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Low-temperature hydrothermal synthesis of zeolite from fly ash and $NaAl(OH)_4$

Нискотемпературен хидротермален синтез на зеолити от летливи пепели и $NaAl(OH)_4$

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Coal is the largest contributor to modern bulgarian energy. Over 50% of the heat and electricity provided come from coal consumption in Thermal Power Plants (TPP). However, the use of coal emits tons of waste material (ash), which creates environmental problems.

Fly ash is a major waste of the combustion (usually 60–88%) of powdered coal in TPP and is collected through flue gas cleaning facilities (usually electrostatic filters) (Carr, 1982). In recent years, the huge amounts of fly ash being released and the low recovery rate (about 25% of the world fly ash release) have provoked various companies and governments to explore their utilization.

One of the most attractive applications of fly ash is its use as a raw material for the production of microporous Al-Si minerals – zeolites (Ye, Yaping, 2008). Zeolites in turn have different applications: additives for industrial and purification waste; extraction of precious metals such as Al, Si, Fe, Ge, Ga, V, Ni; strengthening the earth’s masses in mining areas; flue gas desulfurization sorbents; fire-resistant materials; filter material for the production of various products; ceramic applications (Querol et al., 2002).

Several successful attempts have been reported in the literature to convert fly ash into a particular type of zeolite (Thuadaij et al., 2012; Feng et al., 2018). Most used are one-stage and two-stage hydrothermal synthesis with NaOH as alkaline reagent. However, many of the widely used synthetic zeolites (Na-A, ZTSM-5, ferrierite, etc.) differ in a lower Si/Al ratio than that typically observed in the amorphous glass phase of fly ash. Such zeolites are synthesized from naturally occurring materials with high Si content (quartz sand, other higher silica zeolites or more acidic volcanic glasses) with the addition of Al obtained from ken processing, Al waste, bauxite (Szostak, 1989; Tounsi et al., 2008). No references were found in the literature reported for the use of $NaAl(OH)_4$ as an alkalizing reagent for the zeolitization of fly ash.

In the present work, the possibility of zeolitization of fly ash (electrostatic filters – fields 1, 2 and 3 obtained from burning of bituminous coal in TPP Varna) applying low-temperature hydrothermal synthesis with $NaAl(OH)_4$ was investigated. The synthesis was carried out as 0.2 g fly ash from each field of electrostatic filters was dispersed in 1 ml 2.5 M or 1.25 M $NaAl(OH)_4$ in a polypropylene sealed tube. The tube was placed at 70 °C for 12 or 24 hours. After completion of the experiment, the material was washed with distilled water to pH 8 of the wash water and dried at room temperature.

The initial fly ash samples and the products of the experiments are characterized by powder X-ray diffraction (PXRD) on TUR M62 diffractometer (CoKα radiation, step 0.02°θ), scanning electron microscopy (SEM) with chemical analysis (JEOL – model JSM-6010PLUS/LA, acceleration voltage 20 kV and size 65 nm equipped with an energy dispersion spectrometer (EDS), and XRF-ICP-AES analysis.

The results of PXRD of the studied ash determined quartz, feldspar, mullite, hematite, magnetite, and mica as the phase composition of the ash (Table 1).

In SEM photographs, quartz and feldspars are seen as poorly formed grains and needle crystals distinguish mullite. In SEM, formless carbon particles and near-perfect spheres of the glass phase

Table 1. Mineral phase's quantity (%) in fly ash samples from the electrostatic filter (fields 1–3) of TPP Varna, determined from x-ray diffraction data

Sample	Quartz	K-feldspar	Plagioclase	Magnetite	Hematite	Mica	Mulite	X-ray amorphous phases
Field 1	9.3	5.3	4.0	2.0	5.1	2.4	6.7	65.2
Field 2	8.8	3.1	3.1	2.0	5.2	2.6	7.1	68.1
Field 3	6.2	2.0	3.6	1.8	5.2	2.0	7.0	72.2

Table 2. Chemical analyses (in %) of fly ash samples from electrostatic filter (fields 1–3) of TPP Varna

