Synthetic Zeolitic Ion-Exchangers from Coal Ash for Decontamination of Nuclear Wastewaters

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Abstract. In this study, the conversion of lignite coal fly ash into zeolite of hydrosodalite type is investigated with aim to obtain alternative materials for entrapping of radioactive ^{137}Cs and ^{90}Sr from nuclear wastewaters. The development of this approach will contribute to resolve severe environmental problems in worldwide scales, such as natural resources economy for count of utilization of waste resources. In a special case of Bulgarian energy branch it concerns the utilization of solid wastes from combustion of domestic lignite coal in the thermal energy complex "Maritza East", supplying cheap materials for decontamination of liquid nuclear wastes from radioactive components in a case of normal exploitation and in a situation of emergency. The obtained materials were analysed by X-ray diffraction and scanning electron microscopy. The optimal synthesis conditions were considered by the electrical consumption for the process at following parameters: NaOH/FA=2/1, 3M NaOH, 24 h magnetic stirring, and hydrothermal activation at 90°C for 4 h.

Keywords: fly ash, hydrosodalite, radioactive waters, synthetic ion-exchangers

1 Introduction

Zeolites are highly valuable natural and synthetic aluminosiclicate materials that are broadly applied in environmental protection systems due to their unique porous structure favourable for surface phenomena that determine their applications as adsorbents, catalytic carriers, molecular sieves, etc. [1]. The structural features, as well as the chemical inertness and resistance of these materials to radiation make them a powerful tool for the decontamination of waters containing radionuclides based on their ion-exchange properties. The use of zeolites with well-pronounced ion-exchange capability such as clinoptilolite, chabazite, linde, etc., in nuclear waste decontamination is a well-established practice. Three big NPP incidents in the near past in NPP Three Mile Island in 1979, NPP Chernobyl in 1986, and NPP Fukushima Daiichi in 2011 have caused damages over a wide range. The consequences have been confined by decontamination of accident radioactive wastewaters using zeolitic ion-exchangers for uptake radioactive caesium (^{137}Cs), strontium (^{90}Sr) and other radionuclides holding them in three-dimensional crystal framework [2,3]. Zeolites react readily with cement and glass systems thus allowing the radioactive waste to be entrapped and contained safely. In NPP Chernobyl, over 500,000 tons of natural clinoptilolite have been dropped into the reactor to capture radioactive metals [4]. After the disaster, enormous amounts of zeolites have been used for the construction of protective barriers, for agricultural applications in polluted areas, for decontamination of potable water of the Dnieper River, as well as for extraction of radionuclides from the drainage water of the encapsulated NPP Chernobyl. Natural zeolites have been also added to animal and human foods to reduce the radionuclide levels in their organisms. The commercial zeolites Ionsiv IE-96 and A-51 have been used effectively for the decontamination of high-level wastewaters generated in the reactor during the Three Mile Island accident [5]. The main challenge in water treatment after the Fukushima accident has been to remove radioactive ^{134}Cs, ^{137}Cs, and ^{90}Sr from reactor water and sea water with high salinity. Kurion Company have built technology proven at Three Mile Island, designing external cooling system for nuclear reactors that allows water recirculation to reduce the additional water. Kurion's solution has been based on ion-exchange between sodium and caesium, using Kurion's Ion Specific Media based on zeolite of hershelite type [6].

The cation-exchange capacity (CEC) of natural and some synthetic zeolites toward radioactive species in liquid solutions are widely studied [5-8]. Cation-exchange capacities of some natural and synthetic zeolites, obtained experimentally in different studies are shown in Table 1.

The selectivity order $Sr^{2+} > Ca^{2+} > Mg^{2+} > Cs^+ > Na^+$ for the synthetic LTA zeolites is published in Ref. [12].

Another utilization of zeolites in nuclear safety systems for control of radioactive iodine and krypton during nuclear fuel reprocessing is revealed in the investigations of Soelberg et al. [14].

