

## PHASE TRANSFORMATIONS IN SYNTHESIS TECHNOLOGIES AND SORPTION PROPERTIES OF ZEOLITES FROM COAL FLY ASH

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Coal fly ash is generated in the course of combustion of coal at thermal power plants. Environmental problems increase sharply without disposing that industrial waste. Technologies were tested of hydrothermal synthesis of zeolites from fly ash forming during combustion of coal at thermal power plants of the Pechora coal basin and dependences were identified of the experiment conditions on physical and chemical properties of the end product. It is demonstrated that synthesizing zeolites from fly ash is the first stage of forming ceramic materials (ceramic membranes), which defines the fundamental character (importance) of that area of studies. It was for the first time that sorption and structural characteristics and cation-exchange properties of fly ash from the Pechora basin coals were studied with respect to  $\text{NH}_4^+$ ,  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$ .

**Key words:** zeolites, fly ash, sorbents, hydrothermal synthesis, ammonia, strontium, barium.

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**Introduction.** Fly ash and slag are products resulting from combustion of coal at thermal power plants and thermal electric plants and belongs to large-tonnage power industry wastes. Fly ash is mostly used in construction industry as an additive to cement, concrete and ceramics. It appears possible to utilize 20-50 % of fly ash that way, the rest remains in ash disposal areas. That is why the issue of recycling such technogenic wastes that occupy large areas and are detrimental to the environment is quite topical.

One of the promising directions of using fly ash is its recycling into zeolites, a valuable material. Zeolites thus produced are cheap but effective sorbents and ion exchangers that may be used, e.g., for soil regeneration, processing of acidic mine waters, purifying water, especially to remove ammonia, heavy metals, radio nucleides and organic matter. Besides, they may be used at coal combusting thermal electric plants themselves for sorption of sulfur dioxide ( $\text{SO}_2$ ) from furnace gases, further to produce sulfuric acid, elemental sulphur and other products from it [1]. A number of studies have been published of the properties of fly ash and possibilities to use it [6-8, 10-13, 15], but there is no large scale recycling happening yet.

The current study presents the results of studying zeolite synthesis from fly ash of thermal electric plants of the Pechora coal basin in dependence of the conditions of hydrothermal reaction (temperature, reaction time, alkali concentration) and sorption and structural parameters are presented of synthesized zeolites and their cation-exchange properties with respect to ammonia, barium and strontium.

**Study objects and techniques.** For experiment purposes we used fly ash formed during combustion of coal from the Pechora coal basin. Foundations of the technique for zeolite synthesis were the results presented in the study [16]. Iron containing phases that do not take part in synthesizing zeolites were initially removed from bulk material using a magnetic separator. Dry fly ash was mixed with sodium hydroxide (NaOH) solution to a prescribed proportion, stirring it thoroughly and then placed the suspension in an autoclave; the products of hydrothermal reaction were then washed with distilled water and dried (Fig. 1).

