

Conference Proceedings

2nd International Conference on Applied Mineralogy & Advanced Materials - AMAM2017

Fly ash of the Pechora basin, Russia: Waste as a resource

Olga Kotova^{1*}, Igor Shabalin², Dmitry Shushkov¹, Yu Wang²

¹*The Institute of Geology, Komi SC, UB, RAS, Syktyvkar, 167982, Russian Federation*

²*The University of Salford, Manchester, M5 4WT, United Kingdom*

**kotova@geo.komisc.ru*

Abstract

The fly ash, a by-product of coal combustion in thermal power plants, is one of the most complex and abundant of anthropogenic materials, which large accumulations represent a serious environmental threat. To reduce the environmental burden and improve the economic benefits of energy production, the science and industry focus on the transformation of coal combustion by-products into new functional materials. The fly ash from power plant burning coal of Pechora basin (Russia) and synthesized products were studied by modern analytical methods. As a result of the hydrothermal reaction several types of zeolites were synthesized from the fly ash: analcime, faujasite (zeolite X) and gismondine (zeolite P). It was shown that the experimental conditions (temperature, reaction time and alkali concentration) have a significant influence on the type of zeolite and its content in the reaction products. The series of experiments resulted in schematic diagram of zeolites crystallization. New data on the sorption-structural characteristics and cation-exchange parameters for uranium, radium, thorium, ammonium, strontium, barium were obtained.

Keywords: Coal Fly Ash; Synthetic Zeolites; Sorption; Radionuclides; Uran; Thorium; Radium; Barium; Strontium; Ammonium

Introduction

The fly ash is a bulk industrial waste of coal combustion in thermal power plants, steel mills, etc. Therefore, the problem of utilisation of this technogenic waste, occupying large areas and causing damage to the environment, is very important. Many papers were published on the properties of fly ash and possibilities of its use (Blisset & Rowson 2012; Yao et al., 2015; Ahmaruzzanman, 2010), but mass utilization lacks. One of solutions may be represented by the synthesis of zeolites from fly ash – important type of sorbents for mining-chemical industry. Conversion products of the fly ash in zeolites has many applications,

including ion exchange, molecular sieves and adsorbents (Nascimento et al., 2009; Kotova et al., 2015; Penilla et al., 2006). Identification of new applications has a real commercial interest: the list of marketable products is expanding and energy costs are reduced, environmental risks are reduced and the efficiency of sustainable development in the region is increased. Technologies of zeolite synthesis from fly ash are being constantly improved in both the experimental (variations of temperature, pressure, co-reagent and other methods of exposure) sphere, and the material composition of the initial raw (Querol et al., 2002; Murayama et al., 2002; Belviso et al., 2009); the quality, application area and cost of final product depend on it.

The aim of this work is to develop scientific base for zeolite synthesis techniques including conditions of hydrothermal reaction (temperature, reaction time, alkali concentration), and also to study sorption-structural parameters of synthesized zeolites and their cation-exchange properties for ammonium, strontium, barium and radionuclides (uranium, radium, thorium).

Objects and methods

For the experiments, the coal fly ash from thermal power plants burning coal of Pechora basin (Russia) was used.

The synthesis methods of zeolites were based on Belviso et al. (2009). Firstly, using a magnetic separator ferriferous phases, which do not participate in the synthesis of zeolites, were removed. Dry fly ash is mixed with the solution of sodium hydroxide in a certain ratio, mixed thoroughly, and the suspension was placed in an autoclave. The resulting products of hydrothermal reaction was washed with distilled water and dried. This resulted in powders consisting of the mixture of zeolite and unreacted residue in various proportions.

The chemical composition of the fly ash and synthesized products was determined by X-ray fluorescence analysis (spectrometer MESA 500 W, Horiba). To study the morphology and chemical composition we used a scanning electron microscope TESCAN VEGA 3 LMH equipped with Oxford Instruments X-Max. The phase composition studies were performed on powder diffractometer (Shimadzu XRD 6000, radiation $\text{CuK}\alpha$). The specific surface area, total pore volume, volume of micropores were measured by the analyzer of the surface area and pore size Quantachrome NOVA 1200e.

Ammonium concentration in the solution was determined by the photometric method with Nessler reagent according to Guiding document 52.24.486.2009. The concentration of strontium and barium was determined by ICP-AES spectrometer Vista MPX Rad.

