

Microspheric Zeolite Obtaining from Vitrocrystalline Cenospheres of Power Station Ashes

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Abstract

For the first time, adding no seeding agent and no structure-forming components, the synthesis of microspheric zeolite sorbents is realized basing on vitrocrystalline cenospheres from power station ashes. As the result of hydrothermal processing the silica-alumina material of the wall of cenospheres undergoes transformation into low-module zeolites conserving the morphology of initial particles. The final product represents hollow spheres 80–200 μm in size whose walls entirely or partially consist of the crystals of NaA, NaX and NaP1 zeolites.

Key words: cenospheres, microspheric zeolites, NaP1, NaX, NaA

INTRODUCTION

At the present time synthetic low-module zeolites are widely used in the industrial processes of gas dewatering, dewaxing, air separation, wastewater treatment, including radionuclide extraction [1]. For today the demand of the industry for low-module synthetic zeolites NaA, NaX, NaP1 and others are satisfied completely due to a certain excess in the manufacturing capacity with respect to them [2]. Nevertheless, the works concerning the search for alternative sources of a cheaper raw material and novel efficient methods for the synthesis of zeolite materials are proceeded.

Many researchers consider volatile ashes by-produced due to coal combustion at power stations as a cheap and accessible initial material for the transformation into zeolites. The process of the ashes transformation into silica-alumina skeleton structures is broadly covered in

scientific, technical and patent publications. About 15 types of zeolites and skeleton aluminium silicates were synthesized from volatile ashes due to the application of alkaline hydrothermal processing at various temperatures [3–5], of alkaline fusion [6] including the use of microwave radiation for heating the reaction mixture [7], and the obtaining of NaP1 zeolite was realized as a large scale process [8, 9].

It is obvious that in order to reproducibly obtain the products with preset properties basing on the components of thermal power station ashes one should use for the synthesis the raw material stabilized in chemical and mineral phase composition, with the minimal content of foreign components. It is known, that there are microspheroidal entities observed in the composition of volatile ashes from thermal power stations; they are microspheres presented by both massive particles, and hollow spheres with a monolithic or porous wall (cenospheres).

The latter are readily formed as a concentrate that could be separated into individual fractions with predictable physical and chemical characteristics [10, 11]. The cenosphere wall consists in the main of XRD amorphous silica-alumina glass with the inclusions of crystalline components [12]. Taking into account a unique microspheroidal design, an opportunity to isolate narrow cenosphere fractions with stabilized composition, as well as the fact that ratio Si/Al in these products (2.47–2.8) is close to low-module zeolites, of a great interest is the obtaining of microspheric sorbents on this basis combining a prescribed type of the zeolite structure with the conservation of the spherical shape inherent in initial cenospheres.

EXPERIMENTAL

Source materials

In this work we investigated cenospheres isolated from the concentrate of volatile ashes of Kuznetsk coal combustion at the Novosibirsk heat and electric power plant TETs-5 (H) and the Tom-Usinsk state regional power station (K). The initial concentrate of cenospheres was successively subjected to grain-size and hydrodynamic classification for the isolation of imperforated products with controlled size and density and the subsequent magnetic separation in order to remove most part of magnetic ferri-ferrous particles.

These processes are described in [11] in detail. For the synthesis of microspheric zeolites