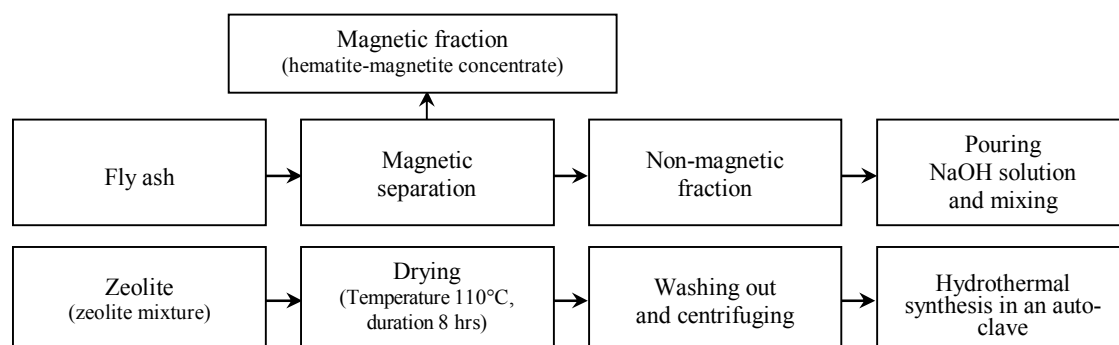


Fig. 1. Flow-chart of producing zeolites from fly ash

Studies of phase composition were conducted with a powder diffractometer ("Shimadzu XRD 6000") in the range from 2 to 65° angles 2θ. Chemical composition was determined in the following way: Na<sub>2</sub>O, K<sub>2</sub>O, FeO, calcination losses, H<sub>2</sub>O<sup>-</sup>, CO<sub>2</sub> obtained by the technique of complete silicate analysis, other components identified using X-ray fluorescence analysis (using the energy dispersion MESA500W, Horiba spectrometer). To study the morphology and chemical composition the TESCAN VEGA 3 LMH scanning electronic microscope with energy dispersion "Oxford Instruments X-Max" attachment was used.

Specific surface area, the total pore volume and that of micropores were measured using the NOVA 1200e surface area and pore size analyzer by "Quantachrome". The cation-exchange capacity (CEC) on barium was defined using the Bobko– Askinasi– Alyoshin technique. To study the kinetics of ammonia and strontium sorption experiments were staged in the exchange of such cations from water solutions of NH<sub>4</sub>Cl and SrCO<sub>3</sub> from 1 to 1,440 minutes. The initial concentration of ammonia and NH<sub>4</sub><sup>+</sup> Sr<sup>2+</sup> was 100 and 25 mg/l, respectively; the solid (S) to liquid (L) ratio was S:L = 1:500. Ammonia concentration in the solution was retrieved using the photometric technique using the Nessler reactant and a KFK-2 photoelectric concentration colorimeter at 440 nm wavelength; strontium concentration was defined using the atomic absorption spectroscopy - induction coupled plasma technique with the "Vista MPX Rad" spectrometer.

**Results and discussion.** *The initial fly ash.* X-ray phase studies have identified quartz, mullite, magnetite and hematite in the initial sample of fly ash (Fig. 2). The wide "hump" (the area of higher background) in the diffractogram in the range of 15-35° angles 2θ points to the presence of amorphous phase (probably of silicate or aluminosilicate glass). The principal components in the chemical composition of the initial sample of fly ash are silicium oxides (57.78 %) and aluminium oxides (18.25 %), ferric oxides make about 9.0 %, oxides of other elements make 7.42 %, losses on calcination are 7.90 % (see the Table). Electron microscopy demonstrates fly ash to consist of globules that are split into aluminosilicate and ferric in their composition [2].

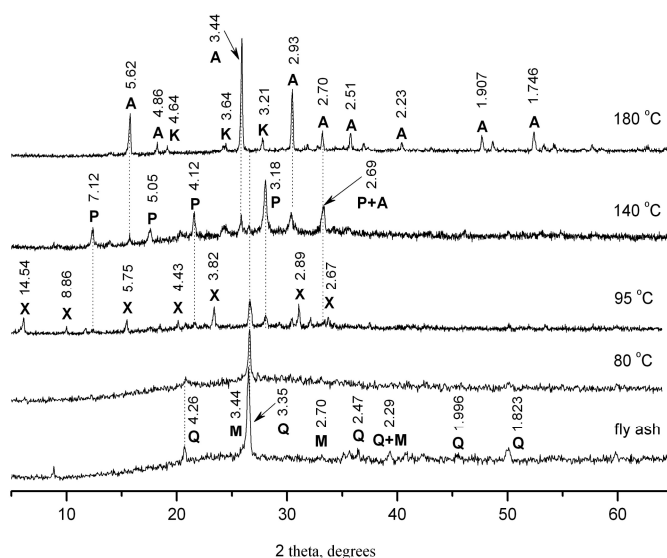


Fig. 2 Diffractograms of products from hydrothermal reaction of 12 hr duration, obtained at reaction temperatures of 80, 95, 140 and 180 °C. Interplane distances are given in Angstroms