Uranium, thorium and radium concentration were determined by luminescent method, photocolometric method using reagent arsenazo III and emanation method (Dobrolubskaya, 1962; Kuznetsov & Savvin 1961; Starik, 1969), respectively. In order to check the ability of zeolites to retain radionuclides the 3rd step extraction (desorption) procedure using processing with distilled water, 1M ammonium acetate ($\text{CH}_3\text{COONH}_4$) and 1M hydrochloric acid was carried out.

Results and discussion

1.1 Initial fly ash

X-ray diffraction showed quartz, mullite, magnetite and hematite in the fly ash. The broad "hump" on the diffraction pattern in the area 15–35 °2 θ indicates the presence of amorphous phase – probably silicate or aluminosilicate glass.

The main components of the chemical composition are SiO₂ (57.78%) and Al₂O₃ (18.25%), iron oxide content is about 9.0%, oxides of other elements - 7.42%, loss on ignition - 7.90%.

The fly ash is represented under the electron microscope by globules, which are divided by the chemical composition to aluminosilicate and iron containing. The aluminosilicate globules composition is predominated by SiO₂ (from 41.82 to 61.27%) and Al₂O₃ (from 17.03 to 22.8%); FeO and Fe₂O₃ (up to 8.31%), MgO (up to 4.83%), K₂O (up to 3.05%), TiO₂ (up to 1.04%) and Na₂O (up to 0.93%) are also present. Globule size varies from the first to about hundred micrometers; on the surface bubbles and elongated structures are observed.

On the surface of iron containing globules both flat areas and skeletal forms are observed, which are significantly different from each other by their chemical composition. The skeletal forms have a high content of iron oxides (68.14-74.66%) and low SiO₂ (1.06-6.22%), Al₂O₃ (1.33-4.17%) and CaO (0.48-3.59%) contents. On the flat areas iron oxides content is greatly reduced (19.29-31.81%), SiO₂ and Al₂O₃ content increases (27.12-37.86 and 2.06-6.22%, respectively); CaO is present in amounts of 10.45-25.3%. Globule size ranges from some to tens micrometers. Globules, which contain smaller globules within, are often observed.

1.2 Hydrothermal synthesis

Two sets of experiments were carried out. In the first set the effect of temperature of hydrothermal reaction on zeolite synthesis was studied (reaction temperature 80, 95, 140 and 180 °C, reaction time 12 hours, the ratio of NaOH: fly ash = 1:1, NaOH concentration 3.0 mol/dm³). The second set of experiments studied the influence of reaction time and concentration of alkali on synthesis process (reaction temperature 140 °C, reaction duration 2, 4, 6 and 8 hours, ratio of NaOH: fly ash = 1:1, NaOH concentration 1.5, 3.0 and 4.5 mol/dm³). Earlier we showed the scheme of transformation of fly ash into zeolites in (Kotova & Shushkov 2015; Kotova et al., 2016). The synthesis results in powders consisting of the mixture of zeolite and unreacted residue in different proportions, in which output was 70-80% of the weight of the initial fly ash.

1.3 Effect of reaction temperature on the synthesis of zeolites

In the result of the reaction at 80 °C, the intense reflections of quartz were diagnosed; no newly formed phases were detected. Electron microscopic studies revealed numerous globules destroyed by alkaline solution.

By increasing the reaction temperature to 95 °C silica the intensity of quartz reflections decreased, i.e. it was dissolved in alkaline solution. Alongside with quartz reflections the intense reflections were determined, which are characteristic for fujasite (zeolite X), and

weak reflections characteristic for gismondine (zeolite P). By Si/Al ratio, the zeolites are low silica: silica-aluminum module of zeolite X varies from 1.51 to 1.57, zeolite P – from 1.65 to 1.69. SEM images present numerous crystals of zeolite X with octahedral shape with the size of 1-3 μm . Zeolite P crystals have a rounded shape, their size is about 5 μm (Kotova & Shushkov, 2015; Kotova et al., 2016).

The diffraction patterns of the reaction products obtained at 140 °C showed zeolite P and analcime, weak quartz reflections were also present. Zeolite P is higher in silica compared to the phase obtained at 95 °C: Si/Al ratio varies slightly from 1.93 to 1.94. Silica-aluminum module of analcime varies from 2.12 to 2.21. SEM images showed that zeolite P formed skeletal crystals with size of 10-15 μm . Analcime crystals with size of 15-20 μm were observed.