Taking into account the mentioned above, it can be considered that the zeolites are the life- and environment saving materials in the nuclear decontamination systems. For preservation of natural zeolitic resources, synthetic analogues have been developed, but more recently, synthetic zeolites are being obtained using aluminosilicate residues. An enormous aluminosilicate source is the coal ash generated by the coal supplied thermal power plants (TPP), which can be readily and cost-effectively transformed into

Table 1. The cation-exchange capacity of natural and some synthetic zeolites toward radioactive isotopes in liquid solutions

| Type of zeolite	Cation exchange capacity, meq/l	Ref.	Type of zeolite	Cation exchange capacity, meq/l	Ref.
Natural clinoptiololite	CEC of ^{137}Cs is 1.95 CEC of ^{90}Sr is 2.20	[9]	Natural chabazite	CEC of ^{137}Cs is 3.55 CEC of ^{90}Sr is 4.80	[11]
Synthetic NaP	CEC of ^{137}Cs is 3.52 CEC of ^{90}Sr is 3.68	[10]	LTA Synthetic A	CEC of ^{90}Sr is 5.50 CEC of ^{90}Sr is 4.60	[12] [13]

Table 2. The chemical composition of investigated fly ash in oxide form

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	MnO	ZnO	Na_2O	K_2O
weight %	52.66	23.37	8.72	5.75	2.75	2.40	0.06	0.04	0.01	0.01

zeolites for industrial applications by alkaline conversion. This technological approach will contribute to several ecological benefits, such as raw material economy, reduction of solid waste disposal from TPPs, production of ion-exchangers and adsorbents for environmental protection systems. In our previous studies, the synthesis of highly-porous Na-A and Na-X zeolites from Bulgarian lignite coal fly ash (FA) have been studied with respect to their application in gas separation systems [15,16].

The aim of this paper is to study the conversion of lignite coal FA into zeolite with ion-exchange properties, which could be applicable for radioactive water decontamination.

Zeolites are natural or synthetic crystalline aluminosilicates with a structural framework built-up of $SiO_{4/2}$ and $[AlO_{4/2}]^-$-tetrahedra linked each to other at the corners by sharing an oxygen bridge. The negative charge at $[AlO_{4/2}]^-$-tetrahedra is compensated by easy replaceable metal-cations such as Na^+, K^+, Ca^{2+}, Mg^{2+}, etc., that determine the ion-exchange ability of zeolites for effective removal of pollutants from contaminated waters [17]. The most common cation in natural and synthetic zeolite structure is Na^+, which can be easily replaced by Sr^{2+} or Cs^+ ions from aqueous solutions through the following mechanism:

$$Sr_{aq}^{2+} + \overline{Na_{solid}^+} \xrightarrow{\Delta G\, Na \to Sr} Sr_{solid}^{2+} + Na_{aq}^+ . \qquad (1)$$
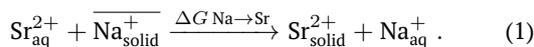
The visualization of the cation-exchange from aqueous solution to solid zeolite structure is shown in Figure 1.

2 Materials and Methods

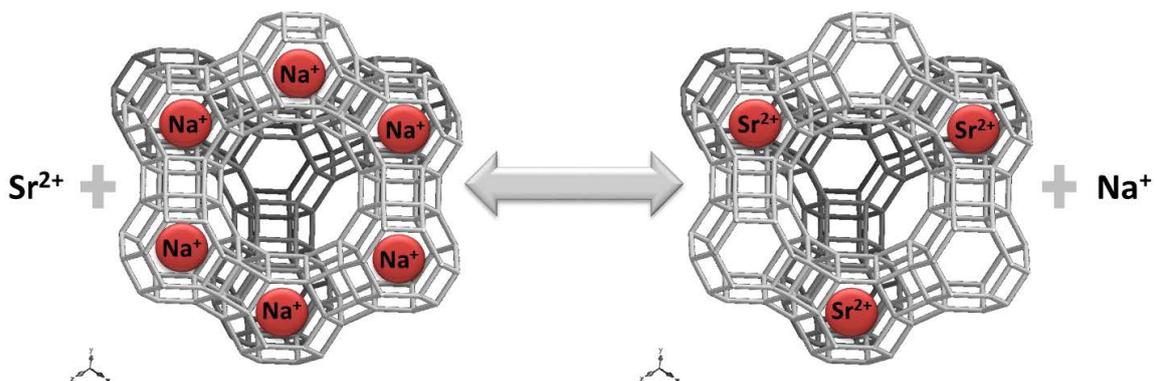FA obtained from electrostatic precipitators of Bulgarian TPP "Maritza East 2" is subjected of zeolitilization. In a previous paper the chemical and structural properties of this material were published [18]. The chemical composition of FA in oxide form is represented in Table 2. The ratio of crystalline vs. amorphous phase is 57/43. The crystal structure consists mainly of quartz, mullite, gypsum, magnetite, and hematite.

