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TRACE ELEMENTS IN SOLUTIONS FROM ZEOLITE SYNTHESIS

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The paper presents the content of selected elements in solutions formed after the synthesis of zeolitic material based on fly ash. Fly ash samples were taken from two pulverized fuel-fired boilers at the Rybnik Power Plant: one boiler fired solely with coal and one co-fired with coal and biomass. The tests conducted have shown that solutions remaining after zeolite synthesis from fly ash generated in boilers co-fired with coal and biomass had higher content of elements than those derived from fly ash generated from burning only coal. It was also found that increasing NaOH concentration of the solution used in zeolite synthesis caused increased content of the individual elements.

Keywords: zeolite, trace elements, synthesis, solutions

1. INTRODUCTION

Zeolite synthesis from fly ash can be achieved by several methods:
– classical alkaline hydrothermal conversion of fly ash,
– alkaline fusion followed by classical alkaline conversion of fly ash,
– dry or molten salt conversion,
– two-stage synthesis.

The hydrothermal synthesis of zeolites from fly ash is the most widely used method. Hydrothermal synthesis is a physicochemical process conducted in an alkaline solution under atmospheric or increased pressure (in that case the process is carried out in an autoclave). Hydrothermal synthesis consists in processing a mixture of fly ash and hydroxide (usually sodium or potassium hydroxide) under defined conditions of temperature and pressure. Additives, such as sodium chloride or potassium chloride are also used. The process involves also filtration, washing and drying of the resultant material. The

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process duration, according to the literature, ranges in the various methods from a few hours to a few days, or even more than ten days. The process temperature range is also wide: from ambient temperature up to several hundred degrees Celsius. The higher reaction temperature, the shorter reaction duration may be [1-4].

In some of the zeolite synthesis methods a solution is generated after the reaction and after washing of the material obtained. No studies have been carried out before to determine the chemical/elemental composition of the generated solutions. These solutions may contain elements that are not present in the synthesized material. Depending on the concentration thereof, they may pose an environmental hazard.

The purpose of this study was to establish the content of selected elements in solutions formed after the synthesis of zeolitic material based on fly ash.

2. SAMPLING AND TESTING METHODS

Fly ash samples were taken from two pulverized fuel-fired boilers at the Rybnik Power Plant: one boiler fired solely with coal (W) and one co-fired with coal and biomass (plant and wood biomass – 8-9%) (Table 1).

Two synthesis trial runs were executed using the hydrothermal method with alkaline activation under the following conditions: synthesis duration – 6 h, synthesis temperature - 170°, fly ash quantity – 100 g, water quantity – 600 mL, NaOH concentration – 2M and 3M. A "blind" synthesis run was carried out for comparison. The conditions of the process were identical as in the two previous trial runs, but alkaline activation was not applied (NaOH concentration 0M). Sample designations are given in Table 1.

Table 1. List of samples of solutions after zeolite synthesis (numbering according to the research plan).

NaOH concentration	Sample no.	
	Boiler fired with coal	Boiler fired with coal and biomass
0.00M	1	15
2.00M	4	18
3.00M	5	19

After each synthesis the material obtained was washed with the same amount of water, enabling thereby comparison of the elemental contents of the

solutions. Distilled water was used both in the synthesis process itself as well as for washing.

The following elements were determined in the solutions: Fe, Cr, Ni, Cu, Zn, Pb, Ti, V, Mn, Cd, Mo, Ba, Ca, Si, Al, Na, K, Mg, Sb, As. Determination was carried out by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a JY 2000 spectrometer.

3. RESULTS

K, Na, Ca, Mn, Mg and Fe were the most numerous elements found in all solutions. The elements concentrations were respectively: K (average concentration 571 ppm), Na (av. conc. 179 ppm), Ca (av. conc. 53 ppm), Mn (av. conc. 39 ppm), Mg (av. conc. 52 ppm) and Fe (av. conc. 19 ppm).

The concentrations of other determined elements found in the solutions were below 10 ppm and included: Cr, Ni, Cu, Zn, Pb, Ti, V, Cd, Ba, Si and Al (rys. 1-4).

The lowest content of elements was determined in the solutions from "blind" synthesis run (with no NaOH activation). There is certain relationship between the content of individual elements in the solutions and the type of fuel used (coal, coal and biomass co-firing), irrespective of NaOH concentration (Figs. 1-10:

- in the case of coal and biomass co-firing - higher content of Fe, Mn, Ca, Mg, V, Mn, Ca, Mg, Na, K, Pb, Ba, Ti and Al, as compared to firing with coal only,
- in the case of coal firing - higher content of Zn, Cr, Cd and Si, as compared to coal and biomass co-firing.

For such elements as Ni and Cu there is no clear relationship between their concentration in solutions and the type of fuel used (coal, coal and biomass co-firing).

