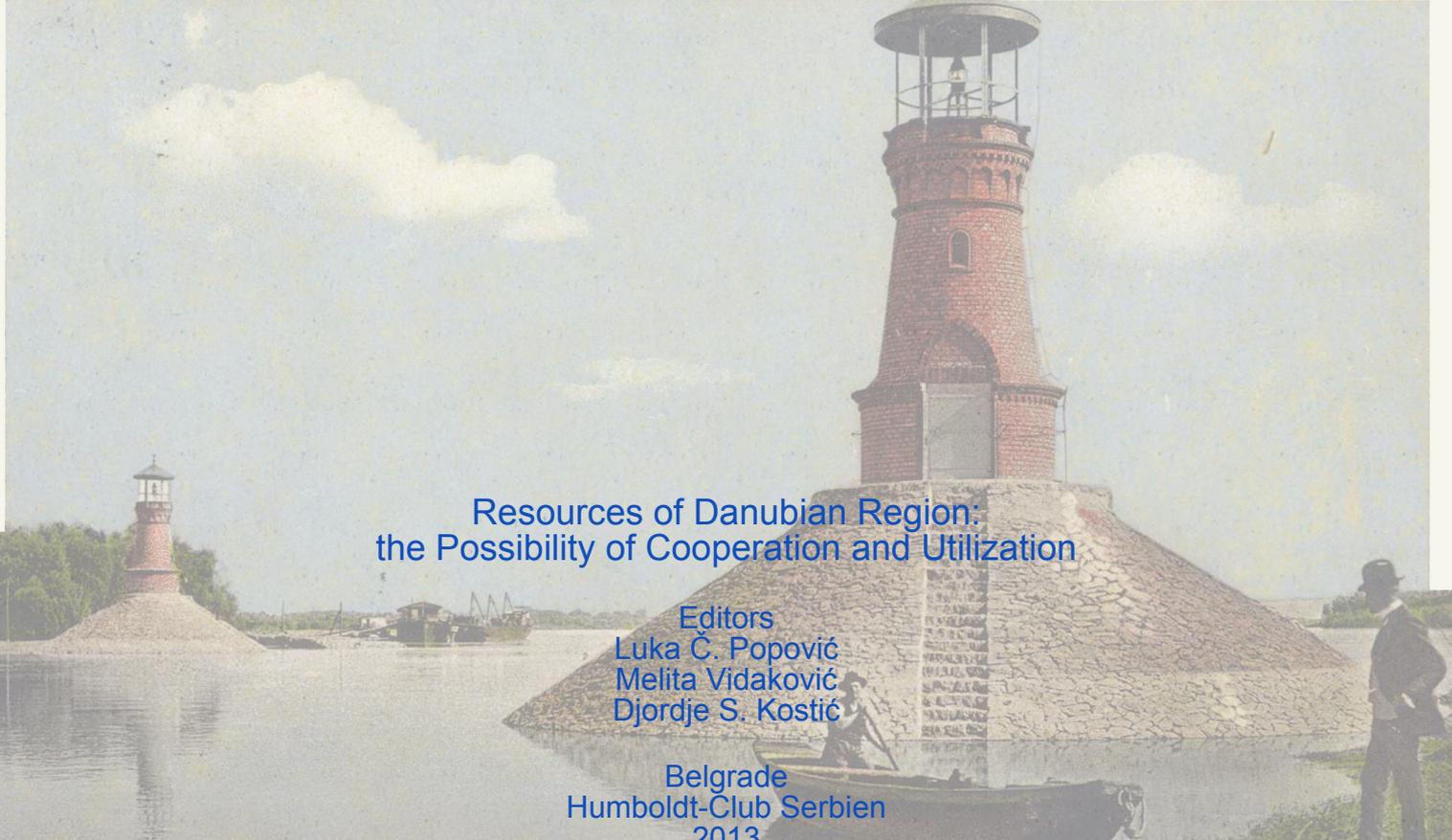**Denitza Zgrureva**
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UTILIZATION OF FLY ASH BYPRODUCT FROM THE COAL COMBUSTION IN ENVIRONMENTAL PROTECTION SYSTEMS

Resources of Danubian Region:
the Possibility of Cooperation and Utilization

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Abstract. Fly ash (FA) from lignite coals burned in the biggest Thermal Power Plant in Bulgaria was used as raw material for synthesis of zeolites. Zeolitization was performed by two-steps fusion hydrothermal synthesis using sodium hydroxide as an alkaline activator. The FA and the treated samples were investigated with respect to their morphology and surface composition. The influence of the synthesis condition on the elemental composition in the surface layer of the samples was studied. FA characterizes with an optimal Si/Al ratio for the synthesis of Na-X zeolite types.
Key words: Fly ash, Synthetic zeolites, Molecular sieves, Hydrothermal synthesis

1. Introduction

Although Bulgaria is not very rich in natural fuels like coals, oil and gas it has very well developed energy sector. Bulgaria is a major producer and exporter of electricity and plays an important role in the energy balance of the Balkans. In 2011, the total electric power generated by different sources in the country is 50682.30 GWh, as 49.6 % of the energy was produced by coal fired power plants, 32.2 % by the Nuclear Power Plant, and the other sources have a smaller contribution to the energy production.

