Preparation of Synthetic Zeolites from Fly Ash

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Abstract

The paper deals with the possibility of utilizing fly ash generated during coal combustion as an input material for the hydrothermal synthesis process in order to prepare a mineral phase. In the hydrothermal synthesis process, we worked with 2M and 3M sodium hydroxide, different process times from 6h to 24h and temperature range 90–110°C. Prior to the experiment, we analysed the input fly ash using XRF, XRD, and SEM. Based on the results, we selected appropriate fly ash and carried out hydrothermal synthesis of zeolites. The resulting mineral phases were analysed by XRD and SEM.

Keywords: fly ash, hydrothermal synthesis, zeolites

Introduction

Fly ash constitutes 65% of the total production of waste related to coal combustion. Worldwide, the combustion of fossil fuels generates approximately 750 million tonnes of fly ash every year. Out of this amount, only 25% are used and the remaining 75% are treated as waste. Fly ash remains one of the most studied pollutants and the obstacle in its wider use lies in its variable composition. Where as it contains hazardous substances or may contain hazardous substances on its surface, unused fly ash must be isolated from the environment to avoid its release into the environment.[1]

The hydrothermal synthesis of zeolites has been of scientific interest for a long time. The disadvantage of this process is the character of the product and the relatively low proportion of the converted fly ash to zeolites. In the presence of OH-, the Si and Al components are dissolved in ash. There are tetrahedra of AlO_5 and SiO_4. Thetetrahedra are the basic building blocks for the zeolite structure. This crystal structure is formed in the presence of Na+, K+ cations. The process of crystallization primarily runs on the undissolved or partially dissolved fly ash particles.[2]

$$\left(Li,Na,K\right)_p\left(Mg,Ca\ ,Sr,Ba\right)_q\left[Al_{(p+2q))}Si_{n-(p+2q)}O_{2n}\right]\times m_oH_2 \quad (1)$$

- p is the number of metal ions with oxidation number I
- q is the number of metal ions with oxidation number II
- n is half of the number of oxygen atoms
- m_o is the number of water molecules

Due to the incipient crystallisation of incompletely dissolved ash particles, the OH- ion approach to the ash surface is limited over time and the ability of the ion to dissolve the ash is reduced. Because of this, the fly ash will not dissolve completely and fly ash will be transferred to the product. The resulting product consists of unreacted fly ash and zeolite crystals. They field of the zeolite thus prepared is not high. [3] Many studies deal with various adjustments to conditions that should increase the ratio of the resulting zeolitic phase. However, the relationships for hydrothermal synthesis are not yet fully defined and hencethe type of zeolite phase at the end of the process is not entirely predictable.[4,5,6]

The convectional Hydrothermal Method can be performed in an open or closed system. Alkaline activation of fly ash uses a closed method in most cases. The closed system is used in an autoclave where the temperature and pressure of the bottles are affected. In the research of alkaline hydrothermal activation of fly ash, different types of alkali are used. The most commonly used are NaOH, KOH and LiOH in various concentrations, at a temperature between 80–200°C and activation time between 3 and 48 hours.[7]

Under the conditions of synthetic hydrothermal synthesis, zeolitic minerals in the original fly ash are found in the range of 20–65% by weight. The parameters (type of fly ash, concentration (NaOH), temperature, residence time in the process, Si/Al ratio, ratio of the solid phase and the liquid phase) are affected by the amount of zeolite minerals prepared.[7]

Materials and Methods

The ash used for hydrothermal synthesis comes from the combustion process from Detmarovice power plant, which belongs to ČEZ, a.s. in the Czech Republic. For combustion in this facility, two-shrinking boilers with a granulating combustion chamber are used at the maximum possible temperature of 1400°C in the boiler. [8]