The synthesis method applied to the FA in this study is classical alkaline hydrothermal treatment [1]. The process consists of consequently dissolution of Al and Si components from FA in liquid alkaline media of NaOH, formation of aluminosilicate hydrogel, and its crystallization into zeolite structure (See Figure 2). The temperature of the process is kept constant.

The steps of the laboratory syntheses are in the following consequence: (1) mixtures of FA, NaOH and distilled water are prepared in respective proportions; (2) the obtained solid/liquid suspensions are subjected to continuous magnetic stirring to accelerate the solubility of Al- and Si-containing components; (3) the reaction mixtures are filled in autoclaves and subjected to hydrothermal treatment at 90°C in a laboratory oven for different duration; (4) the synthesized materials are washed with distilled water, separated by filtration and dried at 105°C for 1 hour. The experimental conditions are listed in Table 3.
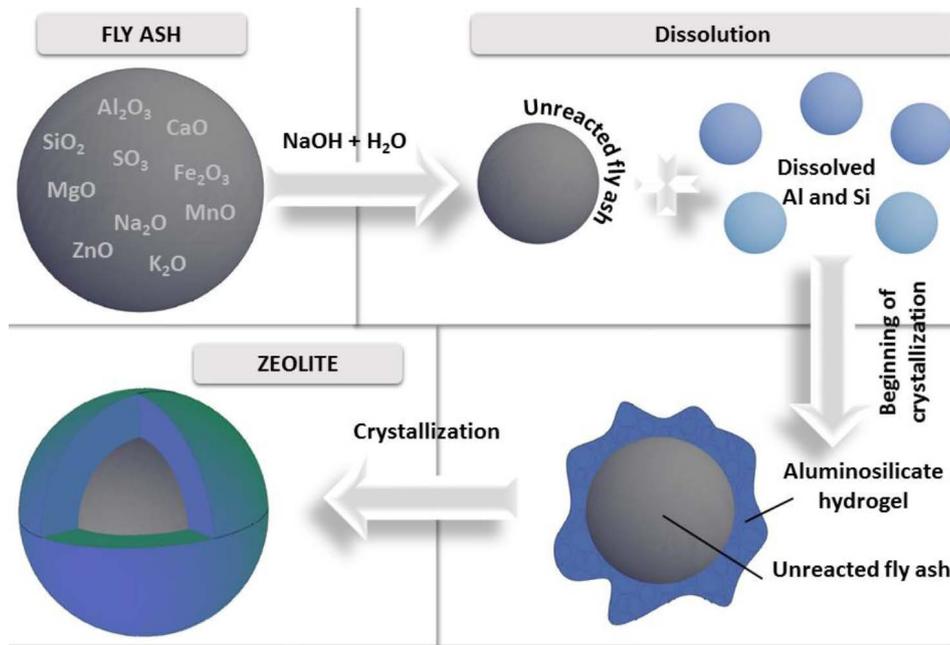

Figure 1. Mechanism of ion-exchange from aqueous solution to solid zeolite structure.

Figure 2. Mechanism of hydrothermal synthesis of fly ash into zeolite.

Table 3. Experimental conditions of fly ash hydrothermal activation

Sample	NaOH/FA	NaOH	Magnetic stirring	Temperature of synthesis	Time of synthesis
No		M	h	°C	h
H-2	1.2	1.5	8	90	3
H-4	2	3	16	90	4
H-5	2	3	7	90	66
H-6	2	3	2	90	4
H-7	2	3	24	90	5
H-8	2	3	0	90	165