Bulk sample (XRF и ICP-AES)	SiO_2	Al_2O_3	Na_2O	MgO	CaO	K_2O	Fe_2O_3	MnO	TiO_2	SO_3	P_2O_5	loss on ignition
Field 1	32.7	16.8	1.0	1.4	2.6	3.1	7.5	0.06	0.4	0.6	0.2	33.64
Field 2	33.1	16.3	0.9	1.8	2.8	2.4	7.7	0.11	0.6	0.0	0.0	34.29
Field 3	34.4	16.7	0.7	1.5	2.7	2.6	7.9	0.08	0.9	0.0	0.1	32.42
Glass particles (EDS)	SiO_2	Al_2O_3	Na_2O	MgO	CaO	K_2O	FeO					
Field 1	57.01	31.14	0.67	1.94	0.13	3.34	5.66					
Field 2	58.13	30.71	0.82	2.33	0.00	3.98	5.03					
Field 3	57.83	30.91	0.54	2.22	0.90	3.73	5.13					

represent the X-ray amorphous phases. Glass globules of different fields differ only in size: 20–30 μm (Field 1), predominantly 10 μm (Field 2), and <5 μm (Field 3).

The determined chemical composition of the studied fly ash from TPP Varna (Table 2) refers it to class F according to the mostly used chemical classification. Following the classification of Vassilev and Vassileva (2007), in which, in addition to the chemical composition, the phase composition is taken into account, the investigated fly ash is defined as a Sialic type with medium acidic tendencies.

In the PXRD patterns of the products obtained from the hydrothermal treatment of fly ash with $NaAl(OH)_4$ at 70 °C, the presence of two zeolite minerals (Na-A and ferrierite) and one feldspathoid (sodalite) was confirmed (Fig. 1). The obtained results show different quantitative relationships depending on the glass phase size, the concentration of $NaAl(OH)_4$, and the duration of the reaction. In the experiments with 1.25M $NaAl(OH)_4$ for 12 hours, the main phase that was recorded was ferrierite. It is known that the process of zeolitization of glass begins with the hydration of the glass, which leads to the release of the highly hydrating ions of Mg^{2+} and Ca^{2+} into the solution. The solution of these ions together with the dissolved Si and Al form ferrierite. Chemical analysis shows that the synthesized ferrierite is Mg-K ferrierite (crystal-chemical composition $Mg_{1.4}K_{1.2}Na_1Ca_{0.5}Si_{10.5}Al_8O_{36}$). The size of the glass globules also influences the zeolitization process. As the globule size increases, the formation of the low-silicon zeolite Na-A is observed. From the SEM photographs it can be assumed that the process proceeds shortly after or almost simultaneously with the formation of ferrierite. Likely, the larger contact surface of the large glass globules in the coarse fraction causes more vigorous interaction of $NaAl(OH)_4$ and the formation of lower silicon Na-A than the depletion of Mg, Ca, K and Si due to the formation of ferrierite. In the SEM photographs, two crystal groups differing in size from both ferrierite and Na-A are observed. The presence of these 2 types of crystals, their size, shape, and relationships, clearly indicate two stages of nucleation (Fig. 1). Most probably, because the formation of zeolites takes place in the boundary layer, due to the large size of the glass globules (Field 1), the interaction of the alkaline solution and the glass phase proceeds in stages.

In the experiments with 2.5M $NaAl(OH)_4$, due to the high normality (equivalent to 10 M NaOH) of the solution, predominantly sodalite was obtained. The quantitative ratios of the phases in the products after the low-temperature treatment of fly ash with $NaAl(OH)_4$ are presented in Table 3. The mineral quantities were determined by semi-quantitative X-ray diffraction analysis using the capabilities of the XPowder program. In SEM micrographs, sodalite is represented by aggregates occupying the spherical surface of the glass globes. This indicates that sodalite crystallizes almost simultaneously with the dissolution of the glass. On the other hand, single crystals of previously formed zeolites are also ob-

