

# Hydrothermal Synthesis of Zeolites from Polish Coal Fly Ash

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## Abstract

A method for the synthesis of NaP1-type zeolite and analcime from Polish fly ash derived from hard coal combustion in pulverized-fuel boilers is applied in this paper. The zeolite synthesis was performed from Opole Power Plant fly ash (Elektrownia Opole S. A.), which were activated with aq 3.6% Na<sub>2</sub>O (1.16 M NaOH) solution within 80 to 320°C. The NaP1-type zeolite and analcime crystallize at 120°C. As the synthesis temperature increases, the NaP1-type zeolite content rises, and for temperatures of 200 to 320°C the analcime share in the synthesis products becomes significant.

The synthesizing capability of zeolites from fly ash has a positive impact on utilization of wastes coming from solid fuel combustion by converting the fly ash into valuable raw material and, simultaneously, accomplishing the lithosphere protection effect.

**Keywords:** fly ash, zeolite, analcime, NaP1, synthesis.

## Introduction

The increasing requirements in the sphere of environmental protection have induced search for more effective, inexpensive and ecologically safe solutions. For the last few years there has been much interest in zeolites, which are molecular-sieve and have sorptive and ion-exchange properties. Zeolites, thanks to properties resulting from their structure, are used in a wide range of environmental engineering processes: from water conditioning and sewage treatment (removal of ammonium ions, radioactive elements, heavy metals, oil-derivative contaminants) to adsorption of water and gases in agriculture and other applications.

Demand for an easily accessible and inexpensive source of zeolites has raised interest in synthesis of these minerals [1-5, 21]. Also, fly-ashes have turned out to be

useful raw material for this purpose [6-15]. The extraction of natural zeolite deposits, despite even better parameters of zeolites, is more expensive and causes considerable degradation of the environment.

Disposal and storage of wastes from the coal combustion process is a large problem to the power generation industry. 39.7 Mt of coal furnace wastes were generated in Poland in 1998-2000. Ash-and-slag mixtures had the largest share (68.5 per cent which accounts for 27.2 Mt) of wastes. Fly-ash from hard coal combustion (12.5 Mt) constitute the remaining part [16]. Currently about 65 percent of furnace wastes are utilized. The dumped fly ash may be a significant resource for zeolite production. Such secondary utilization of the wastes supports activities aimed at lithosphere protection being consistent with guidelines to so-called balanced development. The zeolitization would recycle in small fraction of coal fly ash production, but the product would have a higher added value than current applications.

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The zeolite synthesis in the process of hydrothermal, alkaline activation of fly-ashes produced by the power generation industry is an alternative for the traditional disposal of wastes [16]. A trial to perform such a synthesis process devised by prior studies [6, 8, 11] based on fly-ash from the Opole Power Station, south Poland, is applied in this paper.

## Experimentals

The process of zeolite synthesis was performed on fly-ash samples from the Opole Power Plant. The chemical composition of the ash, for the major oxides present in it, has been determined with the help of an X-ray fluorescence (XRF) method. Mineral constituents were also identified (transmitted light microscopic, X-ray diffraction).

The process was carried out in order to optimize the zeolite synthesis conditions, i. e. to get as much zeolite as possible in a short time [17]. Preliminary activation of the fly ash was carried out at room temperature with NaOH solution, calculation in% Na<sub>2</sub>O. On the bases of information from references and initial experiments (conditions of experiments: time – 6-48 h, concentration – 0.6-4.6% Na<sub>2</sub>O, liquid/solid ratio – 4:1 – 7:1 g/ml and fixed temperature 120°C) it was found that the best results received to 6 h, concentration 3,6% Na<sub>2</sub>O (1.16 M NaOH), liquid/solid ratio 6:1 g/ml (100 g sample size of fly ash in each experiment). In the following experiments these parameters were fixed but the temperature was variable.