The reaction at 180 °C resulted in the formation of analcime and cancrinite; no quartz reflections were diagnosed. Si/Al ratio of analcime varies from 2.00 to 2.15. The analcime crystals are formed by tetragonal faces, their size ranges from 15 to 25 μm . Cancrinite columnar crystals with length of up to 2 μm and about 200-300 nm in diameter are often observed on the surface of analcime, indicating later crystallization of cancrinite.

These results indicate that the reaction temperature influences the type of synthesized zeolite, which differs by pore size, and according to classification (Chelischev et al., 1987), they are divided into narrow, medium and wide porous types. It is determined that increasing reaction temperature results in the formation of narrow porous zeolites: at 95 °C zeolites X formed that are related to wide porous type, at 140 °C – zeolite P, related to medium porous type, and at 180 °C – analcime related to narrow porous type. Pore size of zeolites was as follows: analcime, 0.26 and 0.42 \times 0.16 nm; zeolite P, 0.31 \times 0.45 and 0.28 \times 0.48 nm; and zeolite X, 0.74 nm.

1.4 Effect of reaction time and alkali concentration on zeolite type

The set of experiments resulted in the schematic diagram of zeolites crystallization at 140 °C, the reaction time from 2 to 8 hours, NaOH concentration 1.5, 2.9 and 4.5 (Kotova & Shushkov, 2015; Kotova et al., 2016). The wide porous zeolites X are formed after 4 hours of reaction at a high concentration of alkaline solution (4.5 mol/dm³). Longer reaction leads to the disappearance of the metastable phases of zeolite X and the occurrence of more thermodynamically stable - zeolite P and then analcime.

Zeolite P is crystallized under a wide range of reaction conditions. At the same time, the fields of crystallization of analcime and zeolite P are significantly overlapped, that is, at the same conditions of the hydrothermal reaction, the mixture of zeolites in various quantitative relations is formed. A higher concentration of alkali results in the increase of the content of narrow porous phases (analcime) compared to zeolite P, and contributes to the formation of hydrosodalite.

1.5 Sorption-structural and ion exchange properties

The specific surface area of the synthesized zeolites varies in a wide range from 28 to 269 m²/g depending on the type of zeolite. The specific surface area of the initial fly ash is 3.2-9.9 m²/g. The wide-porous zeolites X (synthetic analogue of natural faujasite) have the largest specific surface area. It should be taken into account that this method cannot measure the specific surface of narrow-porous zeolites, such as analcime, since the pore

size of the analcime (0.26 and 0.16×0.42 nm) is smaller than the diameter of the nitrogen molecule (0.32-0.35 nm). The specific surface area of pure analcime was only 1.5 m²/g.

The total volume of pores (0.02977-0.1526 cm³/g), the volume of mesopores (0.02172-0.05058 cm³/g) and micropores (0.01042-0.1323 cm³/g) also increase in comparison with the initial fly ash (0.00373-0.00595; 0.00285-0.00539 and 0.00113-0.000374 cm³/g, respectively) and depend on the type of synthesized zeolite and its content in the mixture. Direct correlation between the total pore volume and the volume of micropores with the specific surface area is observed.

The synthesized zeolites are characterized by high sorption activity for natural long-lived radionuclides - uranium, radium, thorium (U²³⁸, Ra²²⁶, Th²²³). From model solutions, where the concentration of radionuclides exceeds the natural concentration, up to 98% of radium, more than 89% of thorium and 80% of uranium were removed (Table 1).

Table 1. Sorption of uranium, radium and thorium by synthesized zeolites

Radionuclide	Initial concentration of radionuclide in solution, g/ml	Concentration of radionuclide in solution after sorption, g/ml	Extraction degree, %	Distribution coefficient, ml/g
Uranium	1.35·10 ⁻⁶	0.25·10 ⁻⁶	81.3	43.53
Radium	28.31·10 ⁻¹²	0.47·10 ⁻¹²	98.34	592.24
Thorium	0.87·10 ⁻⁶	0.09·10 ⁻⁶	89.36	84.54

The study of desorption characteristics showed that the sorbents possess a low desorption of radium and uranium (about 5 and 10%, respectively). Thorium is retained by zeolites the least strongly, 35% of the radionuclide was desorbed into the solution. The combination of high sorption activity and ability to hold radionuclides strongly is an important characteristic of a sorption material in terms of its practical use, since it avoids secondary (reverse) contamination of the environment by radionuclides. The obtained sorbents can be used to capture and retain radionuclides in solutions in a wide range of concentrations. This also increases the scope of the sorption material - from low-concentration natural waters to high-level radioactive liquid wastes from nuclear power plants.