The main local energy source is lignite coals from "Maritza East" Basin, from where around 86 % of the total fired coals are mined. The conventional Thermal Power Plants (TPP) supplied by these lignite coals provides 40 % of the annually produced energy in Bulgaria [1]. The incineration of pulverized fossil fuel generates solid residues consisting of 80 % fly ash (FA) and 20 % slug. For the European Union (EU), the amount of FA produced by TPP overcomes 34 million tonnes per year. FA is a serious environmental pollutant, especially for the hydrosphere and lithosphere. In the last decades different approaches for its conversion in valuable products have been developed (Figure 1) [2].

Unfortunately, the utilization of FA in EU is less than 25 % of the totally generated residue, which means that 25.5 million tonnes of FA are annually disposed in open land areas [3]. The integration of large-scale technologies for utilization of FA, which will reduce significantly the proportion of the disposed residues, is a matter of great importance for all countries producing electricity from coals. In the recent years, hard work has been done towards the FA conversion in synthetic zeolite materials stipulated by its major constituents, namely 52-90 % aluminosilicates (for FA produced in Europe). Generally, the synthesis of zeolites is a transformation of the aluminosilicate glass in crystalline phases under the influence of alkalizing reagents [4]. Different zeolite forms (up to 15) can be obtained by one

and the same FA composition, varying the synthesis conditions: the type and combination of alkaline reagents, alkaline reagent/FA ratio, solution molarities, temperature, reaction time and pressure [5]. The zeolites are high porous materials with variable pore size for different zeolite types (2.1 Å to 7.3 Å for A, X and Y zeolites), which make them suitable materials especially for molecular sieves (Figure 2) [4]. These pore sizes allow the adsorption of large gaseous molecules, such as NH_3, H_2, Cl_2, N_2, SO_2, CO, CO_2, CH_4, etc., which diameters are in the range 2.5 Å - 5.1 Å.

The present research is emphasized on our initial studies on the conversion of FA derived from the lignite coal incineration in TPP „Maritza-East 2" in Bulgaria in large porous zeolites.

2. Experimental

The FA is thoroughly investigated with respect of its chemical composition, morphology and structure. To obtain zeolites, the FA was passed through primary fusion stage (calcinations with NaOH) and subsequent hydrothermal synthesis. The first stage was performed at three temperatures 550, 750 and 850 °C for 1 hour. Thereafter, the sintered alloys were crushed, mixed with distilled water and subjected to magnetic stirring for 12 hours. Such prepared water suspensions were filled into an autoclave, where the hydrothermal synthesis stage was performed at different temperatures and with different duration.
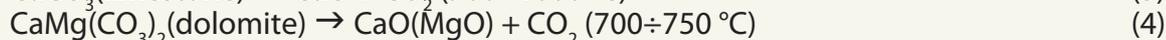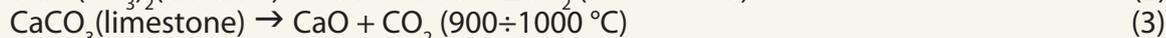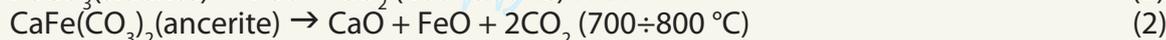
The nature of the obtained synthetic materials was proved by the help of scanning electron microscopy (SEM-EDX), model JEOL JSM6390, coupled with energy-dispersive X-ray (EDX) analyzer, Oxford Instruments.

## 3. Composition and characteristics of FA as a raw material for zeolite synthesis

During the incineration process, the minerals in the coal composition undergo chemical transformations. The most spread minerals consisting coals are listed in Table 1.

Under heating up to 500÷600 °C, the clays and the micaceous minerals firstly loose the water from their crystal hydrates, and then their crystalline lattices are destroyed forming secondary minerals (mullite, spinel, etc.) at ~1100 °C. At further heating, the mineral constituents come to melting [6].

Carbonates (dolomite, limestone, siderite) decompose in the thermal interval 400÷900 °C, forming high melting oxides, such as FeO, CaO, MgO, K_2O, Na_2O, etc.

$$FeCO_3 (siderite) \rightarrow FeO + CO_2 \ (400÷500\,°C) \quad\quad (1)$$
$$CaFe(CO_3)_2 (ancerite) \rightarrow CaO + FeO + 2CO_2 \ (700÷800\,°C) \quad\quad (2)$$
$$CaCO_3 (limestone) \rightarrow CaO + CO_2 \ (900÷1000\,°C) \quad\quad (3)$$
$$CaMg(CO_3)_2 (dolomite) \rightarrow CaO(MgO) + CO_2 \ (700÷750\,°C) \quad\quad (4)$$