The true process of zeolitization of the ash suspension was carried out in a 1l PROLABO autoclave with a stirring (electromagnetic system) with pressure and temperature control (Fig. 1). The synthesis conditions were: temperature 80, 120, 140, 150, 170, 180, 200 and 320°C

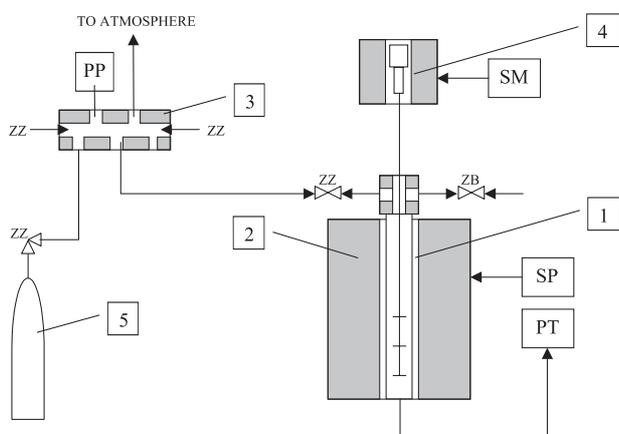


Fig. 1. The autoclave equipment. Description: 1-autoclave, 2-furnace, 3-changeover switch, 4-mixer drive, 5-cylinder, SM-mixer controller, SP-furnace controller, ZZ-cut-off valve, ZB-safety valve, PT-temperature measurement, PP-pressure measurement.

at 6h reaction time. The process pressure was equal to the pressure of the steam generated in the course of heating the suspension.

After the process completion, the solution containing products of synthesis was cooled to room temperature and then decanted. After decantation, the zeolitization product was rinsed with hot distilled water in order to remove the excess NaOH and then was dried at 100°C. Next, a grain-size analysis was performed with the use of a LAU-10 laser analyzer. The identification of mineral components of the fly ash before the synthesis and of the synthesis products was performed using the following methods:

- transmitted light microscopic examination on Zeiss AXIOSKOP mineralogical microscope,
- X-ray-diffraction on HZG4 diffraction apparatus using a Cu lamp, at 4 to 50° 2-theta range,
- derivatographic analysis on Paulik-Paulik-Erdey derivatograph, at: TG-200, DTG-1/5, DTA-1/5, T-1000°C, sample mass-400mg, time-100 minutes. Cation exchange capacities (CEC) were determined for all zeolitic product using ammonium solutions following the methodology of the International Soil Reference [18].

## Results and Discussion

The chemical composition of the fly ash was presented in Table 1. Predominant chemical components of the fly ash are SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. This fly ash has a high Al/Si ratio when compared with most fly ashes. High content of the compounds has an advantageous influence on the process of zeolitisation. Among the remaining components only the contents of MgO and Fe<sub>2</sub>O<sub>3</sub> exceed 6 wt%, whereas the rest appear in small quantities.

The following mineral components were identified in

Table 1. Chemical composition of fly ash from the Opole Power Plant.

Chemical compound	Content [% wt]
SiO <sub>2</sub>	47.09
Al <sub>2</sub> O <sub>3</sub>	33.13
Fe <sub>2</sub> O <sub>3</sub>	6.56
CaO	3.84
MgO	6.07
Na <sub>2</sub> O	0.25
K <sub>2</sub> O	0.11
H <sub>2</sub> O	0.52
Stotal	0.35
LOT	2.39
Total	99.93

the fly ash by means of transmitted light microscopy: quartz, mullite, glass, magnetite, hematite as well as unburned coal grains.

The size of quartz grains ranges from 20  $\mu\text{m}$  to 250  $\mu\text{m}$ , yet 20- $\mu\text{m}$  grains predominate. They have shapes diversified from sharp-edged and elongated to oval and spherical forms but grains of a nearly globular shape prevail. In the thin cross-section the mineral shows transitional light dimming. Some grains have very slight anisotropy, which resemble the high-temperature forms of  $\text{SiO}_2$ , i. e. tridymite or cristobalite. The size of mullite grains ranges from 60  $\mu\text{m}$  to 420  $\mu\text{m}$ , mostly showing characteristic pillar-like, single forms. The mullite is colourless and shows cleavage according to (010), that was observed only in large crystals.