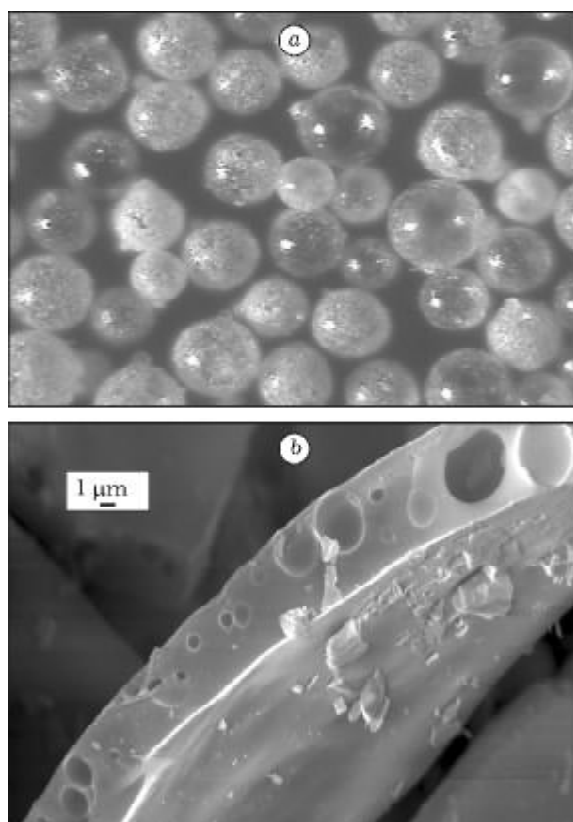


Fig. 1. Appearance (a) and wall cross section (b) of the initial cenospheres from K series.

we used a cenosphere fraction 0.08–0.18 mm in size, with the bulk density of 0.37–0.39 g/cm³. According to the optical and scanning electron microscopy data, this fraction represents a mixture of hollow entities with the shape close to spherical one (Fig. 1). Chemical composition of the initial cenospheres is presented in Table 1.

TABLE 1

Chemical composition of the initial cenospheres and the cenospheres exposed to hydrothermal processing under various conditions

Sample	Solubility in acid, %	Chemical composition									Atomic ratio	
		SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	CaO	MgO	K ₂ O	TiO ₂	Σ	Si/Al	Na/Al
Initial H	1.5	66.5	20.7	0.6	3.67	21	1.9	2.9	0.5	98.8	2.73	0.05
Initial K	2.6	67.6	21.0	0.9	3.0	22	1.8	2.8	0.2	99.8	2.75	0.07
K-100-1.5-24	66	54.1	23.1	10.5	3.8	25	2.1	2.1	0.3	98.6	2.0	0.7
K-100-1.5-72	75	53.7	22.2	12.1	3.5	25	2.4	2.1	0.2	98.7	2.0	0.9
K-100-0.5-24	16	63.6	21.2	3.2	3.1	22	2.9	2.9	0.3	99.4	2.5	0.2

Note. The abbreviations of sample names used include a letter (the source of cenospheres) and three numbers corresponding to process temperature (°C), alkali concentration (NaOH, mol/L) and the synthesis duration (h).

Zeolite synthesis

The process of hydrothermal synthesis of zeolites (zeolitization) was carried out in polypropylene vessels 0.2–0.5 L in volume (at the temperature lower than 100 °C) or in hermetic Teflon beakers 0.02–0.2 L in volume, placed into steel autoclaves (at the temperature >100 °C). For the synthesis of zeolites an alkali solution with the concentration of 0.5–8 mol/L was used. A weighed sample of cenospheres was covered with NaOH solution (the mass ratio the liquid to the solid = 10 : 55); the reaction vessel was put into a thermostat and was held at a temperature of 50–250 °C to an accuracy of ± 1 °C and autogenic pressure during 6–72 h.

In a number of experiments the reaction mixture was stirred by rotating the reaction vessel around a longitudinal axis, the rotation frequency was equal to 30 min⁻¹. After the reaction completing we separated a sediment from the liquid, washed the former on a filter with distilled water up to alkaline pH and then dried it at 60 °C during 24 h.

Methods

The determination of phase composition of the initial and hydrothermally processed cenospheres was carried out by means of XRD technique using a DRON-4 X-ray diffractometer with CuK α radiation, the scan rate being of 1.0°/min; the identification of phases occurring was carried out with the help of the International Centre for Diffraction Data (ICDD) database. The morphology of zeolite layers formed was investigated using the methods of scanning electron microscopy (SEM) with the help of LEO-32 devices (Germany) and optical microscopy (BIOLAM, Russia). The content of an acid-soluble part in samples was determined from the mass of insoluble residue after sample treatment with 6 M HCl solution at room temperature; the specific surface area was determined using a standard technique of argon thermal desorption.