Q – quartz, M – mullite, X – zeolite of faujasite type, P – zeolite of gismondite type, A – analcime, K – cancrinite

Chemical composition of fly ash and products of hydrothermal reaction, mass %

Component	Fly ash	Products of hydrothermal reaction obtained at different reaction temperatures (°C)			
		80	95	140	180
SiO <sub>2</sub>	57.78	43.57	40.80	43.11	45.81
TiO <sub>2</sub>	1.04	0.98	0.90	1.11	1.11
Al <sub>2</sub> O <sub>3</sub>	18.25	15.98	17.22	17.12	17.28
Fe <sub>2</sub> O <sub>3</sub>	5.95	4.13	3.57	4.13	4.53
FeO	2.70	0.45	0.11	0.19	0.09
MnO	0.03	0.03	0.04	0.04	0.03
MgO	2.52	2.92	2.57	2.49	3.44
CaO	1.63	2.18	1.76	1.79	1.10
Na <sub>2</sub> O	0.91	9.58	9.21	9.48	12.14
K <sub>2</sub> O	1.29	0.75	0.52	0.91	0.23
P <sub>2</sub> O <sub>5</sub>	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Calcination losses	7.90	19.43	23.30	19.62	14.24
Total	100.00	100.00	100.00	100.00	100.00
H <sub>2</sub> O <sup>-</sup>	0.41	7.50	10.21	8.42	2.16
CO <sub>2</sub>	<0.1	3.33	1.79	1.52	1.14

**Hydrothermal synthesis.** Two series of experiments were run. In the first series the effect was studied of the temperature of hydrothermal reaction on zeolite synthesis (reaction temperature of 80, 95, 140 and 180 °C, reaction time was 12 hrs, the ratio NaOH:fly ash = 1:1, NaOH concentration 3.0 mol/dm<sup>3</sup>). The second series of experiments studied the effect of reaction duration and alkali concentration on the process of synthesis (reaction temperature was 140 °C, reaction time was 2, 4, 6 and 8 hrs, the ratio NaOH:fly ash = 1:1, NaOH concentration was 1.5, 3.0 and 4.5 mol/dm<sup>3</sup>). Synthesis resulted in producing powders that are a mixture of zeolites and non-reacting residual in various quantitative proportions, with product output of 70-80 % of the initial amount of fly ash.

**The effect of reaction temperature on zeolite synthesis.** In the result of reaction at 80 °C intense quartz reflexes were diagnosed, no newly formed phases were detected (Fig. 2). Electron microscopy studies have identified numerous globules, destroyed under the effect of alkali solution (Fig. 3, a, b). With the reaction temperature increasing to 95 °C the intensity of quartz reflexes lowers, i.e. it starts dissolving in the alkali. Along with quartz, intensive reflexes were identified corresponding to zeolite of the faujasite type (zeolite X) and weak reflexes typical for the gismondi type zeolite (zeolite P). In their Si/Al ratio the obtained zeolites are of low siliceous type: the silica-aluminium module of zeolite X varies from 1.51 to 1.57, that of zeolite P – from 1.65 to 1.69. Images produced by electronic microscope (Fig. 3, c, d) demonstrate numerous crystals of zeolite X of octahedric shape, 1-3 µm in size. Zeolite P crystals are of rounded shape, their size around 5 µm.

Diffractiongrams of reaction products obtained at 140 °C manifest zeolite P and analcime and also weak reflexes of quartz are present. Zeolite P is of higher silica content compared to the phase obtained at 95 °C: the Si/Al ratio varies insignificantly (changing between 1.93 to 1.94). The silica- aluminium module of analcime varies from 2.12 to 2.21. As seen from Fig. 3, e, f, zeolite P forms skeleton crystals of 10-15 µm in size. Crystals of analcime are observed of 15-20 µm size.