The diameters of glass grains range from 10 to 100  $\mu\text{m}$ . The glass occurs most often in spherical (Fig. 2) or almost spherical concentrations, but also spheroidal forms happen. Most often the glass is colourless but yellow, slightly brown, or greenish forms were observed (particularly spherical concentrations). Inclusions of magnetite and organic substances often occur in the glass.

The size of magnetite grains ranges from 5 to 15  $\mu\text{m}$ . Magnetite occurs in the form of nearly spherical grains. Individual magnetite grains may be surrounded by a hematite rim, resulting from magnetite oxidation, showing red and brown internal reflections. Hematite grain sizes range from 5 to 10  $\mu\text{m}$ , sporadically to 1000  $\mu\text{m}$ . Most often, it occurs in the form of spheroidal aggregates or the above-mentioned rims.

Undurned coal particles mostly take irregular and jagged forms. The size of grains ranges from 22 to 150  $\mu\text{m}$ .

Mullite and hematite were identified in the initial sample of the fly ash by means of x-ray diffraction. The rise in background angle at 11-19° 2-theta (Fig. 3) indicates the occurrence of an amorphous substance (glass and not uncombusted coal).

The thermal analysis curves obtained for initial sample (Fig. 4) are typical for fly ashes, i. e. show minimum loss of mass (no thermal effects on the DTG curve), very slight thermal effects on the DTA curve, resulting from burning out of organic matter, as well as from transformation of glass.

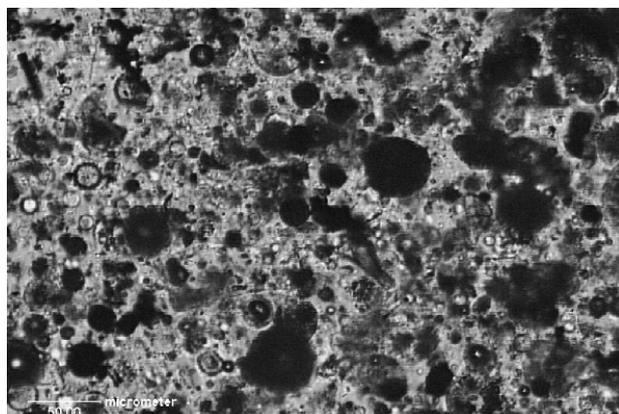


Fig. 2. Microphotograph of raw fly-ash from coal combustion plant, transmitted light, parallel polars, magn. 200x.

Results of a grain size analysis of the post-synthesis products were presented in Fig. 5. The results show the prevalence of the 10-20  $\mu\text{m}$  size range, which in each sample constituted >30% mass, with the exception for the product produced at 180°C. In the latter case, the 40-50  $\mu\text{m}$  size range has the largest share – 23% mass. The grain size distribution curve of each of the tested synthesis samples shows two distinct peaks, indicating domination of two size ranges: 5-15  $\mu\text{m}$  and 35-60  $\mu\text{m}$ . Moreover, there is a clear trend to decrease the share of the 35–60- $\mu\text{m}$  size range in favour of finer sizes. It seems that the main reason for this is dissolution of glass and mullite during synthesis process, simultaneous with crystallization of small size zeolites.

Synthesis at temperature of 80°C leads to an almost complete decomposition (dissolution) of glass, which is indicated by a flattening of diffraction background within the 11-19° 2-theta angle (Fig. 3). It seems that the presence of NaOH in the solution plays the most important role in the dissolution of the glass. The microscopic examination also showed the effects of glass dissolution in the shape of irregular boundaries as a result of chemical corrosion of the spherical aggregates. Moreover, at 80°C mullite and quartz also are dissolved.

