEM–EDS and X-ray method, respectively. Textural characterization of the materials was carried out with a low-temperature nitrogen adsorption–desorption method.

The mineral composition was determined via powder X-ray diffraction (XRD) method using a Philips X'pert APD diffractometer (with a PW 3020 goniometer), Cu lamp, and a graphite monochromator. The analysis was performed within the angle range of 5–65 2 θ . Philips X'Pert Highscore software was used to process the diffraction data. The identification of mineral phases was based on the PDF-2 release 2010 database formalized by the ICDD.

The morphological forms and the chemical composition of the main mineral components were determined by the means of a scanning electron microscope (SEM) FEI Quanta 250 FEG equipped with a system of chemical composition analysis based on energy dispersive X-ray-EDS of EDAX company.

The chemical composition of the fly ashes used for the synthesis reactions was determined by XRF method with the use of a Philips spectrometer PW 1404. An X-ray tube equipped with dual Cr–Au anode with a maximum power of 3 kW was the excitation source.

Nitrogen adsorption–desorption measurements were carried out at 77 K using an ASAP 2020 volumetric adsorption analyzer (Micromeritics). The BET specific surface areas (S_{BET}) of the investigated samples were evaluated using the standard Brunauer–Emmett–Teller (BET) method for nitrogen adsorption data in the range of relative pressure p/p_0 from 0.06 to 0.3. The total pore volumes were estimated from single-point adsorption at a relative pressure of 0.98. The pore-size distributions were

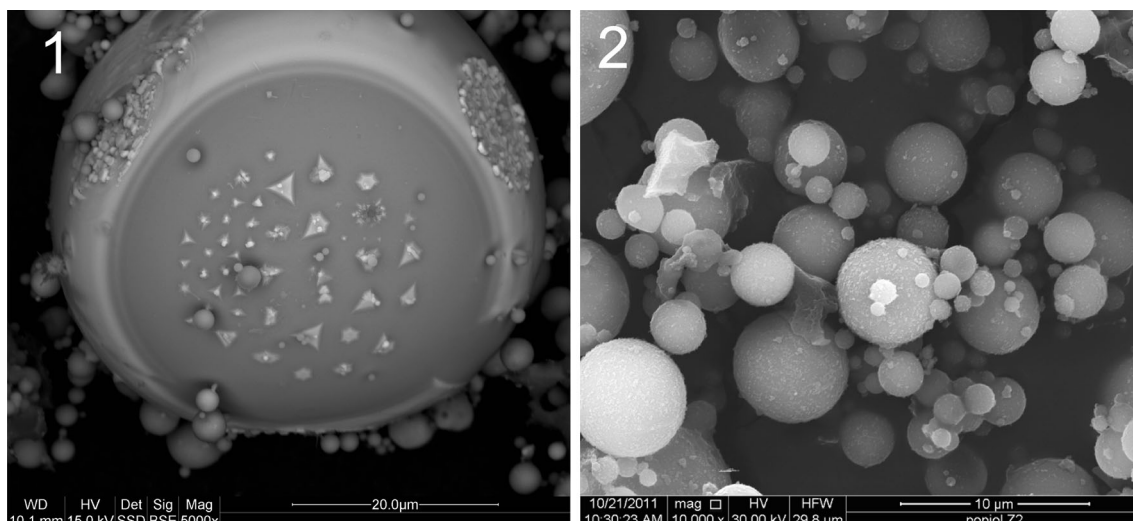


Fig. 1 SEM images of fly ash used for the synthesis. 1 Magnification 5000×, 2 magnification 10000×