Structural analysis of the obtained solid powders was performed by X-ray diffraction (XRD) technique on a Brucker D2 Phaser diffractometer with CuK_{α}-radiation and a Ni filter. Morphological observations were carried out by Scanning Electron Microscopy (SEM), model JEOL JSM6390, coupled with an Oxford Instruments energy-dispersive X-ray (EDX) analyser. For the evaluation of the economical parameters of the different synthesis conditions, the electricity consumption of the processes considered was estimated with an energy measurement device Brennenstuhl PM231 E. The obtained results are attributed to the specific consumption per mass unit of FA zeolite (FAZ) in kWh/kg FAZ.
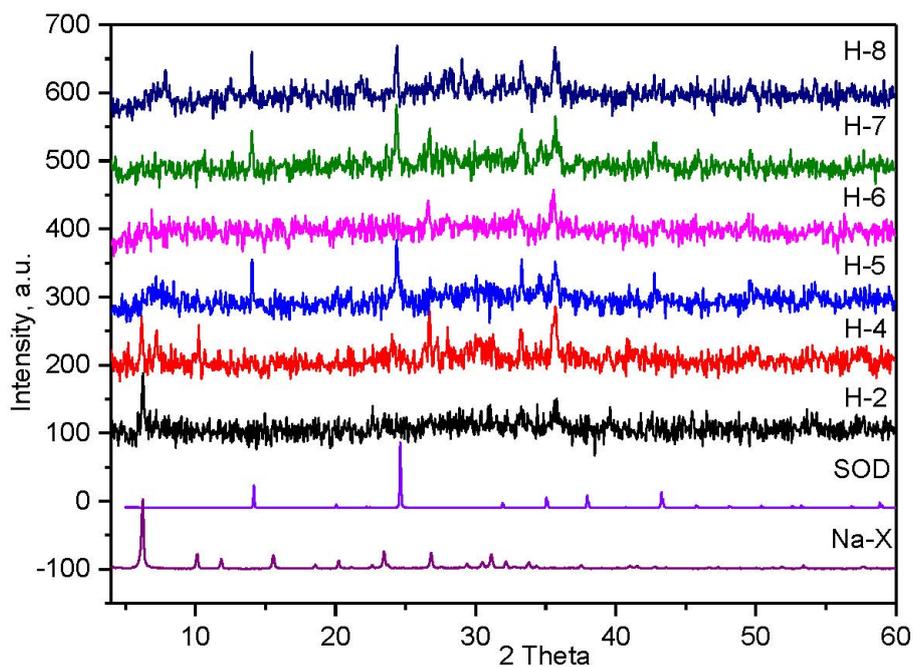

Figure 3. XRD patterns of the obtained synthetic materials, referent Na-X and SOD zeolites.
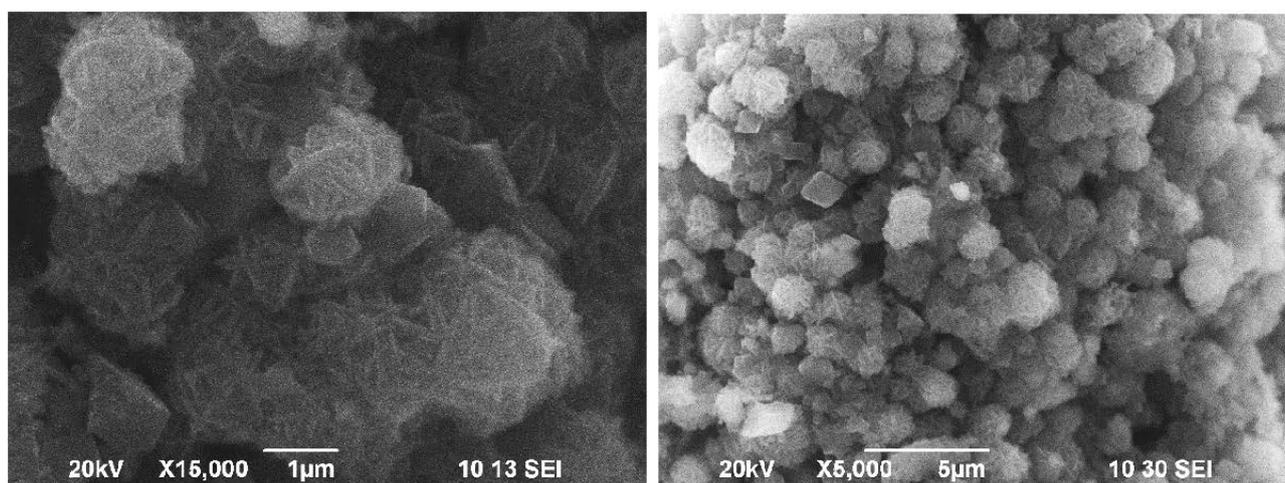
Figure 4. SEM images of the obtained hydrosodalite zeolite from fly ash.