There is a certain relationship between the occurrence of Mo, Sb and As only in solutions formed in the course of the synthesis from fly ash generated during coal and biomass co-firing:

- Mo is present only in samples nos. 18 and 19, that is in solutions formed in the course of synthesis in 2M and 3M NaOH solution,
- Sb and As are present only in the solution formed in the course of synthesis in 3M NaOH solution.

The results of element content determination in solutions formed in the synthesis of zeolitic material also indicate that the content thereof depends on

the NaOH concentration in the activating solution, irrespective of the type of fuel burned (Figs. 1-4):

– 3M NaOH solutions have higher concentrations of Mn, Mg, Cr, Cd, Na, K, Ba and Ti than the 2M NaOH solutions,
– 2M NaOH solutions have higher concentrations of Ca, Ni, Al and Si than the 3M solutions.

For elements such as V, Cu and Pb there is no clear relationship between their concentration in solutions and the concentration of NaOH in solutions used in the synthesis process.

The decrease of Si and Al content with increasing NaOH concentration (in solutions used in the synthesis) found in solutions after the synthesis may be an indicator of increasing efficiency of zeolite crystallization in the synthesis process. At the same time increasing Na content is observed when NaOH concentration is increased, which suggests that some sodium does not participate in the synthesis reaction.

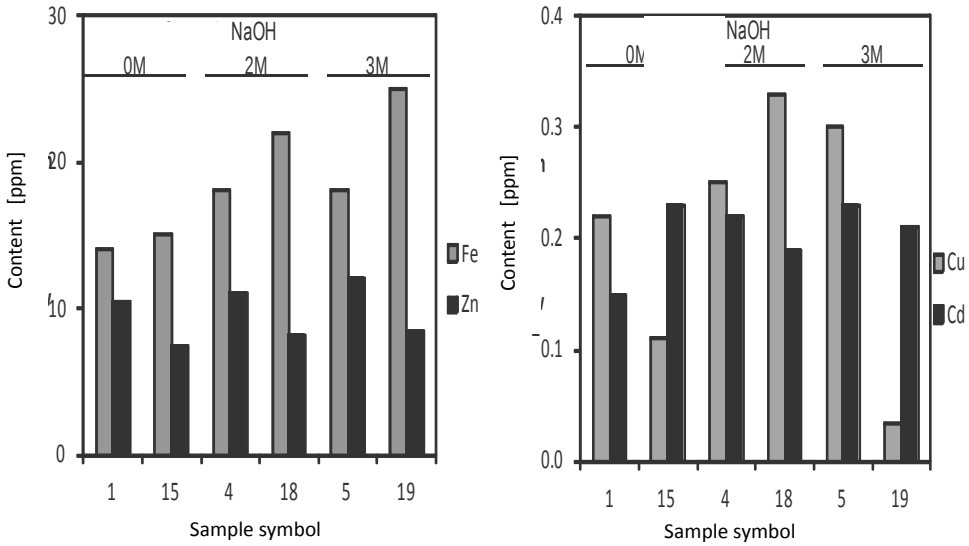

Fig. 1. Content of Fe, Zn, Cu and Cd in solutions after zeolite synthesis from fly ash from the Rybnik Power Plant.

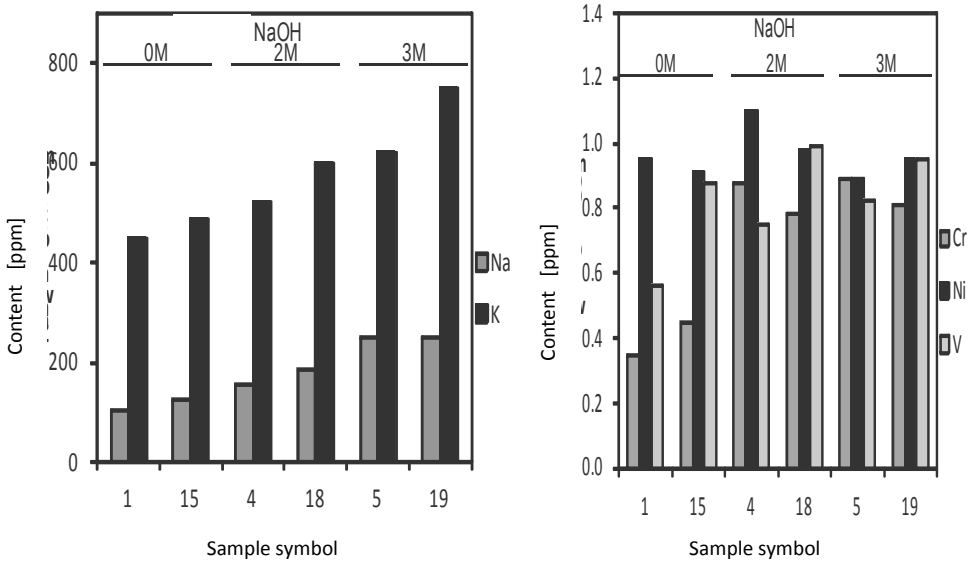

Fig. 2. Content of Na, K, Ni, Cr and V in solutions after zeolite synthesis from fly ash from the Rybnik Power Plant.