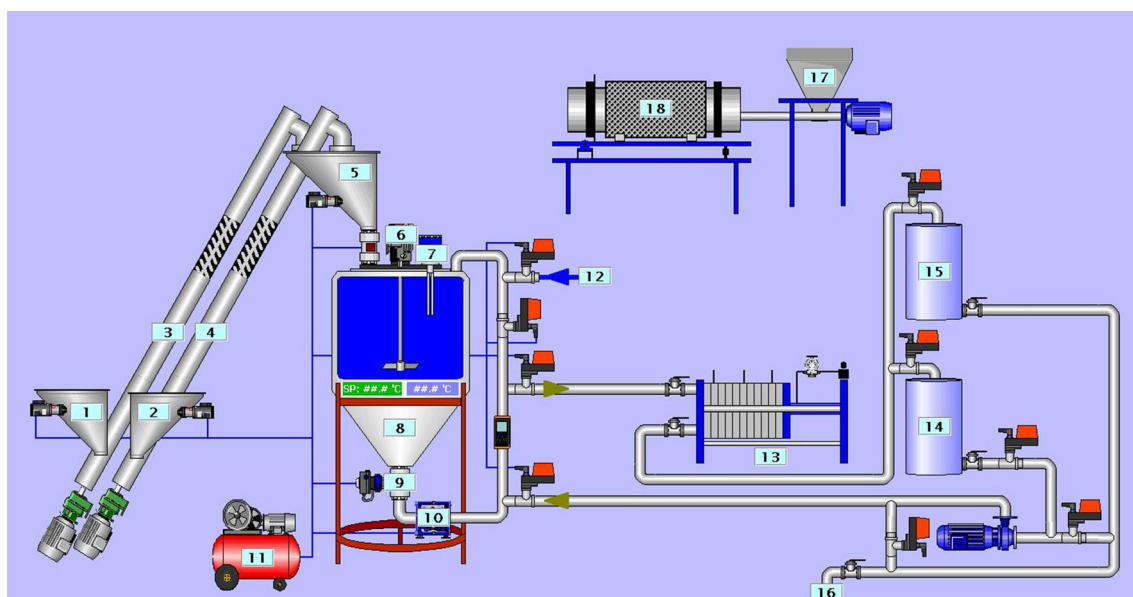


Fig. 2 Technological scheme of the prototype line for the synthesis of zeolites: 1 NaOH storage tank with the vibrator, 2 fly ash storage tank with the vibrator, 3 screw conveyor transporting NaOH, 4 screw conveyor transporting fly ash, 5 weighting tank suspended on three-strain gauge weight sensors with the vibrator, 6 mechanical stirrer, 7 heater with the control system of the reactants level and reaction

temperature, 8 reaction vessel, 9 pneumatic membrane valve, 10 membrane pump, 11 compressor, 12 water supply with the control volume by means of flowmeter, 13 hydraulic press, 14 NaOH aqueous solution of the synthesis reaction, 15 water solution from flushing of zeolite material in the press, 16 waste for disposal, 17 feed to the calciner, 18 calciner

obtained from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) procedure.

Technological line for the conversion of fly ashes into zeolites

Figure 2 presents the photography of a device for the production of zeolites at a pilot-plant scale. The synthesis process

can be divided into four stages: a stage of the reactor loading, a reaction stage, a stage for the separation of reaction products, and a stage for final processing of the obtained material.

The stage for the reactor loading takes place in two storage tanks, where granulated NaOH and fly ash are stored. These tanks are connected with a weight tank by means of two worm gears; the purpose of each worm gear is the transport of fly ash and sodium hydroxide granules from the storage tank to the weight tank.

The tank is made of stainless steel. It has the shape of a converse cone-head ended by a roller. In order to avoid excessive dusting of the room, the tank is closed by a cap. To provide suitable amount of substrates for the synthesis reaction, the tank is mounted on three-strain gauge weight sensors. In order to improve the drop of substrates (NaOH, fly ash) to the synthesis reaction tank, the worm gears and the weight tank are equipped with pneumatic piston vibrators.

The conversion process of fly ash into zeolites takes place in the reaction tank which is the main component of the described line. The total volume of the tank is 130 dm³ (working volume is 100 dm³). The tank is equipped with a system of three heaters (2 kW each), a probe for controlling the reaction temperature, and the level of tank filling probe, and a stirrer that is sequentially switched on and is responsible for the homogenization of the material and prevents the aggregation of the material during the reaction process. A pneumatic membrane that pumps the zeolite material during and after reaction is installed at the tank outlet.

The separation of the products block consists of a filter press and two tanks in which the post-reaction aqueous solution of NaOH as well as materials rinsing solution are stored. The aqueous solution from the first rinsing of the reaction products is directed to the storage tank and then pumped back to the reactor for further synthesis. The solution from rinsing is returned to its original composition and is directed to the next reaction cycle.

The volume of water during loading and the volume of solution after modification process and recycling are controlled by flowmeters.

The final processing stage occurs in a ribbon feeder and a rotary furnace. The rotary furnace is used to dry the zeolite material obtained by filtration of the solution and for its calcination.

The whole process is fully automated and controlled by a computer, and touch screens are located in the cabinets of each technological blocks.

Mineral characterization and textural properties of the obtained zeolite

By using the designed technological line, a number of zeolite synthesis reactions were carried out. The monomineral zeolite Na-P1 was obtained in the following reaction conditions: 20 kg of fly ash, 12 kg NaOH, 90 dm³ of H₂O, temperature of the process 80 °C, and duration 36 h. Obtained zeolite materials were fully characterized by scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), powder X-ray diffraction, and nitrogen adsorption–desorption isotherm.