Reaction at the temperature of 180 °C results in the formation of analcime and cancrinite, no quartz reflexes are diagnosed in the diffractiongram. The Si/Al ratio for analcime varies between 2.00 and 2.15. Crystals of cancrinite are of pole shape, up to 2 µm in length, 200-300 nm crosswise and they are often observed on the surface of analcime crystals which are 15 to 25 µm in size (Fig. 3, g, h) which testifies to cancrinite crystallizing at a later stage than analcime.

The products of hydrothermal reaction presented in the Table are characterized by high content of Na<sub>2</sub>O (9.21-12.14 %) and high calcination losses (14.24-23.30 %), as compared to the initial fly ash (0.91 and 7.90 %, respectively), which is related to the formation of zeolites containing H<sub>2</sub>O and Na<sup>+</sup>

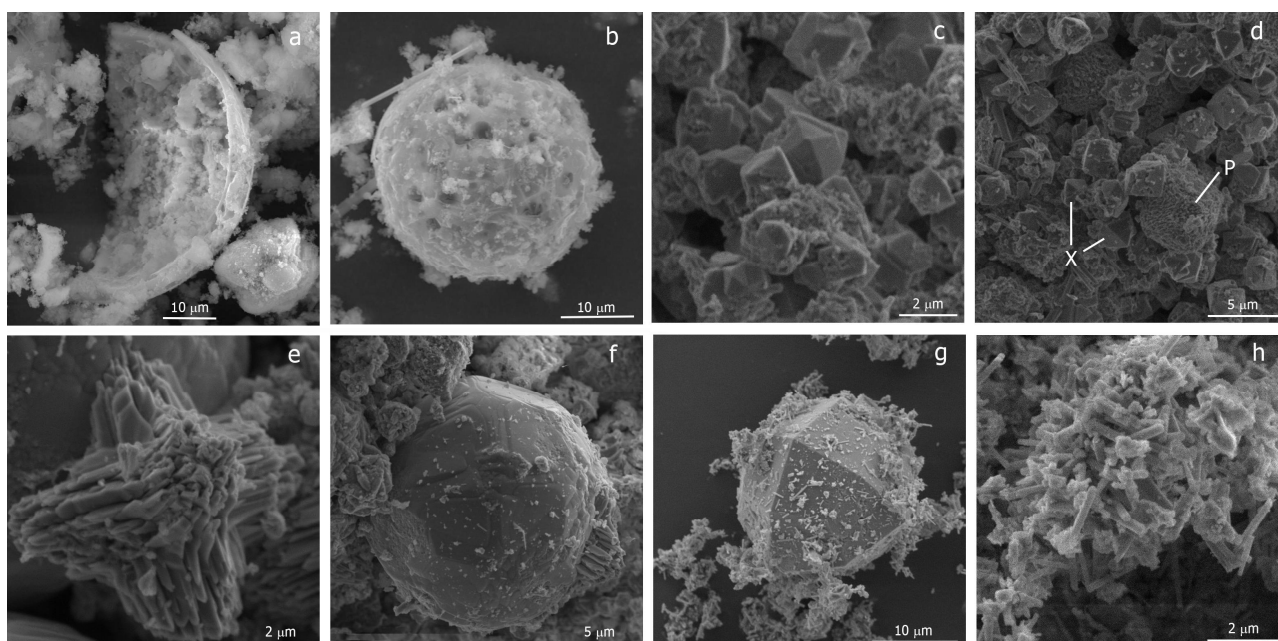


Fig. 3. Products of hydrothermal reaction obtained at reaction temperatures 80 °C (a, b), 95 °C (c, d), 140 °C (e, f) and 180 °C (g, h): a, b – globules affected by the alkali solution; c – an agglomerate of zeolite X crystals ; d – crystals of zeolites X and P; e – separate crystal of zeolite P; f – crystals of analcime and zeolite P; g – separate crystal of analcime; h – agglomeration of cancrinite crystals

