



Magnetic zeolites from coal fly ash

Магнитни зеолити от въглищна летлива пепел

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All natural and synthetic zeolites (crystalline microporous aluminosilicates) are valuable adsorbents and cation exchangers (Querol, 2002). The magnetically modified zeolites (MZ) are of special interest for treatment of high volume effluents of waste water because they can be easily removed from the medium by magnetic separation (Oliveira, 2004; Shoumkova, 2011a). The typical MZ synthesis refers either to decoration of the zeolite surface with magnetic metals or iron oxides, or to zeolite immersion into solution of iron ions. The main disadvantage of these methods is their complexity. An original and simple method was developed, which combines the low-temperature hydrothermal zeolitization of fly ash (FA) with an extraction of magnetic zeolitic composite by magnetic separation.

FA from coal burning thermal power station “Maritsa 3” (Dimitrograd) was explored for obtaining of zeolitic composite with magnetic properties. Recently the alkali activation of FAs from several Bulgarian power plants was investigated by applying of different procedures (Shoumkova et al., 2011). The used here FA has relatively high content of Fe (8–9 wt.%) and large specific surface (15–16 m²g⁻¹), facilitating the dissolution of Si and Al, and thus making it appropriate for zeolitization at lower temperatures (Shoumkova, 2011b).

The zeolitized FA (ZFA) was synthesized by heating of 10 g FA in 100 ml 3.1 m NaOH at 80 °C for 7 hours, then dried and washed (Shoumkova, Stoyanova,

2013). The magnetic zeolitic product (MZFA) was extracted by wet low intensity (0.1 Tesla) magnetic separation, and then washed and dried. For comparison, FA was subjected also to magnetic separation under the same conditions to obtain MFA.

Morphology of the initial FA and the obtained products (MFA, ZFA and MZFA) was examined by scanning electron microscope (SEM), model JSM6390, using regimes of secondary (SEI) and backscattered (BEI) electrons image. The SEM was coupled with energy-dispersive X-ray analyzer (EDX), Oxford Instruments, used for estimation of the average elemental composition on the base of integral spectra, taken at 20 keV and 30x magnification for 300 s from a surface comprising several thousand ash particles. The phase compositions of FA and its products were identified by powder X-ray diffraction (XRD), Philips PW 1050 with CuK α radiation and scan steps 0.02°(2 θ). The results are given in Table 1, Fig. 1 and 2, respectively.

In the obtained 40 wt.% MFA, Fe is present mainly as oxides, incorporated into glassy particles (Fig. 1a) or crystallizing on their surface (Fig. 1b) (magnetic fly ash microspheres); rarely as aggregates of iron oxide (magnetic) and iron-lean (non-magnetic) particles (Fig. 1c) or as individual Fe particles.

The primary FA minerals (quartz, maghemite/magnetite, hematite) were present in ZFA also (Fig. 2), the aluminosilicate glass phase was partially dissolved

Table 1. Chemical composition (in wt.%, normalized) and yield (in %) of FA, MFA, ZFA and MZFA

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Yield (%)
FA	2.15	2.58	22.54	38.71	4.87	1.48	7.80	0.71	19.17	100
MFA	0.00	2.74	23.06	35.39	0.00	0.00	5.66	0.91	32.23	40
ZFA	6.95	2.56	26.14	38.73	0.49	0.68	11.26	0.12	13.07	103
MZFA	5.61	3.41	24.74	39.60	0.00	0.00	12.76	0.38	13.50	53

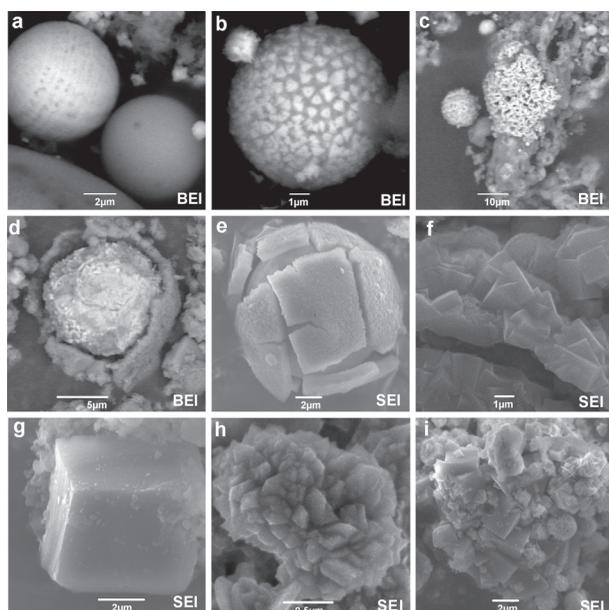


Fig. 1. Morphology of MFA and MZFA particles

and the others – completely. The main newly formed zeolite phase in ZFA (Fig. 2) was zeolite A (Fig. 1g) with traces of zeolite P (Fig. 1h).