The concentration of alkali and soluble silicates in the liquid phase was calculated from potentiometric titration data obtained for 0.1 M HCl solutions with the use of a glass electrode. The cationic composition of solutions was de-

termined using an atomic absorption spectroscopy technique; the chemical composition of the initial cenospheres and the products of their transformation was determined by means of a chemical method after sample dissolution according to the State Standard GOST 5382–91.

RESULTS AND DISCUSSION

General laws of cenosphere zeolitization process

As it is known, the formation rate and the chemical nature of zeolite phases formed under the conditions of hydrothermal transformation as well as the crystallinity level depend on a variety of factors such as Si/Al ratio in the initial mixture, the presence of seeding agents, the nature of a mineralizer and a structure-forming agent, solution alkalinity and temperature, relative amounts of the liquid and the solid phases, the sequence of reagent mixing and the intensity of reaction [13].

The process of cenosphere transformation into zeolite structures was carried out in alkaline NaOH solutions with no adding any seeding agents and structure-forming components, as against [14], where mineralizing additives were used. The experiments have demonstrated that the material of cenosphere walls (silica-alumina glass) is rather chemically inert, thus a long processing duration at elevated temperature is required for its activation. So, the interaction cenospheres at 45 °C with 2.5 M NaOH solution during 72 h did not result of occurrence of new phases, being accompanied only by perforating a part of cenospheres and by increasing in the specific surface area from 0.2 (initial cenospheres) to 1.2 m²/g. The XRD profiles obtained for these samples are similar to XRD profiles of initial cenospheres wherein one can distinctly observe only the reflexes corresponding to quartz are (Fig. 2). This fact is in a good agreement with the results of works concerning the synthesis of zeolites from naturally occurring and synthetic glasses presented in the literature [15] in detail.

At the processing temperatures higher than 80 °C and the durations longer than 24 h one can observe a considerable increase in the specific surface area and the occurrence distinct reflexes in XRD profile those indicate the for-

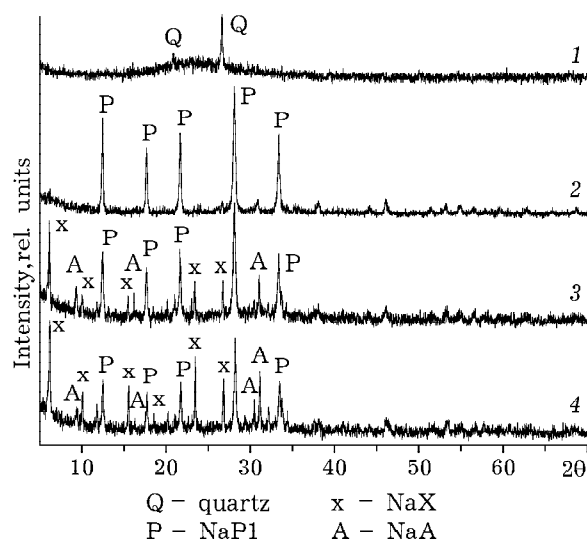


Fig. 2. XRD profiles for samples of the initial cenospheres from H series (1) and for cenospheres subjected to hydrothermal processing (2-4): 2 - with stirring (H-100-2.5-72); 3, 4 - under static conditions (H-100-2.5-72 and K-100-2.5-72, respectively).

mation of zeolites. In most cases a simultaneous formation of zeolites of several structural types is observed, among those according to XRD data we have identified NaX (FAU, JCPDS 12-0228), NaA (LTA, JCPDS 43-0142), NaP1 (GIS, JCPDS 40-1464), chabazite (CHA, JCPDS 12-0194), analcyme (ANA, JCPDS 19-1180) and hydroxysodalite (JCPDS 11-401). The ratio between individual zeolite phases varied depending on the concentration of alkali, treatment duration and process temperature. The influence of these parameters upon the formation of a certain type zeolite skeleton corresponds for the most part to commonly known tendencies [9, 15]. So, at low temperature values, NaA and NaX zeolites are mainly formed; the rise in temperature promotes the transformation of cenospheres into NaP1, whereas at the temperature >150 °C the formation of analcyme begins. At intermediate temperature values (80–120 °C) the low concentrations of NaOH (0.5–1.5 mol/L) promote the prevailing formation of a skeleton with gismondine topology (NaP1), at NaOH concentration of 2.5–3 mol/L NaA and faujasite are formed; a higher concentration of alkali is favourable to the formation of hydroxysodalite structure. Depending on the conditions, the transformation of the most part of cenospheres requires from

24 to 72 h to spend, and the level of vitrocrySTALLINE substrate conversion into zeolite is amounting to 96 %.