Diffraction pattern of the material synthesized at 120°C points to the presence of mullite and hematite reflections; however, reflections of analcime appear for the

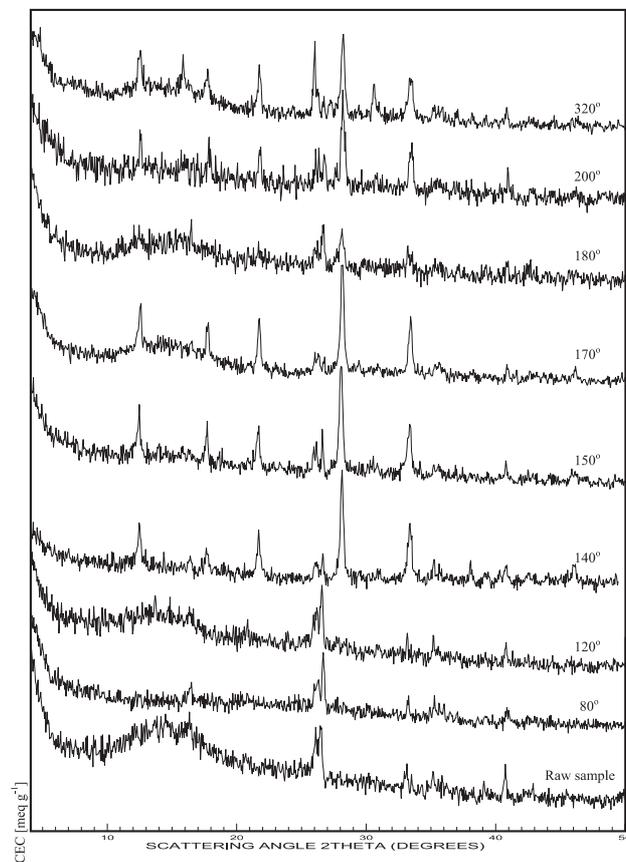


Fig. 3. Diffraction patterns of synthesis products based on fly-ash from Opole Power Plant.

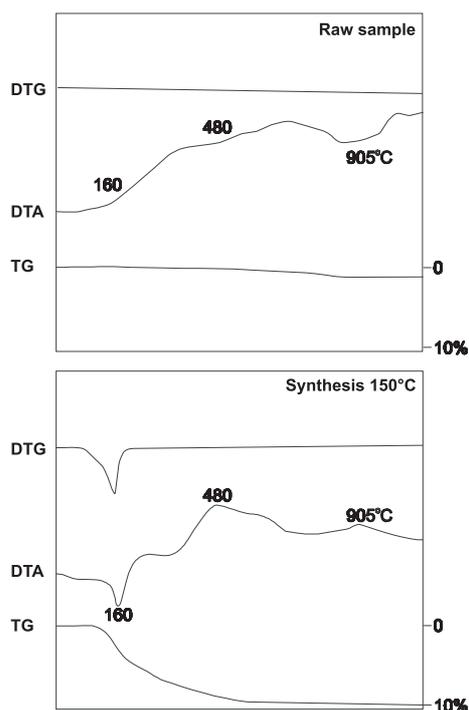


Fig. 4. Thermal analysis curves of the samples under research.

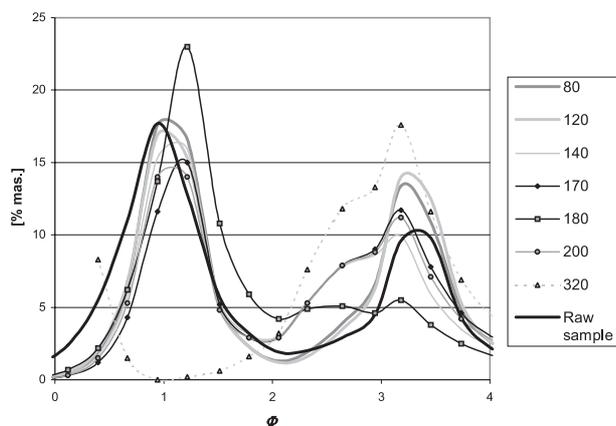


Fig. 5. Grain size curves of the synthesis products.  
Legend:  $\phi = -\lg 2d$ , where  $d$  – diameter of grains in millimetres.