Pyrites (FeS_2) is oxidized above 400 °C and it is fully burned at 700÷800 °C undergoing in Fe_2O_3.

$$2\ FeS_2 \xrightarrow{\ 5,5O_2\ } Fe_2O_3 + 4\ SO_2 \tag{5}$$
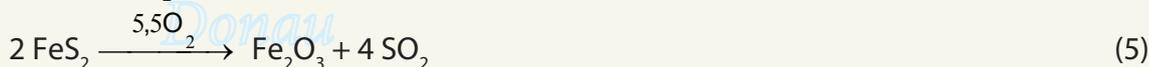
Insoluble sulphates also decompose at ~1000 °C, forming metal oxides.

$$CaSO_4 \rightarrow CaO + SO_3 \tag{6}$$
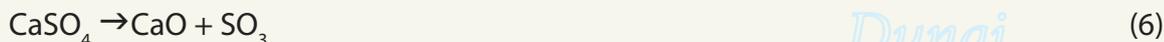
Hence, the silicates, aluminosilicates and the metal oxides are the constituents of ash residues. Ash remains on the bottom in the incineration cameras (bottom ash) or it is carried by the flue gas flow (fly ash). FA separates from flue gases by electrostatic precipitators, cyclones or mechanical filters. It consists of fine powder with spherical particles with 0.5÷100.0 µm in size. FA posses a mixed amorphous-crystalline nature composed mainly of amorphous SiO_2 (a-SiO_2) and some crystalline phases as quartz (α-SiO_2), mullite ($2SiO_2.3Al_2O_3$), hematite (α-Fe_2O_3), magnetite (γ-Fe_3O_4), etc. [6,7].

According to the International Crystallographic Standard of the American Society for Testing and Materials ASTM C618, FA is specified in two types (F and C) depending on the amounts of CaO, Al_2O_3, SiO_2 and Fe, which determine its practical applicability.

Due to its complicated nature and composition, the characterization of FA from coals is a quite difficult task [8].

FA used as a raw material for our studies was found to contain 52.66 wt.% SiO_2 and 23.37 wt.% Al_2O_3, as the amorphous phase is presented in 43 % versus crystalline. The grain size distribution of the FA particles, determined by sieve separation, was found to be between 125 and 250 µm. The measured density of the FA is ~3.07 g/cm³. The results from the compositional and crystallographic studies were published elsewhere [9]. As the total content of $SiO_2+Al_2O_3+Fe_2O_3>70$ % and the content of CaO is rather low (5.75 mass %) the investigated FA refers to the class F. This chemical composition of FA is favourable for it conversion into zeolites.

SEM micrographs of FA particles are presented in Fig. 3. The observed typical species can be classified in several types: oval-shaped with relatively smooth surface (Fig. 3,a), spongy like (Fig. 3,b) and spherical species, as well as plerospheres covered and filled with gypsum orthorhombic crystals (Fig. 3,d). The results from the performed EDX analysis of the elemental composition on the particle surface are listed on the corresponding images.

The data from the EDX analyses for different FA species reveal comparative small Si and Al surface concentrations, while high Fe content was observed, which is indicative that they are covered by crystallized ferrous oxides.

4. Synthesis of zeolites

Figure 4 shows the visualisation of hydrothermal synthesis: dissolution of Al^{3+} and Si^+ ions from FA particles and formation of aluminosilicate hydro gel [2]. As the condensation reaction proceeds, the aluminosilicate gel rapidly starts to deposit on the particle surface like a big flake. Then, the aluminosilicate

gel begins to transform to a zeolite crystal. When the hydrothermal synthesis was completed, solid part was separated by filtration, thoroughly washed by distilled water and dried at 105 °C. Syntheses were carried out under different conditions varying the fusion temperatures and the time of hydrothermal treatment (Table 2).

SEM micrographs of crystallized zeolites form the investigated FA are presented in Fig. 5. Crystallites shaped typically for several zeolite forms were observed. Zeolites from type A (Linde) are presented by cubic crystals (Sample 11), zeolites from type P (Phillipsite) aggregates in ball crystals with silky surface (Sample 14), octahedrons are typical for Na-X (Faujasite), while flower shaped crystals are characteristics for hydrosodalite (Sample 4).

The obtained results clearly showed strong influence of the synthesis conditions on the type and the yield of the synthetic zeolite. Increasing the time of the hydrothermal synthesis, which is the time required for the crystallization of the amorphous phase, the formation of more stable zeolite forms is expected, thus Zeolite X transforms in Zeolite A.

The elemental composition on the surface of the synthesized samples was studied by EDX and the obtained concentrations are listed in Table 3.

The influence of the synthesis parameters on the compositional variation on the sample surface was studied. The obtained dependences are plotted in Figs. 6 and 7.