3 Results and Discussions

The XRD patterns of the obtained synthetic materials, the referent Na-X and SOD zeolites are shown in Figure 3. Some peaks that correspond to the raw FA components can be observed on the diffractrograms of the all samples. The intensive peaks of unreacted mullite are registered at $2\theta = 26.59$ and $2\theta = 33.28$. The magnetite does not participate in the zeolitization process and its main peak is appeared at $2\theta = 35.59$. The existence of these reflections is expected because of the low solubility of mullite and magnetite at low temperature conditions.

XRD analysis of the sample H-2 shows very low zeolitilization of FA represented by a single peak of Na-X zeolite. For process optimization the molarity of NaOH was increased from 1.5M to 3M. Samples from H-4 to H-8 were obtained at the same experimental conditions in regards to the NaOH molarity and the temperature of the hydrothermal synthesis. The duration of the magnetic stirring and the crystallization time were varied to obtain optimal economical parameters. On the XRD patterns of the sample H-4, intensive peaks of Na-X and SOD are registered. The decrease of the time of magnetic stirring from 16 h for H-4 to 0 h for H-6, leads to lack of any zeolitic phase. The solubility of Al and Si components from FA is realized during the hydrothermal treatment. It was established, that the duration of 4 h is not enough for the subsequent crystallization of hydrogel. At the synthesis of sample H-8, magnetic stirring is also skipped while the hydrothermal incubation is drastically increased from 4 h to 165 h. On the XRD pattern of sample H-8, all of the intensive peaks of SOD are observed. The results from XRD analysis of samples H-5 and H-7 are identical to those for H-8. The synthesis conditions for H-5 and H-8 differ in the shorter magnetic stirring for 7 h and the two times shorter crystallization. At sample H-7, the duration of the stirring and synthesis is in opposite. The obtaining of SOD with equal intensity of XRD peaks at the samples H-5, H-7, and H-8 is indicative for a correlation between the prolongation of magnetic stirring and hydrothermal activation. The morphological observations of these three samples are in good agreement with the XRD results. Typical SEM images of the obtained materials are shown in Figure 4 in different approximation. The sample surface is well covered with typical for SOD "rose-shaped" individual crystals with size around 1.5 μm.

The evaluation of optimal synthesis conditions for samples H-5, H-7, and H-8 was performed by measuring the electrical power applied for magnetic stirring and hydrothermal activation, attributed to the treatment of 1 kg FA. The electricity consumption for drying of the samples is omitted because of its constant value. The results are listed in Table 4.

Table 4. Electricity consumption for magnetic stirring and hydrothermal activation to obtain hydrosodalite by fly ash zeolitilization

Sample No	Magnetic stirring kWh/kg FA	Hydrothermal activation at 90°C kWh/kg FA	Total electricity consumption kWh/kg FA
H-5	0.359	28.743	29.102
H-7	1.230	1.742	2.972
H-8	0.000	71.875	71.875

As the consumption of electricity for the thermal treatment in the laboratory oven is higher than by the magnetic stirring, the optimal conditions are obtained at the shorter time of hydrothermal activation.

4 Conclusion

Zeolite analogies of natural ion-exchangers were synthesized from lignite coal ash through classical hydrothermal activation at different conditions. The obtained samples were analysed with respect to their crystallography and morphology by XRD and SEM. The obtained synthetic zeolites are of hydrosodalite type that could be applied successfully as ion-exchangers in systems of nuclear safety for trapping radioactive ^{137}Cs and ^{90}Sr. The optimal preparation conditions were evaluated on the base of the electrical consumption for the synthesis process, as the following parateters were considered as the most economical: NaOH/FA=2/1, 3M NaOH, 24 h magnetic stirring, and hydrothermal activation at 90°C for 4 h. The develop-

ment of this approach will give a cheap alternative material for removal of radioactive components from liquid nuclear wastes. Moreover that, the resources of natural ion-exchangers will be saved, while solid coal ash residues will be reduced.

Acknowledgments

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