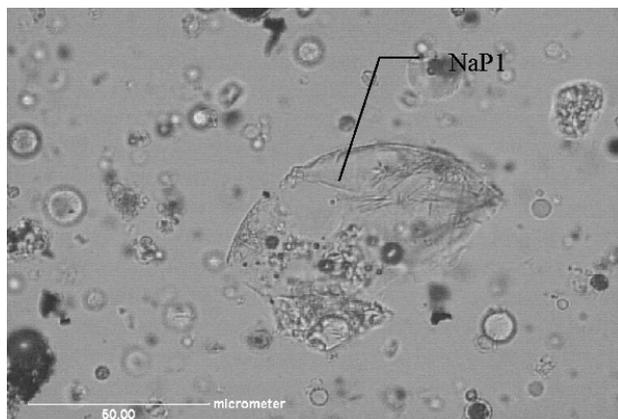


Fig. 6. Microphotograph of fly ash synthesis products at 80°C, transmitted light, parallel polars, magn. 400x.

first time. The intensity of analcime reflections grows with the increase of process temperature due to the increasing share of analcime in the products of synthesis. Microscopic examination showed single NaP1 zeolite pillars that crystallize directly from glass (Fig. 6). Their length may reach 100  $\mu\text{m}$ .

Simultaneously, first reflections of the NaP1-type zeolite appear on diffraction patterns at 120-140°C. Their intensity increases along with the growth of synthesis temperature up to 150°C and higher, the quantity of NaP1-type zeolite prevails over analcime. It should be emphasized that the presence of reflections coming from a given type of zeolite on the diffraction patterns is not fully reflected by microscopic identification. This is because crystals are usually smaller than 20  $\mu\text{m}$ . Therefore, attention should be paid to the NaP1 zeolite crystals, which may grow up to 30  $\mu\text{m}$  at higher temperatures of the synthesis (Fig. 7). Microscopic analysis proved that, at increased temperatures, higher intensity of the NaP1 crystallization may lead to the formation of the zeolite not only on glass aggregates but also around the grains of uncombusted coal.

Zeolites such NaP1, X, Y and others have a high industrial application potential due to the high cation exchange capacity (CEC) values but not analcime, sodalite and others that have a very low CEC [6, 8, 19].

A particular element of the zeolite crystallization is appearance of microscopically perceivable analcime crystals formed at 200°C and higher (Figs. 8-10). The crystals display isometric shapes with maximum dimension of 30  $\mu\text{m}$ , often twinned. High analcime products may be synthesized, but these have very low potential application since these have very low CEC.

Mullite and hematite disappear with the growth of synthesis temperature. Semi-quantitative content of constituents presented in Table 2 was determined on the basis of x-ray diffraction analysis.

Thermal analysis curves obtained for the post-synthesis material indicate high content of zeolites (Fig. 4). The DTA curve of the material synthesized at 150°C shows several thermal effects. The first endothermic effect with its maximum at 160°C is connected with water release

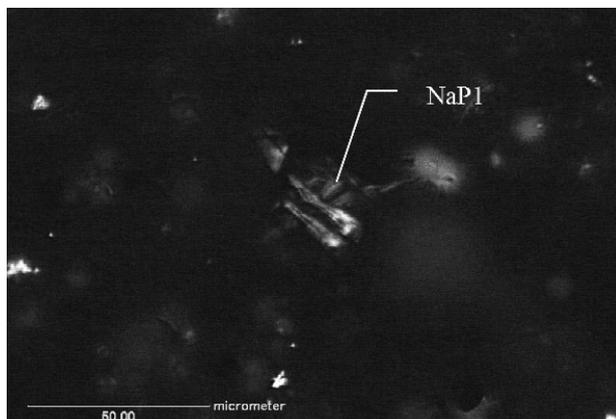


Fig. 7. Microphotograph of fly ash synthesis products at 170°C, transmitted light, crossed polars, magn. 400x