The ratio of Si/Al, measured on the surface of the resultant phases, decreases when the fusion temperature is increased: Si/Al=1.56 at t=550 °C; Si/Al = 1.46 at t=750 °C and Si/Al=1.46 at t =850 °C. Significant (Si+Al)/Na ratios are registered at samples, at which no or negligible crystallization process is carried out and their surface is covered by gelatinized mass. The highest value of 9.55 is measured at Sample 9, and values of 3.86 and 3.65 are obtained for Samples 1 and 4. The surface morphology of Sample 9 is revealed by SEM image in Fig. 5. Because of the low NaOH/FA ratio and the comparatively short duration of the hydrothermal synthesis at these samples, the gelatinized Si-Al-Na-O system is not crystallized. The composition of Na-X zeolite is given as $[Na_{88}(H_2O)_{220}[Si_{104}Al_{88}O_{364}]$, which correspond to the molar ratio of $4.2Na_2O:Al_2O_3:3SiO_2$ or expressed in wt.% is 34.33Na:11.57Al:16.43Si (2.97Na:Al:1.42Si) or Si/Al ratio 1.42 and Si+Al/Na ratio 0.81. FA used as raw material for zeolite synthesis ensures an appropriate Si/Al ratio for the synthesis of Na-X zeolites (Fig. 6,a), while the used NaOH as an alkaline activator is under the required quantity for the fully crystallization of the Al-Si matrix (Fig. 6,b).

It is also evident that the surface concentration of Fe sharply increases at the highest fusion temperature, while those of Si, Al and Na have minimal values (sample 16). Thermal behaviour of FA in the thermal region 20-950 °C has been studied in our previous work [10]. It has been established pseudomorphous magnetite→hematite transformations taking place through intermediate stages. Evidently, at high-temperature fusion step the hematite agglomerates on the surface of the FA species and hinders the aluminosilicate dissolution. Thus the low concentration of the Al- and Si-ions into the reactant solution results in a mixture of zeolite forms. The fusion temperature below 750 °C does not affect the dissolution of aluminosilicates and at the all other samples Fe surface concentration does

not change drastically. The lowest Fe content is observed at higher NaOH concentration (sample 13). Exceeding the NaOH/FA ratio up to 2.4, Na concentration on the surface of the reaction product elevates sharply. This leads to fast crystallization of the Al-Si-Na-O gelatinized mixture in nanocrystalline structures (Fig. 5, sample 13).

The longer hydrothermal syntheses result in reduction of the Al and Si concentration at the expense of Na increase in the material surface layer.

It was revealed by SEM analyses that at elevated fusion temperature and longer hydrothermal time, while other synthesis conditions were kept constant, crystals with larger geometric dimensions were obtained. Zeolite crystals with average sizes of 1.025 µm, 1.784 µm and 2.529 µm were obtained by fusion at 550 °C, 750 °C and 850 °C, correspondingly, providing hydrothermal synthesis for 4 h. As a result of the performed experiments, the highest degree of zeolitization of FA was observed at 2.4 ratio of NaOH/FA

Conclusions

Investigated lignite coal fly ash is an appropriate raw material for preparation of synthetic zeolites, as the Si/Al ratio is optimal for the synthesis of large pore zeolite types (Na-X). A fusion temperature above 850 °C retards the dissolution of sodium silicates and aluminates because of the block surface effect from iron oxide sintering. The established (Si+Al)/Na ratio values reveal an insufficient sodium concentration in the surface layer of the samples, which is the main reason for the partial zeolitization of the aluminosilicate constituents.