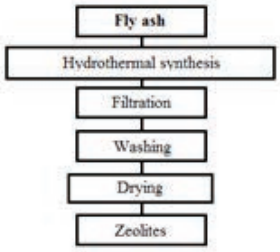


Fig. 1. Schematic of conventional hydrothermal synthesis

Rys. 1. Schemat konwencjonalnej syntezy hydrotermalnej

Tab. 1. XRF fine and coarse ash

Tab. 1. XRF frakcji drobnej i grubej popiołu lotnego

	Fine ash	Coarseash
	[Weight%]	
Na_2O	0.59	0.39
MgO	1.93	2.01
Al_2O_3	23.3	20.3
SiO_2	52.6	55.0
P_2O_5	0.18	0.11
SO_3	0.69	0.21
Cl	0.01	0.00
K2O	3.52	3.67
CaO	4.02	5.45
TiO_2	1.07	1.20
MnO	0.12	0.17
Fe_2O_3	7.90	10.6
	[mg/kg]	
V	191	193
r	166	169
Ni	122	113
Cu	134	124
Zn	245	100
Rb	154	177
Sr	321	271
Zr	188	326
Ba	1171	893
Pb	131	43

From this process, ash is collected in two devices, electrostatic and mechanical separators. Two types of fly ash were used for each experiment. These ashes differed in their chemical composition (table 1) and particle size.[8]

Hydrothermal synthesis

After basic analyses (XRD,XRF,SEM), the ash was homogenised. In 250 ml PTFE containers, we take ash, to which we added NaOH at 2 and 3M concentrations. S/l ratio was 1:7.5. The prepared samples were placed in a laboratory drier and the hydrothermal synthesis was set to proceed for 6 to 24 hours at 90, 100, 110°C. Upon completion of the synthesis, the samples were filtered and washed with distilled water to lower the pH value below 10. The samples were dried. Samples were homogenised and subjected to XRD and SEM analysis. To obtain zeolitic minerals using hydrothermal synthesis from fly ash, the following equations were respected.

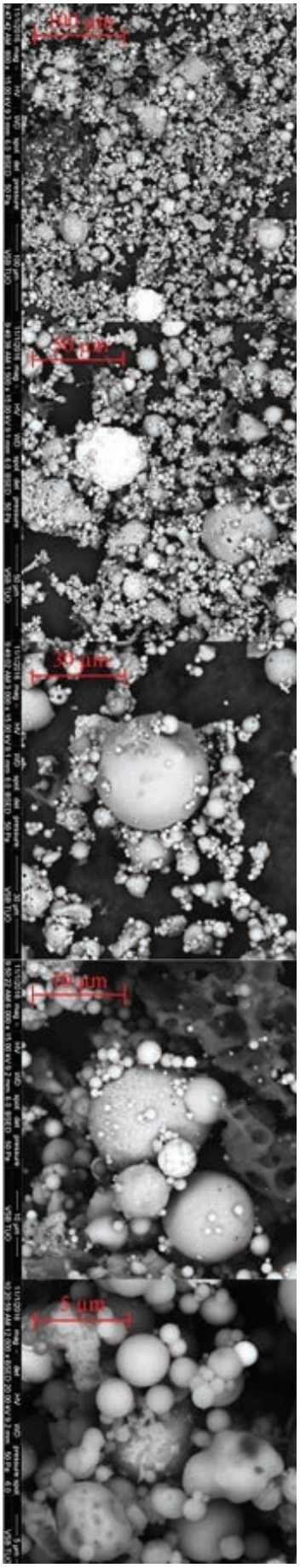
$$FLY\ ASH + x\,mol.dm^{-3}NaOH \xrightarrow[Temperature]{Time} Zeolite + residuum \quad (2)$$

where x is the concentration of NaOH solution

Results and Discussion

Table 1 shows the XRF results of both fly ash types. Figures 2 and 3 show SEM fragments of fly ashes.