from NaP1 zeolite, accompanied by sudden loss of mass. It seems that an exothermic effect at 480°C may be connected with partial decomposition of the material. Usually a process of crystal decomposition is of exothermic character. Moreover, in certain cases it was observed that decomposition of zeolites is related to the collapse of free duct spaces at this temperature [20]. Such a situation may take place in case of the largest ducts (0.320 nm) in NaP1

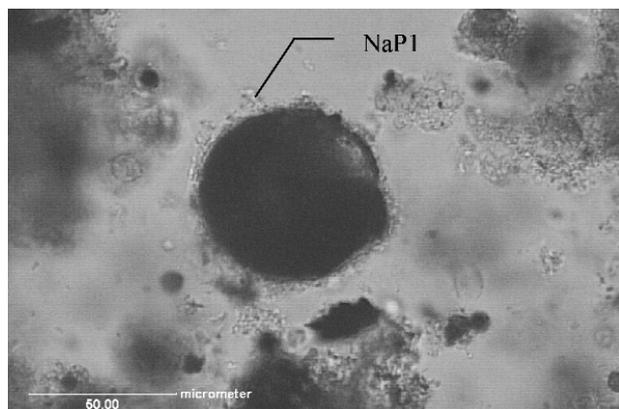


Fig. 8. Microphotograph of fly ash synthesis products at temperature of 190°C, transmitted light, parallel polars, magn. 400x.

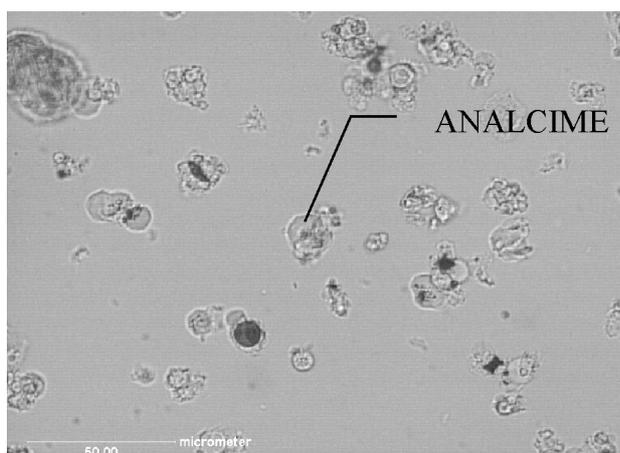


Fig. 9. Microphotograph of fly ash synthesis products at temperature of 200°C, transmitted light, parallel polars, magn. 400x.

zeolite crystals. Beginning at around 500°C only slight loss of mass is noted, the sample mass finally stabilizes around 700°C. This clearly indicates completion of dehydration within this temperature range. Most probably a complete destruction of crystalline lattice of zeolites takes place at about 700°C, whereas at 905°C crystallisation of a new phase will occur. No examination was performed to identify the phase but research on natural zeolites shows nepheline is likely to crystallize in such a case [21].

Simultaneously with the development of synthesis methods of zeolites, research has been carried out on their potential application. High industrial application potential due to the high CEC values. CEC value of NaP1-type zeolites is usually 2.7 meq g<sup>-1</sup> [8]. Initial investigation CEC of raw material (fly ash from the Opole Power Plant) and products of zeolitization indicate value 0.4 for fly ash and maximum value 1.8 meq g<sup>-1</sup> in the product of synthesis at 170°C (Fig. 11).