cations in their cavities and canals. Decrease of the amount of silica in reaction products (40.80-45.81 %) as compared to the initial fly ash (57.75 %) indicates that not all of silicium takes part in the process of zeolite crystallization, some part of it remains in the solution. In contrast to silicium, practically all of aluminium is used in the process of zeolite formation, since its content in reaction products is only 1-2 % lower than in fly ash. A drop in the content of FeO and Fe<sub>2</sub>O<sub>3</sub> is the result of magnetic separation which worked to separate part of iron containing phases (magnetite and hematite).

The results obtained indicate that the reaction temperature influences the type of zeolites synthesized, differentiating them by the effective diameter of their entry windows, so they are separated into narrow-, medium- and wide pore zeolites. It is found that higher reaction temperature results in the formation of zeolites with narrower pores: at 95 °C zeolites X are formed, which belong to wide pore zeolites, at 140 °C – these are zeolites P, which belong to the medium-pore zeolites, while at 180 °C analcime is formed which belongs to the narrow-pore zeolites [3].

*The effect of reaction time and alkali concentration on the zeolite type.* In the result of a series of experiments a schematic diagram was plotted of crystallization of zeolites and other phases (hydrosodalite) at 140 °C, reaction time from 2 to 8 hr and NaOH concentration of 1.5M, 2.9M and 4.5M (Fig. 4).

As seen from Fig. 4, wide pore zeolites X are formed in the result of 4 hr reaction at high concentrations of alkali solution (4.5 mol/dm<sup>3</sup>). Increasing reaction time results in vanishing of meta-stable phases of zeolite X and the appearance of thermodynamically more stable ones: first zeolite P and then analcime. Zeolite P crystallizes within a wide range of reaction conditions. Meanwhile crystallization fields of analcime and zeolite P overlap significantly, so under the same conditions of hydrothermal reaction mixtures of zeolites are formed of different quantitative composition. Increasing the concentration of alkali results in higher content of analcime as compared to zeolite P and also provides for the formation of a non-zeolite phase: hydrosodalite.

*Sorption, structural and ion exchange characteristics.* When comparing Fig. 5a with the schematic crystallization diagram (see Fig. 4) one notes the dependence of specific surface of the reaction products on the zeolite type and its content in the mix. In this case one has to keep in mind that the BET technique (low temperature sorption of nitrogen) is incapable of measuring specific surface of narrow pore zeolites, such as analcime, since the diameter of analcime canals (0.26 and 0.16 × 0.42 nm) is smaller than the diameter of the nitrogen molecule (0.32-0.35 nm). The measured specific surface of pure analcime appeared to be only 1.5 m<sup>2</sup>/g.

In the result of a 2 hr reaction the specific surface increases by a factor of 4-6 compared to specific surface of the initial fly ash, which is 5.6 m<sup>2</sup>/g, though zeolite phases were not identified in those products. A smooth increase of specific surface of reaction products with reaction time obtained for the NaOH concentration of 1.5M, is related to the increase of zeolite content in the mix. In a series of experiments with the NaOH concentration of 3.0 M the specific surface reaches its maximum after 4 h of reaction and then stays at approximately the same level with reaction time extended further. Due to formation of zeolite X which belongs to wide pore zeolites, reaction products obtained for the reaction duration of 4 h and NaOH concentration of 4.5M are characterized by high specific surface equal to 269 m<sup>2</sup>/g. A sharp drop of specific surface at longer reaction times is a result of extinction of zeolite X and the appearance of thermodynamically much more stable zeolite P and analcime. The total pore volume and the volume of micropores (Fig. 5b, c) are directly proportional to specific surface and are also defined by the type of synthesized zeolite and its content in the mix.