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Fig. 1.
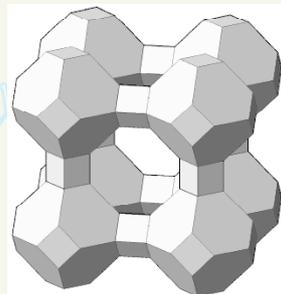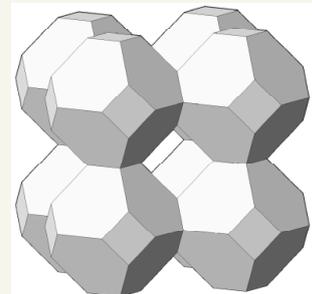Different approaches for FA conversion in valuable products.
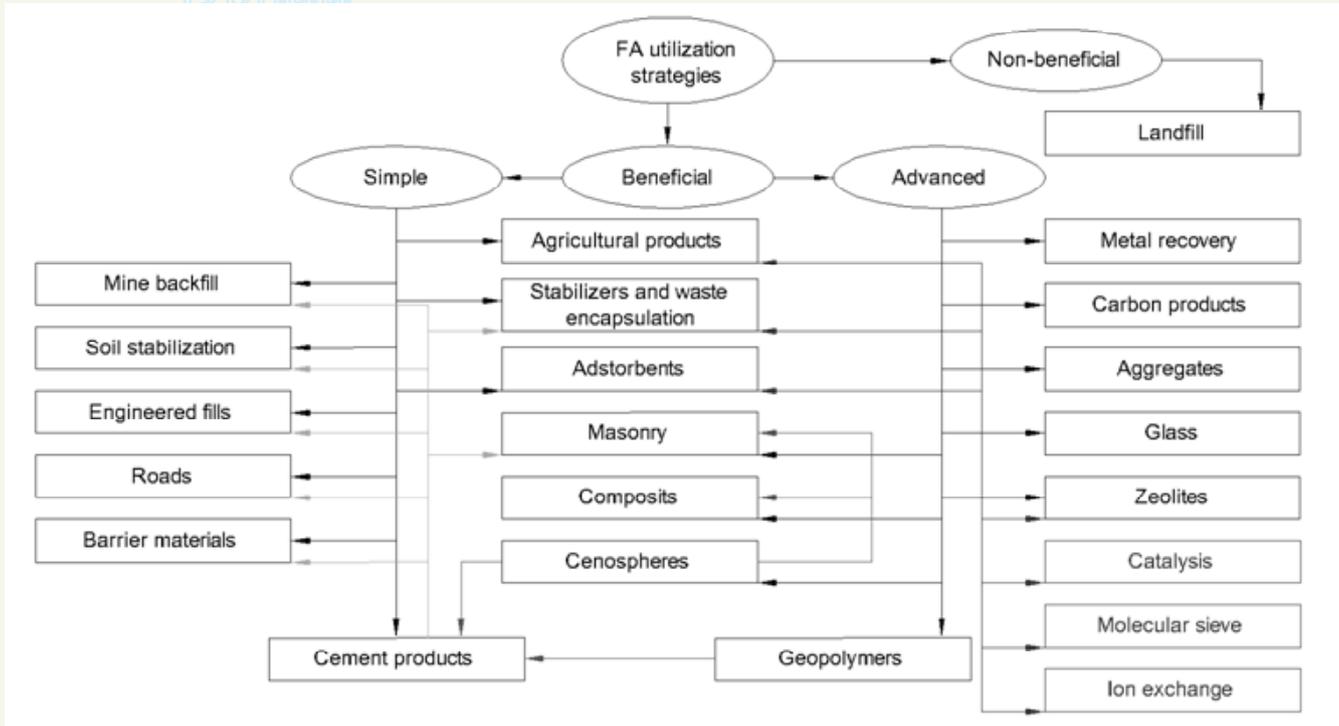
Fig. 2.
The channel diameter of zeolites is dependent on the structure. The sodalite cage (truncated cube – octahedron) is the base unit of A, X zeolite and hydroxy-sodalite, but depending on the arrangement of the polyhedral unit, the structures have channels with very different diameter [4].
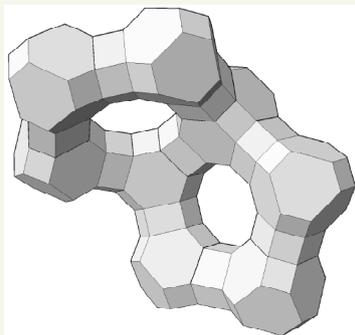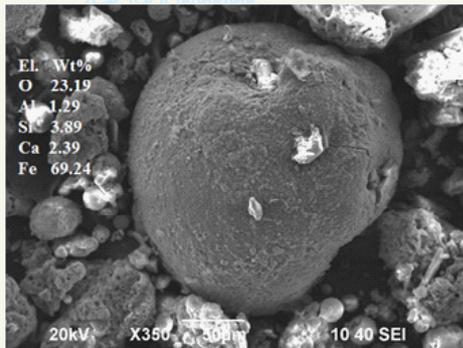

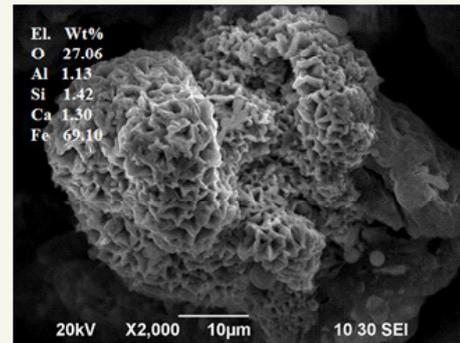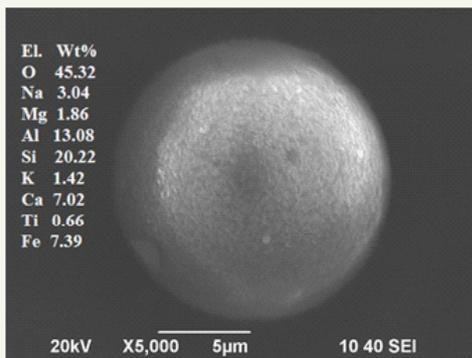**Zeolite X, Y (7.3 Å)**   **Zeolite A (4.1 Å)**   **Sodalite (2.3 Å)**

Fig. 3.
SEM micrographs of typical particles in the studied FA.