A particular significance in the manufacture of the products of certain composition based on naturally occurring components is attached to the possibility of obtaining reproducible results of the synthesis, first of all, under changing the source of raw material or when using different raw material batches from the same source.

The experiments carried out have demonstrated that the zeolitization of H and K cenospheres, isolated from coal combustion ashes of the Kuznetsk coals at different thermal power stations results in a qualitatively identical structure of zeolites formed. However, despite of a close chemical composition for the initial H and K cenospheres (see Table 1), some differences are observed in the amount zeolite phase formed (in case of monomineral composition) or in the ratio between different zeolite phases (under the conditions when several types of zeolites are formed).

So, only NaP1 zeolite phase was revealed in samples H-100-2.5-72 and K-100-2.5-72 obtained with the stirring of the reaction mixture. The content of acid-soluble part in these samples amounts to 90 and 86 %, respectively, which indicates a different content of low-module zeolites. Under the same conditions in the absence of stirring one can observe predominant formation of NaX, NaP1 zeolites mixture as well as an insignificant amount of chabazite, the ratio between those was different for H and K cenospheres (see Fig. 2, c, d). Furthermore, H and K cenospheres exhibit also a different content of acid-soluble fraction (93 and 86 %, respectively).

The reproducibility of the results for the synthesis of zeolites from cenospheres taken from the same source was examined for sample K-100-2.0-68 (with stirring) whose synthesis was repeated several times. According to the XRD data, in all the cases there is only zeolite phase NaP1 in the product. In order to characterize the reproducibility, we used the specific surface area (S_{sp}) whose average value, according to the results of 11 measurements, amounted to $70.1 \text{ m}^2/\text{g}$ (the standard error being of $1.4 \text{ m}^2/\text{g}$). The minimal and maximal S_{sp} values amounted to 64.3 and $78.0 \text{ m}^2/\text{g}$, respectively; the deviation from the average value does not exceed a 12 %.

Thus, the results presented confirm the possibility of transforming the cenospheres of thermal power station ashes into individual zeolites or into a mixture of zeolite phases in the course of hydrothermal processing. The obtaining of reproducible results for the zeolitization of cenospheres from various thermal stations is caused by a preliminary raw material preparation as well as by narrow cenosphere fractions used for the synthesis, stabilized in physical properties and in chemical composition.

Stoichiometry of zeolite phase formation

As the experiments have shown, the main zeolite phases formed under the alkaline hydrothermal processing of cenospheres are presented by NaP1, NaX and NaA.

According to the chemical analysis of zeolitization products (see Table 1), with the increase in the processing time or in the concentration of alkali one can observe an increase in the level of cenosphere material conversion into zeolites. This fact is indicated by the reduction of the acid-insoluble residue fraction as well as the ratio of Na/Al \sim 1, which is inherent in sodium zeolite species. Simultaneously, a reduction is observed for the Si/Al ratio value and the SiO₂ content in the samples.

As known from the literature, for NaA zeolite the atomic ratio Si/Al \sim 1.0, whereas for NaP1 this value can change ranging from 1 to 2.5. Within a much wider range the Si/Al ratio can change for the faujasite skeleton. The use of a known relationship between the crystal lattice parameter a_0 and the aluminium content within the unit cell N_{Al} [13] allows us to estimate the Si/Al ratio in the synthesized zeolites with the faujasite skeleton:

$$a_0 = 0.00868N_{Al} + 24.191 \quad (1)$$

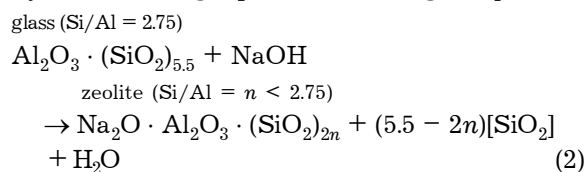
$$N_{Al} = 192/(1 + R), \quad R = N_{Si}/N_{Al}(1)$$

Here a_0 is the crystal lattice parameter; N_{Al} , N_{Si} stand for the number of aluminium and silicon atoms within the unit cell, respectively.