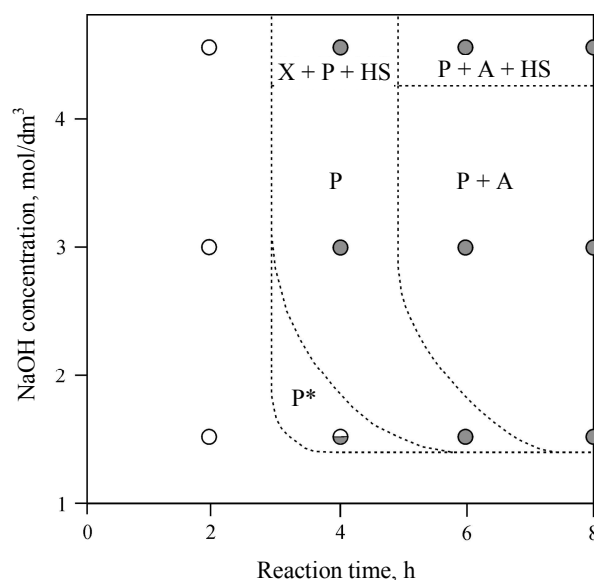


Fig. 4. Schematic flow-chart of zeolites crystallization



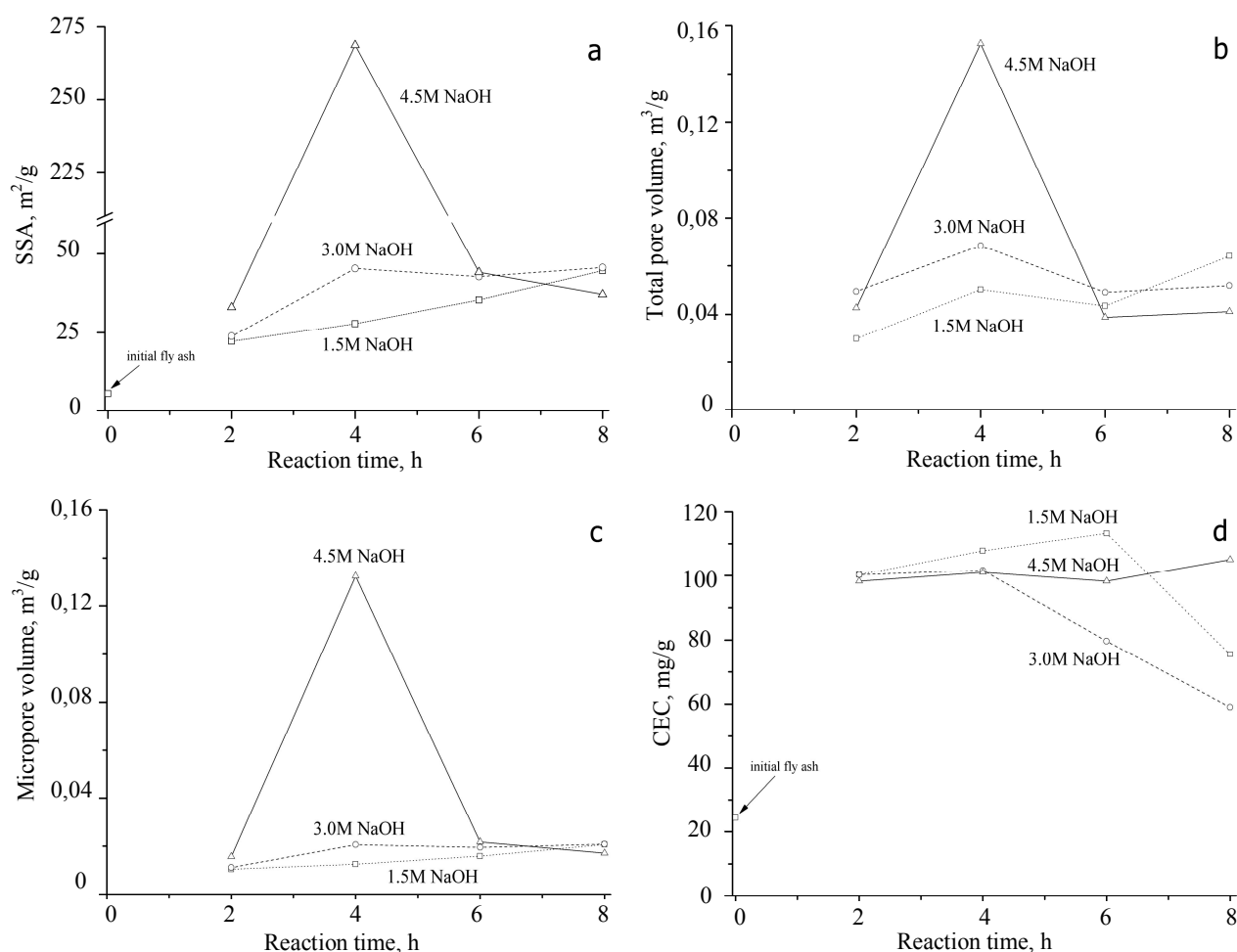


Fig. 5. Specific surface (a), total pore volume (b), micropore volume (c) and cation exchange capacity for barium (d) of the initial fly ash and products of hydrothermal reaction obtained at the temperature of 140 °C, alkali concentrations of 1.5; 3.0 and 4.5 mol/dm<sup>3</sup>, and reaction time of 2 to 8 h

Fig. 5, d demonstrates the barium cation exchange capacity of the initial fly ash and products of hydrothermal reaction in dependence of the reaction duration and alkali concentration. Cation exchange capacity (CEC) of products obtained in the result of 2 h reaction increases more than four-fold (to 98.2-100.2 mg/g) against the CEC of the initial fly ash, though zeolite phases were not detected in the mix. The alkali solution concentration being 1.5 mol/dm<sup>3</sup> CEC is increasing gradually for longer reaction times, reaching 113.3 mg/g, but further on it lowers considerably to 75.5 mg/g in the result of 8 h reaction. With alkali concentration of 3.0 mol/dm<sup>3</sup> the drop in exchange capacity is observed after 6 h of reaction. The most probable reason for the decrease in the cation exchange capacity is a drop in the content of zeolite P and formation of analcime which features low exchange capacity with respect to barium (14.4 mg/g). The CEC of products produced in the 4.5M solution of NaOH remains practically unchanged with larger reaction times.