a)

b)

c)
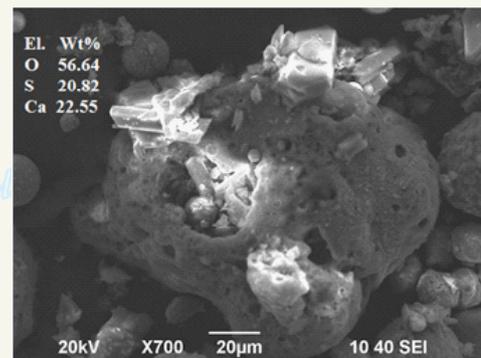
d)

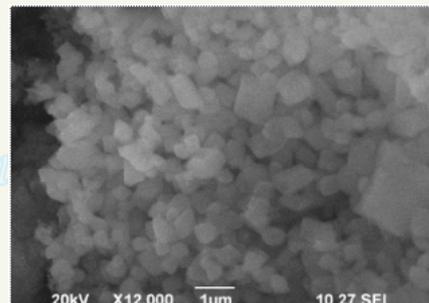**Fig. 4.**
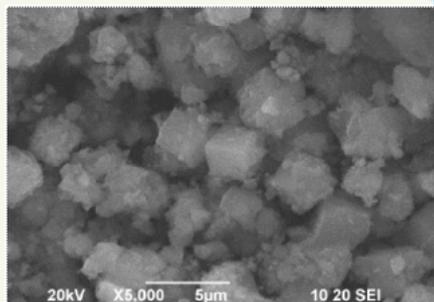Visualisation of hydrothermal synthesis
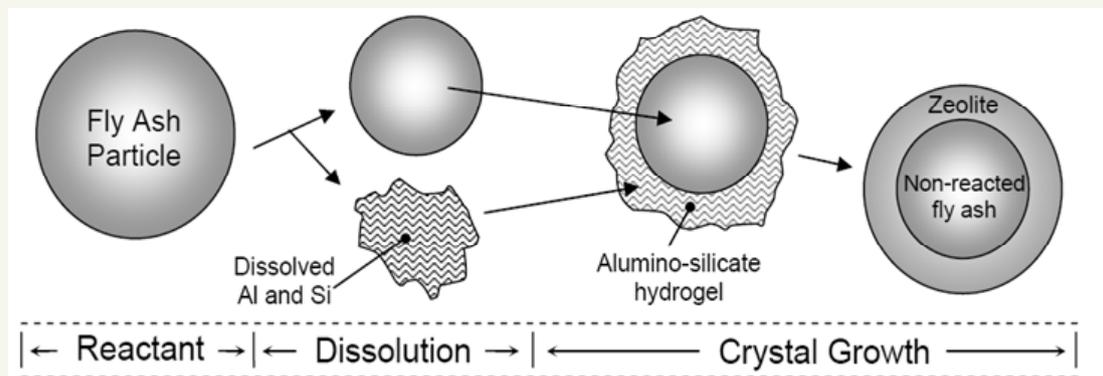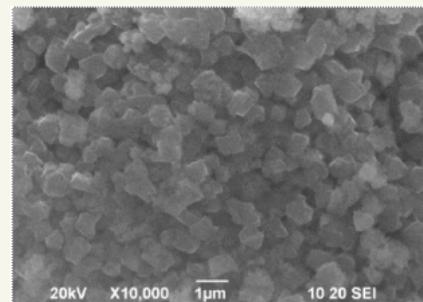
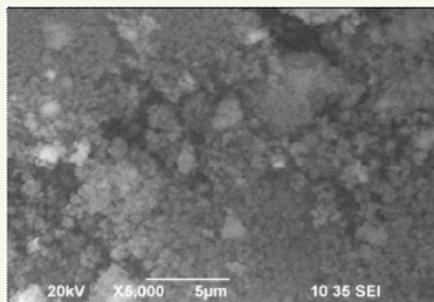**Fig. 5.**
SEM micrograph of zeolite phases obtained
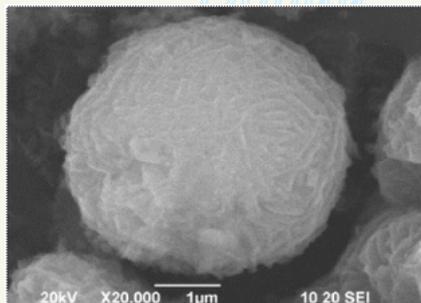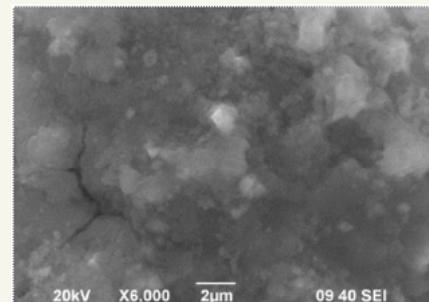