We determined that the sorption capacity of barium were from 113 to 157 mg/g (1.65-2.29 mg-equiv/g), depending on the type of zeolite. The sorption capacity of strontium reached 86 mg/g (1.94 mg-equiv/g), ammonium – 32 mg/g (1.78 mg-equiv/g). When the sodium hydroxide was added to the solution, the sorption selectivity of strontium decreased, the sorption capacity decreased to 57 mg/g (1.31 mg-equiv/g). The exchange reactions had a high rate, so after only 5 min the extraction degree of the cations was more than 90%.

Conclusions

Efficient sorbents have been synthesized on the basis of technogenic materials resulted from the burning of coal of thermal power plant (Pechora coal basin, Russia). Synthesized product is represented by powders - mixture of zeolite and unreacted residue in various proportions, which yield was 70-80% to the weight of the initial fly ash. The influence of hydrothermal reaction (temperature, alkali concentration, reaction time) on the type of zeolite was presented. It was shown that the sorption-structural characteristics of the synthesized products depend on the type and content of zeolite in the mixture. The

synthesized zeolites exhibited a high sorption activity to radionuclides and ability to retain them strongly. Sorption capacity of cations was as follows: $Ba^{2+} > Sr^{2+} > NH_4^+$.

Acknowledgements

The authors express gratitude to the common use center “Geonauka” for their help in analytical work. This work was supported by the Program of UB RAS (project 15-18-5-45).

References

- Ahmaruzzaman M. (2010). A review on the utilization of fly ash. *Progress in Energy and Combustion Science* 36, 327-363.
- Belviso C., Cavalcante F., Lettino A., Fiore S. (2009). Zeolite synthesis from fused coal fly ash at low temperature using seawater crystallization. *Coal Combustion and Gasification Products Journal* 1, 8-13.
- Blisset R.S., Rowson N.A. (2012). A review of multi-component utilization of fly ash. *Fuel* 97, 1-23.
- Chelischev N.F., Berenstein B.G., Volodin V.F. (1987). *Zeolites as a new type of mineral raw*. Moscow, p 14. (in Russian).
- Dobrolubskaya T.S. (1962). *Luminescent method (Analytical chemistry of uranium)*. Moscow, pp 143-165 (in Russian).
- Guiding document 52.24.486-2009. *Mass concentration of ammonium and ammonium ions in waters. Methods of photometric measurements with Nessler reagent*. (in Russian).
- Kotova O.B., Shabalin I.L., Shushkov D.A., Ponaryadov A.V. (2015). Sorbents based on mineral and industrial materials for radioactive wastes immobilization. *Vestnik of the Institute of Geology of Komi SC of UB of RAS* 2, 32-34. (in Russian).
- Kotova O.B., Shabalin I.N., Shushkov D.A., Kocheva L.S. (2016). Hydrothermal synthesis of zeolites from coal fly ash. *Advances in Applied Ceramics: Structural, Functional and Bioceramics*, 115, 3, pp. 152-157.
- Kotova O.B., Shushkov D.A. (2015). A process of zeolite production from fly ash // *Obogashchenie Rud* 5, 60-63. (in Russian).
- Kuznetsov V.I., Savvin V.B. (1961). Delicate photometrical determination of thorium with reagent arsenazo III. *Radiochemistry* 1, 79-86 (in Russian).
- Murayama N., Yamamoto H., Shibata J. (2002). Mechanism of zeolite synthesis from fly ash by alkali hydrothermal reaction. *International Journal of Mineral Processing* 64, 1-17.
- Nascimento M., Soares P.S.M., Souza V.P. (2009). Adsorption of heavy metal cation using coal fly ash modified by hydrothermal method. *Fuel* 88, 1714-1719.
- Penilla R.P., Bustos A.G., Elizalde S.G. (2006). Immobilization of Cs, Cd, Pb and Cr by synthetic zeolites from Spanish low-calcium fly ash. *Fuel* 85, 823-832.
- Querol X., Moreno N., Umana J.C., Alastuey A., Hernandez E., Lopez-Soler A. (2002). Synthesis of zeolites from coal fly ash: an overview. *International Journal of Coal Geology* 50, 413-23.
- Starik I.E. (1969). *Fundamentals of radiochemistry*. St. Peterburg, 247 pp. (in Russian).
- Yao Z.T., Ji X.S., Sarker P.K., Tang J.H., Ge L.Q., Xia M.S., Xi Y.Q. (2015). A comprehensive review on the application of coal fly ash. *Earth-Science Reviews* 141, 105-121.