The crystal lattice parameter calculated from XRD data for NaX zeolite entering into the composition of samples H-100-2.5-72 and K-100-2.5-72 is equal to 24.885 and 24.869 Å, respectively. This corresponds to the ratio Si/Al = 1.4–1.46, *i.e.* the zeolites formed during hydrother-

mal cenosphere processing belong to the group of so-called low-module zeolites.

The atomic ratio Si/Al for all the zeolites formed is lower as compared to the Si/Al ratio value for the initial cenospheres (2.7–2.8, see Table 1). In this connection the transformation of the amorphous silica-alumina cenosphere material into the zeolite skeleton should be accompanied by the segregation of excess SiO₂. The overall transformation, thus, can be presented by the following equation of total gross process:



The excess [SiO₂] could partially remain in the solid phase being in an amorphous or crystalline state in the form of quartz, whose weak reflexes are observed almost for all the samples after the reaction. However, its dissolving and passing into the solution as silicates is considered to be more likely.

The chemical analysis of the liquid after 72 h of zeolitization process at 100 °C in 1.5 M NaOH solution has demonstrated that, except for ions K⁺ whose content in the solution rose in some cases during the reaction up to 1 g/L, the metals are present in the solution in insignificant amounts (7 and 1.8 mg/L for aluminium and iron, respectively, and <0.02 mg/L for Mg²⁺ and Ca²⁺). Thus, almost all the cations of the metals those are present in the initial raw material, remain in the solid. The low content of aluminium in the reaction solution is most likely caused by its binding to form silica-alumina structures during the formation of the zeolite skeleton.

Figure 3 demonstrates the potentiometric titration curves for initial NaOH solution and for the solution after cenosphere processing for 72 h at 100 °C. The concentration of alkali due to the reaction decreased within the range of 10–50 % depending on initial NaOH concentration as well as the process duration and temperature. Furthermore, there is a pronounced “shoulder” on the titration curve for the reaction solution, which indicates the presence of some species with weak acidic properties in liquid phase, with the concentration of 0.08–0.43 g-eq/L. Taking into account the chemical com-

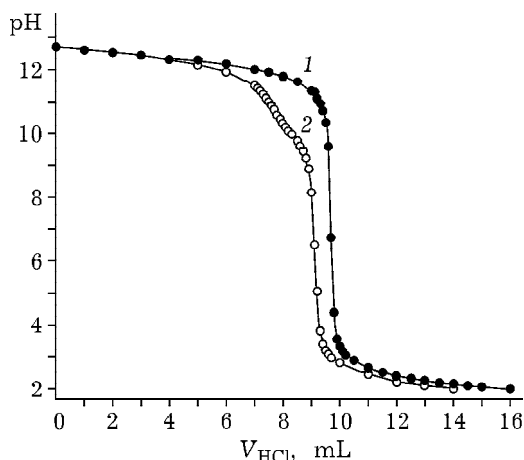
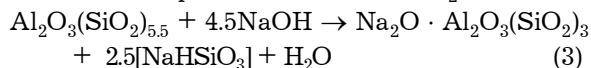


Fig. 3. Potentiometric titration curves for the initial NaOH solution (1) and the solution after the synthesis of the sample K-100-2.5-72 (2).