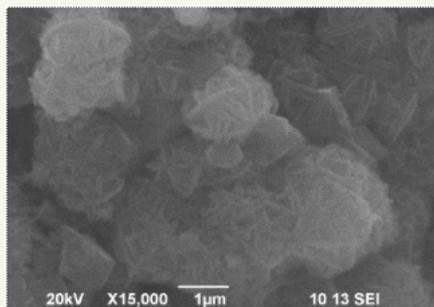Sample 14

Sample 16

Sample 11
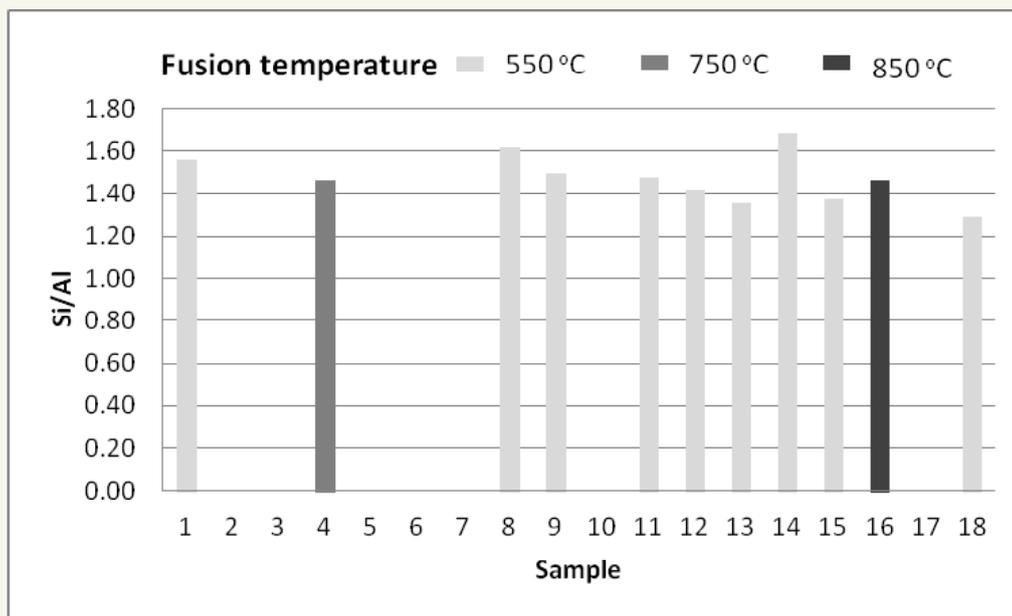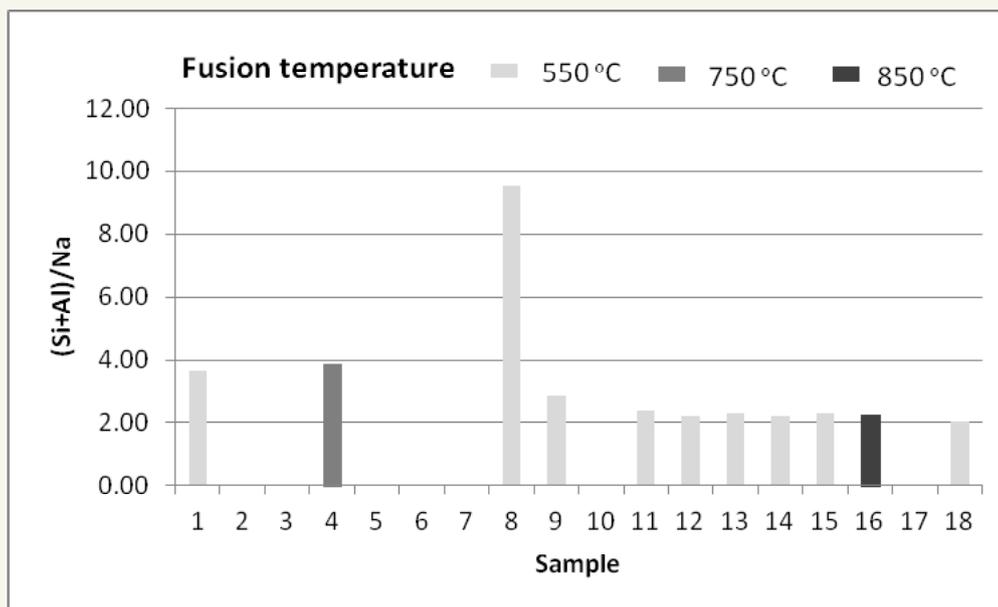

Sample 12

Sample 13

Sample 9

Sample 4

Fig. 6.
Dependence of surface Si/Al (a) and (Si+Al)/Na (b) ratios on the synthesis conditions.

a)

b)