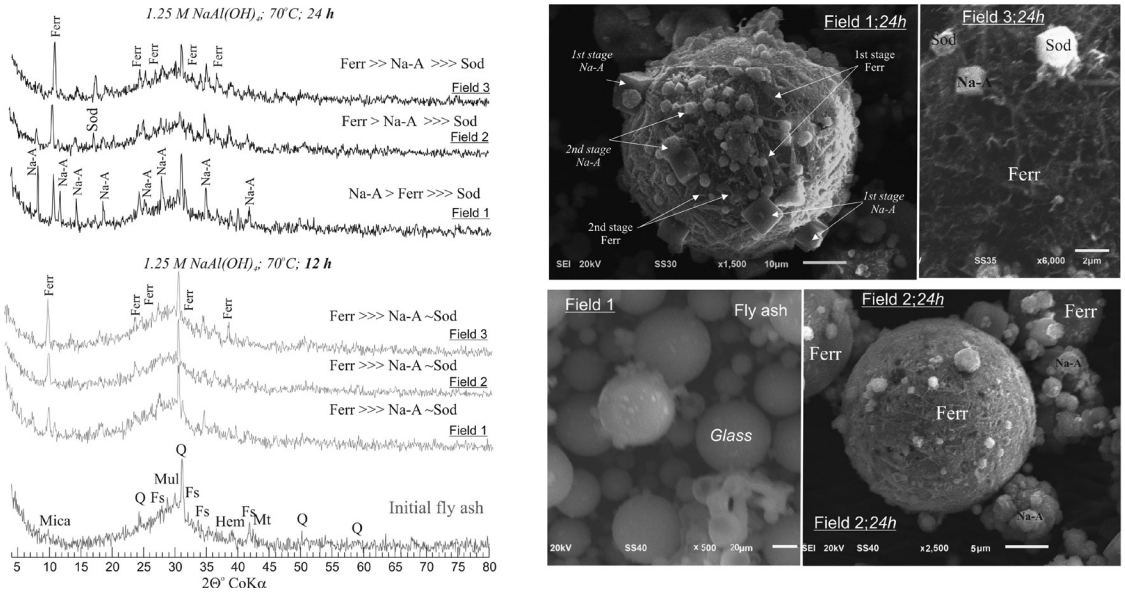

Fig. 1. PXRD patterns and SEM micrographs of the products obtained from the low-temperature (70 °C) hydrothermal treatment of fly ash with 1.25M $NaAl(OH)_4$

Table 3. Mineral phase's quantity (%) in zeolitized fly ash samples from the electrostatic filter (fields 1–3) of TPP Varna, determined from x-ray diffraction data

	Na-A	Ferrierite	Sodalite	Q	Fs	Fe-oxides	Mica	Mulite	X-ray am. phase	% of transf.
Field 1	**25.5**/*6.6*	**8.8**/*4.4*	**2.1**/*15.3*	**5.9**/*5.7*	**4.9**/*4.4*	**4.2**/*4.5*	**1.7**/*1.5*	**7.1**/*5.1*	**39.8**/*52.5*	**39**/*20*
Field 2	**10.5**/*5.4*	**13.6**/*4.2*	**3.4**/*32.6*	**7.3**/*6.9*	**6.5**/*5.9*	**3.6**/*3.9*	**2.4**/*2.3*	**7.5**/*3.9*	**45.2**/*34.9*	**34**/*49*
Field 3	**3.4**/*2.6*	**18.4**/*1.4*	**4.8**/*39.4*	**7.6**/*6.5*	**6.1**/*6.0*	**5.3**/*5.1*	**2.9**/*2.1*	**9.3**/*3.1*	**42.2**/*33.8*	**42**/*53*

Notice: bold – data from the experiment with 1.25 M $NaAl(OH)_4$ and italic – data from the experiment with 2.5 M $NaAl(OH)_4$

served: cubic crystals of Na-A and rod-shaped crystals of ferrierite.

In conclusion, through low temperature (70 °C) hydrothermal synthesis with 1.25M $NaAl(OH)_4$, two types of zeolites (zeolite Na-A and ferrierite) and feldspathoid mineral sodalite were successfully synthesized from fly ash from TPP Varna. Two stages of nucleation of zeolite Na-A and ferrierite were identified. The influence of various factors (reaction duration, solution concentration, and size of the glass globules) on the type and amount of different zeolites (Na-A, ferrierite, and sodalite) was recorded.

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