Diffraction patterns that show the mineral composition of the zeolite material are presented in Fig. 3. The presence of

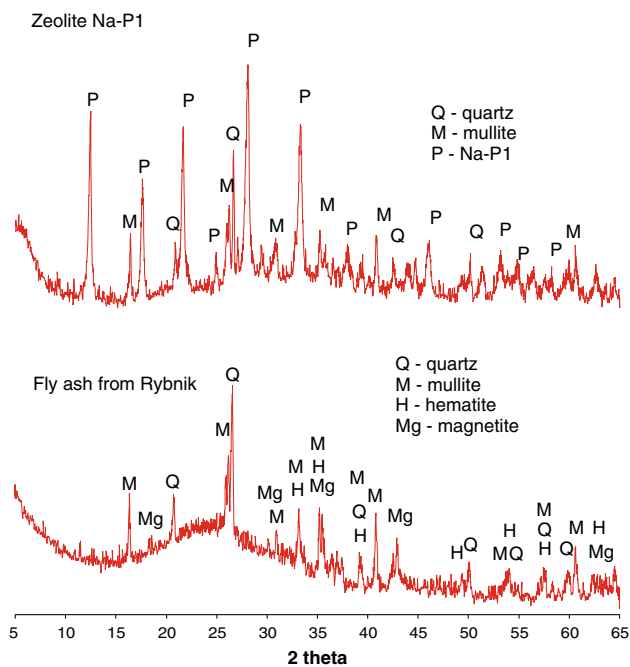


Fig. 3 X-ray diffraction patterns of fly ash and zeolite material. 1 Fly ash EC Rybnik, 2 zeolite material. Clarifications: *P* Na-P1, *Q* quartz, *M* mullite, *H* hematite, *Mg* magnetite

Na-P1 zeolite phase in the reaction products was determined based on the characteristic interplanar distances $dhkl = 7.10; 5.01; 4.10; 3.18 \text{ \AA}$. The content of pure-zeolite phase in the product obtained under given conditions was 81 %.

The morphologies of the fly ash used for the synthesis reaction and the obtained zeolite Na-P1 are shown in Fig. 4. Chemical analysis in the micro-area revealed that sodium is the main-exchange cation in the zeolite structure, which balances the charge of aluminosilicate framework. Average ratios of individual cations obtained by EDS are as follows: $\text{Na} + \text{K} + \text{Ca} + \text{Mg}/\text{Si} = 0.44$; $\text{Si}/\text{Al} = 1.42$.

Textural properties [nitrogen adsorption–desorption isotherms and pore-size distributions (PSD) obtained by BJH method] are presented in Fig. 5.

Fly ash has a low-specific BET surface area (15 m²/g). Nitrogen adsorption–desorption isotherm for fly ash can be classified as type II isotherm according to the IUPAC classification and is characteristic for macroporous materials with relatively small-specific surface area. In addition, the pore-size distribution indicates a low porosity of fly ash.

Whereas, Na-P1 zeolite has a BET specific surface area of 88 m²/g, which is almost six times higher with respect to fly ash. A high-specific surface area is preferable for providing large adsorption capacity, so it means that zeolite may be used as adsorbent of many pollutant in such as heavy metals, radionuclides, or some gases etc. Its nitrogen adsorption–