Fig. 7.
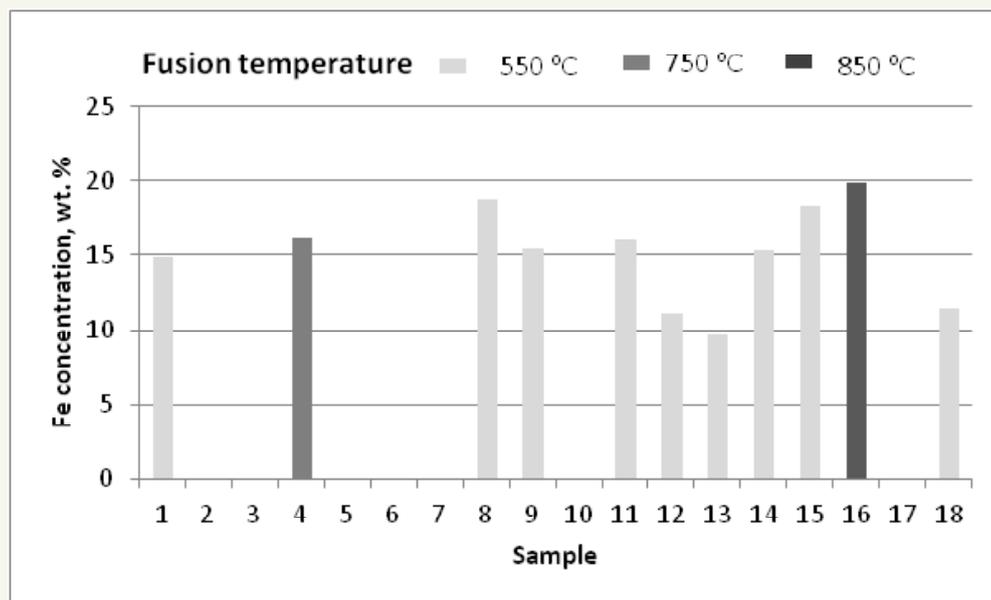Dependence of surface Si/Al (a) and (Si+Al)/Na (b) ratios on the synthesis conditions.

Tabele 1.
Mineral composition of coals

Mineral	Composition	Mineral	Composition
Kaolinite	$Al_2O_3.2SiO_2.H_2O$	Pyrite	FeS_2
Illite	$K_2O.3Al_2O_3.6SiO_2.2\ H_2O$	Gypsum	$CaSO_4.2H_2O$
Muscovite	$K_2O.3Al_2O_3.\ 6SiO_2.2\ H_2O$	Quartz	SiO_2
Biotite	$K_2O.MgO.Al_2O_3.3SiO_2.H_2O$	Hematite	Fe_2O_3
Orthoclase	$K_2O.Al_2O_3.6SiO_2$	Magnetite	Fe_3O_4
Albit	$Na_2O.Al_2O.6SiO_2$	Rutile	TiO_2
Calcite	$CaCO_3$	Halite	NaCl
Dolomite	$CaCO_3.MgCO_3$	Sylvite	KCl
Siderite	$FeCO_3$		

Tabele 2.
Synthesis conditions

Sample	Procedure	Temp.°C	Time	NaOH, M	FA, g	NaOH, g	H$_2$O, ml
1	Fusion	550	1h	1.5	5	6	100
	Hydrothermal synthesis	90	4h				
4	Fusion	750	1h	1.5	5	6	100
	Hydrothermal synthesis	90	4h				
9	Fusion	550	1h	1.5	5	6	100
	Hydrothermal synthesis	90	2h				
11	Fusion	550	1h	2	5	8	100
	Hydrothermal synthesis	90	2h				
12	Fusion	550	1h	3	5	10	100
	Hydrothermal synthesis	90	2h				
13	Fusion	550	1h	4	5	12	100
	Hydrothermal synthesis	90	2h				
14	Fusion	550	1h	1.5	5	6	100
	Hydrothermal synthesis	90	6h				
15	Fusion	750	1h	1.5	5	6	100
	Hydrothermal synthesis	90	6h				
16	Fusion	850	1h	1.5	5	6	100
	Hydrothermal synthesis	90	4h				
17	Fusion	550	1h	1.5	5	6	100
	Hydrothermal synthesis	100	4h				
18	Fusion	550	1h	3	5	10g	100
	Hydrothermal synthesis	90	4h				

Tabele 3.
Elemental composition of FA and zeolitizied samples (in wt.%, normalized)

Sample	O	Na	Mg	Al	Si	Ca	Ti
FA	43.02	1.11	1.80	9.94	14.44	7.16	0.43
1	45.57	6.86	1.65	9.77	15.24	5.99	-
4	43.23	6.48	1.44	10.17	14.87	7.13	0.46
8	43.44	2.54	1.80	9.26	15.00	7.87	0.51
9	44.73	8.39	1.31	9.57	14.30	6.25	-
11	42.08	9.99	1.54	9.65	14.24	5.99	0.44
12	42.06	12.61	1.03	11.57	16.43	5.22	-
13	41.91	13.02	0.67	12.81	17.37	3.65	0.42
14	46.52	9.49	1.55	7.77	13.04	5.89	0.42
15	42.55	9.62	0.8	9.29	12.75	6.72	-
16	46.22	8.40	1.15	7.72	11.3	4.87	0.45
18	46.39	12.01	0.94	10.67	13.77	4.35	-

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