We worked with two kinds of fly ash. Based on the tests we eliminated coarse ash which came from the mechanical step of treating the flue gas to be unsuitable be-



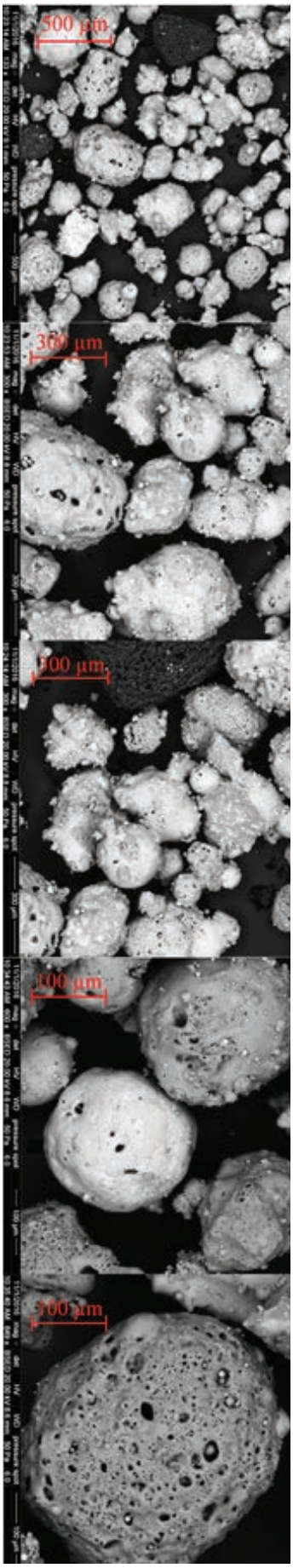


Fig. 2. SEM of fine fly ash

Rys. 2. SEM frakcji drobnej popiołu lotnego

Fig. 3. SEM of coarse fly ash

Rys. 3. SEM frakcji grubej popiołu lotnego

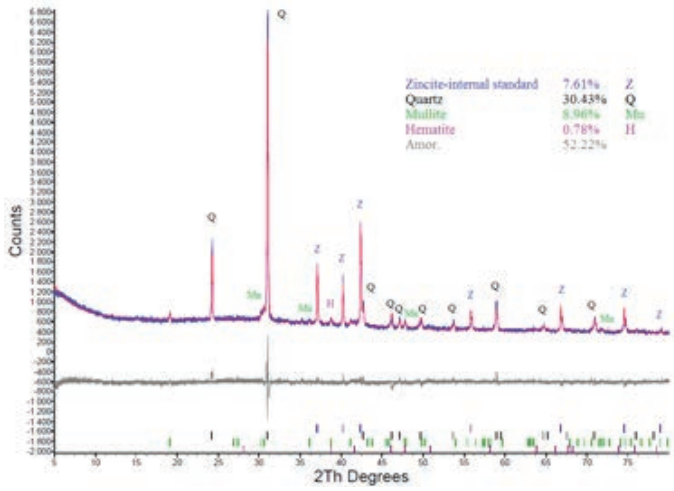


Fig. 4. XRD of coarse fly ash

Rys. 4. XRD frakcji grubej popiołu lotnego

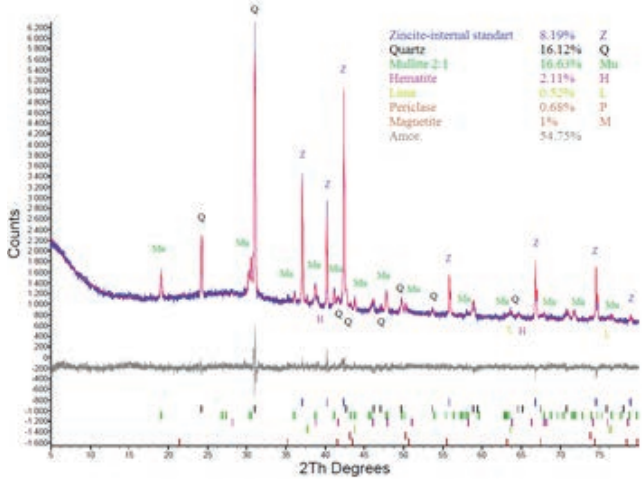


Fig. 5. XRD of fine flyash

Rys. 5. XRD frakcji drobnej popiołu lotnego

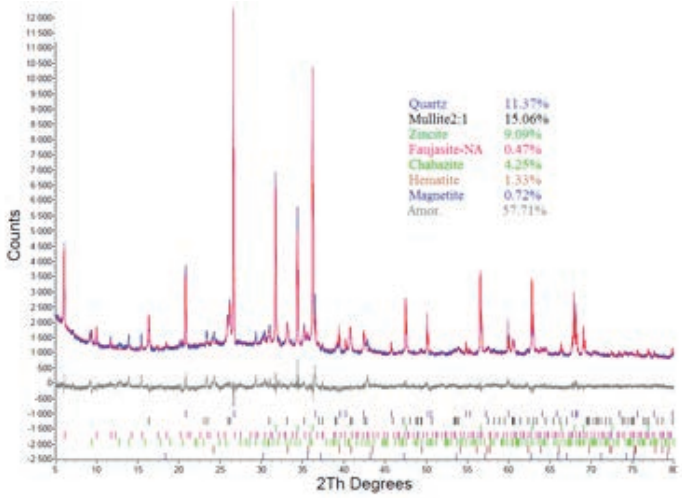


Fig. 6. Fine fly ash after conventional hydrothermal synthesis

Rys. 6. Frakcja drobna popiołu lotnego po konnwencjonalnej syntezie hydrotermalnej

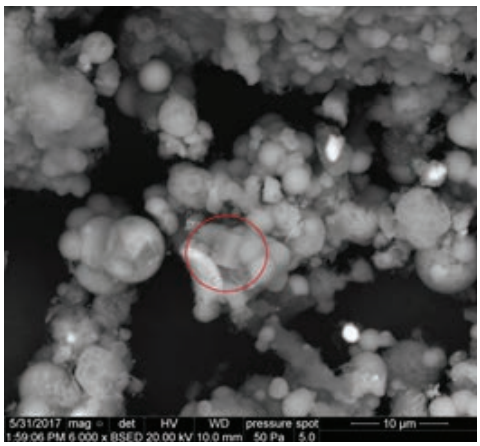


Fig. 7. SEM of chabazite

Rys. 7. SEM próbki chabazitu

cause hydrothermal synthesis particle size when not adequately dissolving fly ash we set time of hydrothermal synthesis process. We also worked only with fine ash, which came from an electrostatic degree of cleaning.

XRD frames in Figures 4 and 5, the original composition of the two fly ash types can be seen before hydrothermal synthesis.