Experiments in cation exchange with ammonia and strontium were done using the sample produced at 140 °C, alkali concentration of 1.5 mol/dm<sup>3</sup> and reaction time of 8 h, its basic mineral phase formed by zeolite P with some analcime present. Both exchange reactions go at high rate so after 1 and 5 min, respectively, the limit concentration of ammonia (31.9 mg/g) and strontium (12.3 mg/g) are achieved already and further increase of exposition time does not bring any changes in the capacity. The degree of extraction NH<sub>4</sub><sup>+</sup> of ammonia and Sr<sup>2+</sup> for these reaction conditions are 63.9 and 95.4 %, respectively.

**Conclusion.** Efficient sorbents are synthesized from technogenic raw material formed in the course of combustion of coal at thermal electric plants (the Pechora coal basin, Russia). End products are powders that are mixtures of zeolites and non-reacting residual in various quantitative ratios, their output being 70-80 % of the mass of the initial fly ash. The effect is identified of the conditions of hydrothermal reaction (temperature, alkali concentration, reaction time) on the zeolite type. It is demonstrated that



sorption structural characteristics of synthesized products depend on the zeolite type and its content in the mix. Additional experiments made it possible to update the crystallization field. It is found that synthesized zeolites manifest quite high activity with respect to cations of  $\text{NH}_4^+$ ,  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$ .

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