pound of the system and $pK_{a,1}$ values for silicic acids (the first step dissociation constant values for orthosilicic acid H_4SiO_4 and metasilicic acid H_2SiO_3 are equal to 9.7 and 9.66, respectively [16]), the presence of the "shoulder" on the titration curves should be most likely connected with the presence of soluble silicates in the solution. Another argument in support of this assumption is presented by the results of the studies using a ^{29}Si NMR technique wherewith silicate ions were revealed in the reaction solution. It is known that there is a number of mono- and oligosilicate ions with various condensation level in an aqueous sodium silicate solution, the ratio between them depending on the ratio $r = SiO_2/Na_2O$. Basing on the analysis of ^{29}Si NMR spectra the authors work [17] ascertain that at $r < 0.16$ there is the only monosilicate ($\delta = -70.4$ ppm against Me_4Si) in the solution completely converted to yield condensed silicates at $r > 3$.

In the case under our consideration the ^{29}Si NMR spectrum of the reactionary solution after zeolitization (sample K-100-2.5-72) exhibits both monosilicate peak ($\delta = -70.8$ ppm) with the intensity about 80 % of the total ^{29}Si intensity, and a series of weak peaks at $\delta = -78.8, -88.7$ ppm those are most likely related to condensed silicates [17]. Thus, it is obvious that the transformation of the amorphous silica-alumina skeleton of cenospheres into low-module zeolites should be accompanied by the dissolution of the superstoichiometric SiO_2 :



Morphological features of cenosphere zeolitization products

The analysis of micrograph images of the samples of cenospheres, subjected to zeolitization under various conditions has demonstrated that the most essential influence upon the shape and localization of zeolite crystals formed is exerted by the intensity of reaction mixture stirring. The zeolitization of cenospheres carried out under static conditions (without stirring) at 100 °C, in all cases resulted in an almost complete destruction of the initial particles (Fig. 4, a), which destruction is accompanied by a profound local wall dissolution and by the formation of the mixture of NaA, NaX and NaP1 zeolites in the form of large (up to 10 μm) separately located crystals with a distinctive crystal habit (octahedrons NaX, spherulites NaP1, see Fig. 4, b). The latter are located both on the residuals of transformed cenospheres, and in the bulk of the reaction solution. Similar results are also caused by a slight periodic stirring of the reaction mixture.

The increase in the intensity of stirring is accompanied by a progressive increase in the percentage of particles those conserved the spherical shape inherent in the initial cenospheres. At the rotation frequency of an autoclave amounting to 30 min^{-1} the final product consists mainly of hollow spherical particles comparable in size with the initial cenospheres (see Fig. 4, c); as this takes place the composition of the zeolite phases formed and the morphology of zeolite crystals are entirely changed. The main zeolite phase in this case is presented by NaP1 whose needle-shaped crystals with the length to cross size ratio ranges within 5–10, are mainly normally aligned to the surface with forming a continuous layer (see Fig. 4, d).

In order to explain the laws of volatile ashes transformation into zeolite products an approach is commonly used in the literature based on the sequence of dissolution and crystallization stages. In particular, the authors of [18] proposed a mechanism which includes the dissolution of initial material, the formation silica-alumina gel, nucleation and the crystallization of zeolite, for the explanation of NaP zeolite formation from volatile ashes under the conditions of hydrothermal synthesis with no stir-