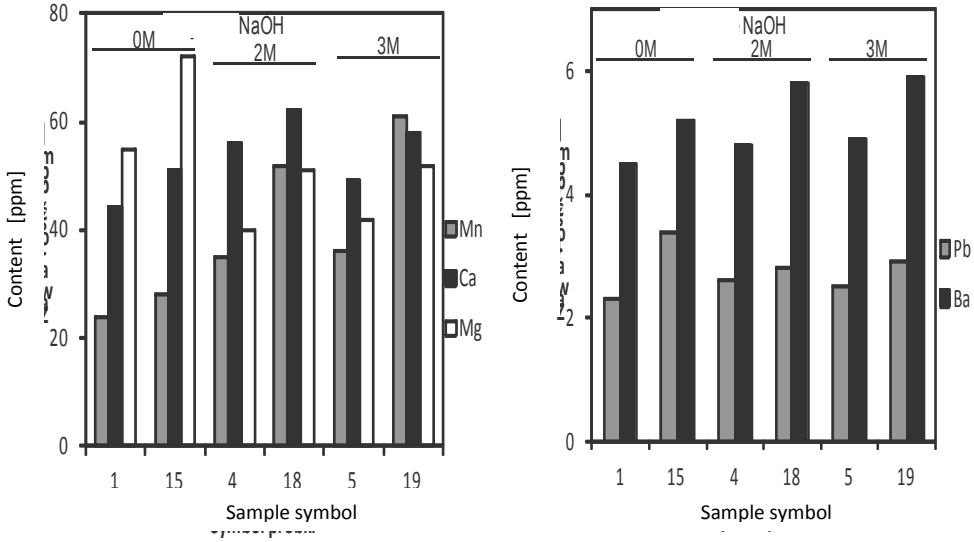

Fig. 3. Content of Mg, Ca, Mn, Pb and Ba in solutions after zeolite synthesis from fly ash from the Rybnik Power Plant.

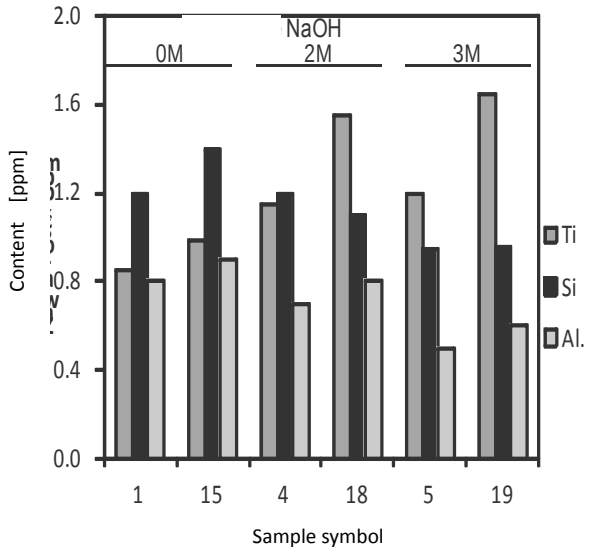

Fig. 4. Content of Ti, Si and Al in solutions after zeolite synthesis from fly ash from the Rybnik Power Plant.

4. CONCLUSIONS

The following conclusions can be drawn from the study of results of elemental analyses of solutions formed in the course of zeolitic material synthesis from fly ash generated by burning coal or by co-burning coal and biomass at the Rybnik Power Plant:

– solutions formed after zeolite synthesis from fly ash generated by co-burning of coal and biomass have higher content of elements than those derived from fly ash generated by burning coal only,
– increasing NaOH concentration of the solution used in zeolite synthesis causes increased content of the individual elements,
– decrease of Si and Al content with increasing NaOH concentration (in solutions used in the synthesis) in solutions after the synthesis may be an indicator of increasing efficiency of zeolite crystallization in the process.

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PIERWIASTKI ŚLADOWE W ROZTWORACH PO SYNTEZIE ZEOLITÓW

S t r e s z c z e n i e

W artykule przedstawiono zawartości wybranych pierwiastków w powstałych roztworach po syntezie materiału zeolitowego na bazie popiołu lotnego. Próbki popiołu lotnego pochodziły z Elektrowni Rybnik z dwóch kotłów pyłowych: opalanego czystym węglem i ze współspalania węgla z biomasą. Przeprowadzone badania wykazały, że wyższe zawartości pierwiastków występują w roztworach poreakcyjnych, powstałych po syntezie popiołów pochodzących ze współspalania węgla z biomasą, niż w roztworach po syntezie popiołów będących produktem spalania czystego węgla. Stwierdzono ponadto, że wraz ze wzrostem stężenia NaOH roztworu zastosowanego do syntezy zeolitów wzrasta ilość poszczególnych pierwiastków.