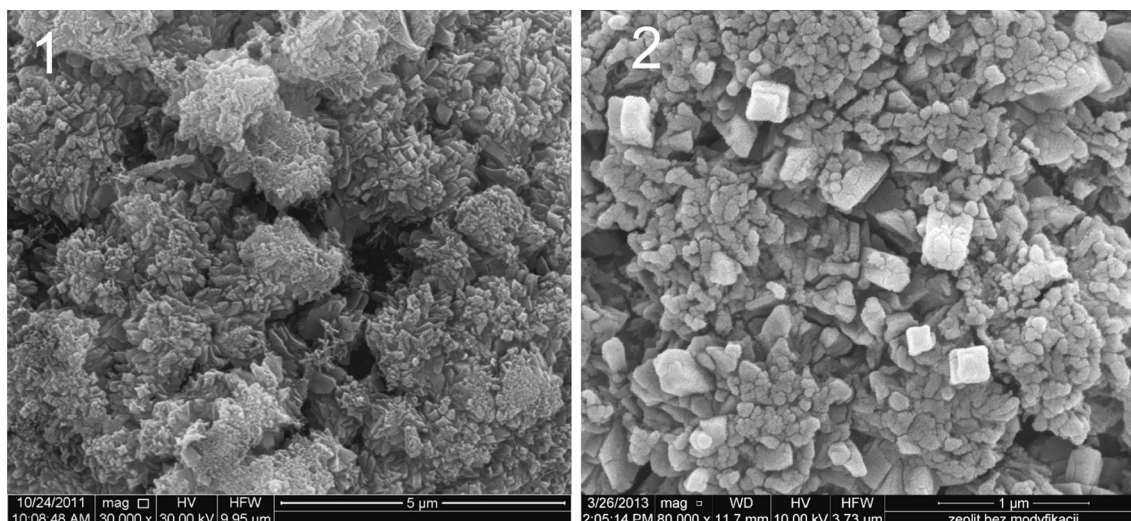


Fig. 4 SEM images of zeolite Na-P1. 1 Magnification 30000×, 2 magnification 80000×

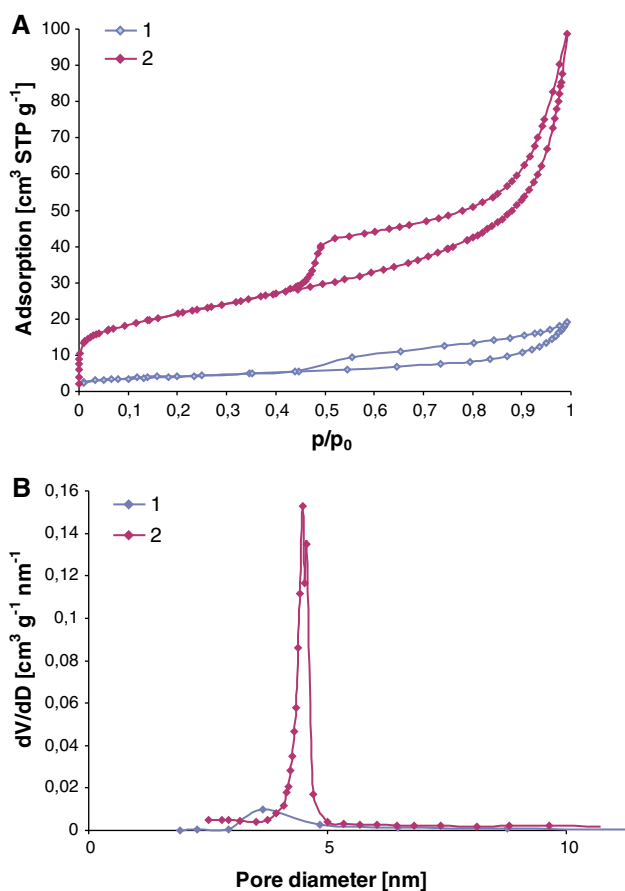


Fig. 5 Textural properties of the materials: 1 fly ash, 2 Na-P1. **a** Nitrogen adsorption/desorption isotherms, **b** pore-size distribution

desorption isotherm shape can be classified as IV type (with hysteresis loop) in IUPAC classification which is associated with capillary condensation in mesopores. The shape of the

hysteresis by de Boer (1958) indicates the type B, which is related to the presence of “bottle shape” pores. The hysteresis loop is most similar to the H3 type in IUPAC classification, which is characteristic for mesopores in the shape of narrow slits. The pore-size distribution by BJH indicates a mesoporous character of the material, where the contribution of individual pores is as follows: micropores (2.76 %), mesopores (61.81 %), and macropores (35.43 %).

Conclusions

The technological line presented in the paper offers promising and long-term results in the search of new solutions for the utilization of waste materials such as fly ash. This line is fully automated and allows to synthesize the high-purity Na-P1 (zeolite content 81 wt%) from the coal fly ash in a very effective and efficient way. The obtained material is mainly mesoporous (c.a. 61 %) and has approximately six times higher the specific BET surface area than the fly ash from which it has been synthesized. These properties indicate a possibility to use the Na-P1 zeolite as an adsorbent for many pollutants, including heavy metals (Wang et al. 2009), radionuclides (Chałupnik et al. 2013), or gases such as CO₂ (Walton et al. 2006).

After changing the synthesis conditions, the same line has been successfully used to produce other types of zeolites such as Na-X and Linde-A.

In summary, the described technological line has some advantages and originality in comparison to previously described systems (Kikuchi 1999; Mainganye et al. 2013; Moutsatsou et al. 2008; Querol et al. 2001). It has full automation of the systems and the what is important zeolite product of reaction have high-purity average 61 %wt of

zeolite. Additionally, the system is enabled to change the condition of reactions simultaneously allowing to obtain various types of zeolite.

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