The obtained MZFA (about 53 wt.% of the initial FA), similarly to ZFA, consisted predominantly

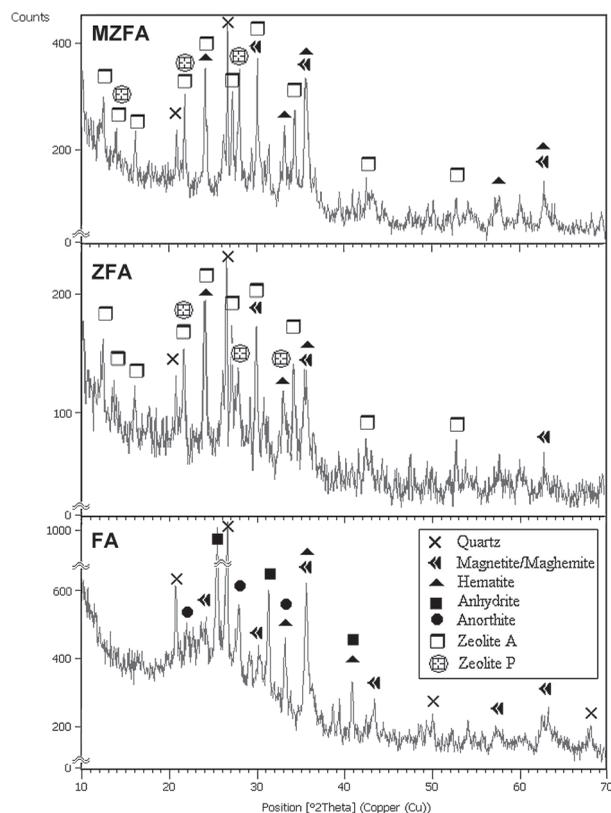


Fig. 2. XRD patterns of FA, ZFA and MZFA

of particles with 10–60 wt.% Fe, covered with a few micrometers thick shell (Fig. 1d, e) of zeolite A crystals (Fig. 1f, g) with quite a constant composition, on which fine zeolite P crystals (Fig. 1h, i) were grown. Compared to ZFA, the only difference was in the relatively higher intensity of magnetite/maghemite XRD peaks of MZFA (Fig. 2). Rarely, uncovered with zeolite iron oxide crystals were detected, indicating the lower affinity of these zeolites to nucleate on particles with iron oxide surface than on aluminosilicate glassy ones. Small iron oxide particles captured in larger iron-lean (<2 wt.%) zeolitized FA particles were also present.

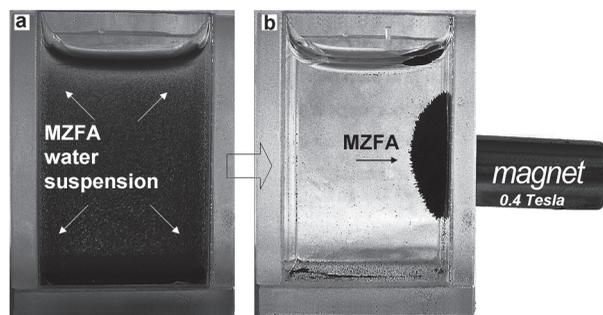


Fig. 3. Water suspension of MZFA (a) and its response to application of magnetic field with induction of 0.4 Tesla (b)

The as-prepared MZFA consists mainly of particles having magnetic core with zeolite A shell (up to 2–3 μm thick), and strong aggregates of magnetic (Fe oxide) and zeolite particles; so it is easily manipulated in water suspensions by application of magnetic field. An illustration of the magnetic behavior of MZFA in the field of a permanent magnet is seen in Fig. 3.

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