In our experiments using a laboratory dryer, we obtained 4.72% ofthe zeolite phase (Figure 6), 20g fly ash, 0.15 dm³ NaOH 2 M, 6h at 110°C. The majority of the zeolitic phase formed was 4.25% chabazite and faujasite 0.47%.

In other experiments, we would like to increase the process temperature within the PTFE capacity and try to add different additives to the ash in order to support the amount of mineral phase formed. We would like to test the sorption capacity for the prepared zeolites.

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Metoda otrzymywania zeolite z popiołów lotnych

Artykuł jest poświęcony możliwości wykorzystania popiołu lotnego ze spalania węgla jako materiału wejściowego do procesu syntezy hydrotermalnej w celu przygotowania fazy mineralnej zeolitu. W procesie syntezy hydrotermalnej wykorzystano 2M i 3M wodorotlenek sodu, proces prowadzono w czasie od 6h do 24h i w zakresie temperatur 90–110°C. Przed eksperymentem przeprowadzono analizy XRF, XRD i SEM popiołu. Na podstawie uzyskanych wyników wybranio odpowiedni popiół lotny i przeprowadzono hydrotermalną syntezę zeolitów. Powstałe fazy mineralne analizowano za pomocą XRD i SEM.

Słowa kluczowe: popiół lotny, synteza hydrotermalna, zeolit