The possibility of the use of NaP1 in waste water purification technology has been investigated [8]. In details NaP1-type zeolites can be used in treatment of acid mine waters (subject of next research by authors). An important limitation for the application of the zeolitic material for

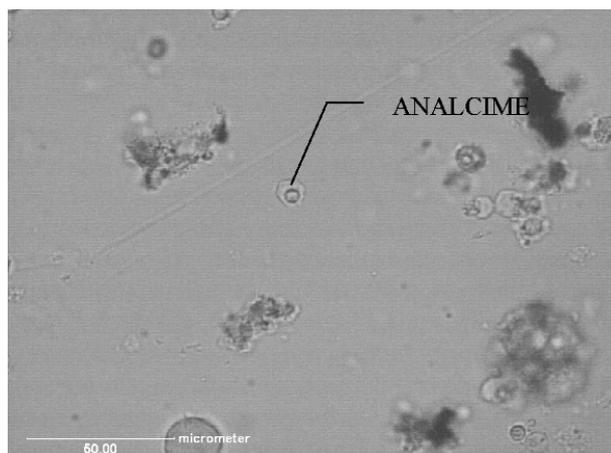


Fig. 10. Microphotograph of fly ash synthesis products at temperature of 320°C, transmitted light, parallel polars, magn. 400x.

Table 2. Semi-quantitative content of the process materials

Constituent	Temperature [°C]								
	20	80	120	140	150	170	180	200	320
Glass	+++	+							
Mullite	+++	++	++	trace	trace	trace	+	+	
Quartz	+++	++	+	trace					
Hematite	++	++	trace	trace	+				
NaP1				+++	+++	+++	++	+++	+++
Analcime			trace	trace	+	trace	trace	+	+++

Explanations: +++ – constituent occurring in a large quantity, ++ – constituent occurring in a quantity less than (+++), + – constituent occurring in a quantity less than (++) , trace – constituent occurring in a trace amounts.

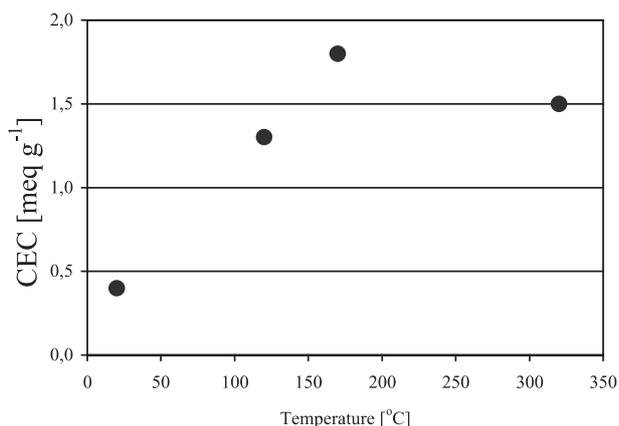


Fig. 11. Effects of temperature on the CEC values of the zeolite synthesis products.

the cation uptake from waste waters is the possible occurrence of potentially hazardous leachable elements (As, Se, Mo, Cu, V, Cr) in the residual fly ash particles when direct conversion products are used.

### Conclusions

A sample of raw fly ash from the Opole coal combustion power plant was examined. The following components were identified: glass, mullite, quartz, hematite and grains of uncombusted coal. The fly ashes under analysis are characterized by a low Si to Al ratio, which enables successful synthesis of zeolites with low Si content (analcime, NaP1), which display high ion-exchange capability and a large volume of pores.

It was confirmed that glass, almost in every synthesis condition, undergoes dissolution, which creates chemical conditions for crystallization of zeolites. It is possible that zeolites crystallize from compounds released into the solution not only from glass but also from quartz and, to a lower extent, from mullite.

At 120°C, at 3.6% concentration of Na<sub>2</sub>O (1.16 M NaOH) solution and in 6 hours time NaP1 zeolite as well as analcime are formed. The amount of newly formed minerals increases along with temperature on account of the disappearance of primarily mullite and glass. At the highest synthesis temperatures (200°C and 320°C) the share of analcime increases significantly.

NaP1-type zeolites can be used in the treatment of acid mine waters [22].

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