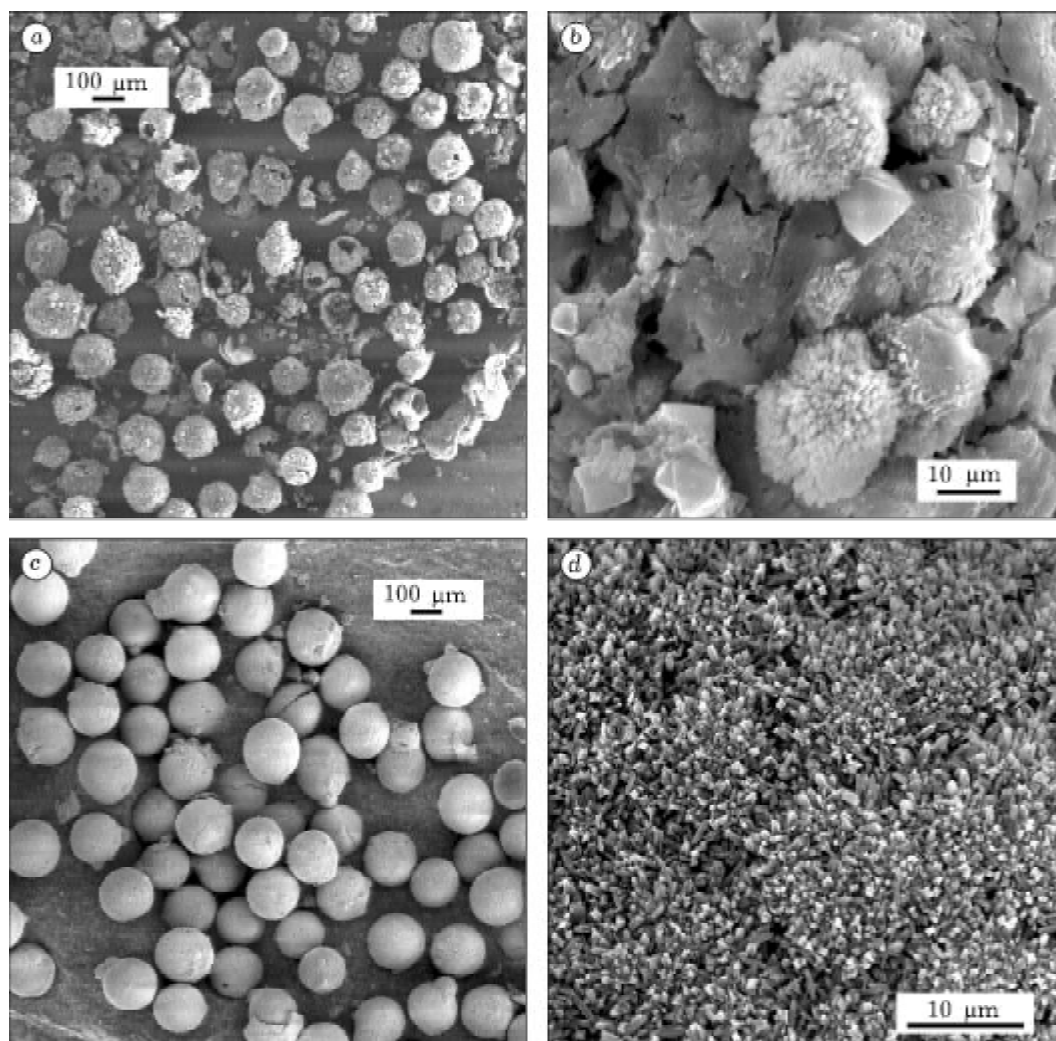


Fig. 4. General view (a, c) and the fragment (b, d) of the cenosphere surface exposed to hydrothermal processing, on an enlarged scale: a, b – sample H-100-2.5-72 processed under static conditions; c, d – sample K-100-2.5-72, with stirring.

ring the reaction mixture. When taken into account that the zeolitization of cenospheres also proceeds through the stages such as glass dissolution–silica-alumina precursor transfer through the solution–nucleation–crystallization, then one should connect the essential influence of stirring upon the morphology zeolite layers formed, to all appearance, with different local conditions determining the formation of the «building units» of the zeolite skeleton *i.e.* of oligomeric silicate and silica-alumina fragments. In the case when the process is carried out with no forced circulation of the solution, the cenospheres and the liquid phase form two distinctly separated layers within an autoclave, the mass transfer between those could be realized by

means of diffusion only. Hence, the concentration of NaOH in the layer of cenospheres should be lower, whereas the concentration of silicate should be higher, than in the bulk of the solution. Correspondingly, in this case the layer of cenospheres should be characterized by a higher level of the liquid phase supersaturation by silica-alumina fragments and by an increased level of their condensation as compared to the conditions when the intense stirring of a reaction mixture weight promotes the efficient equalization of concentration. Such influence of the liquid phase composition upon the co-crystallization NaY, NaP zeolites and hydroxysodalite, NaA zeolite and hydroxysodalite is described in the literature [19], as well

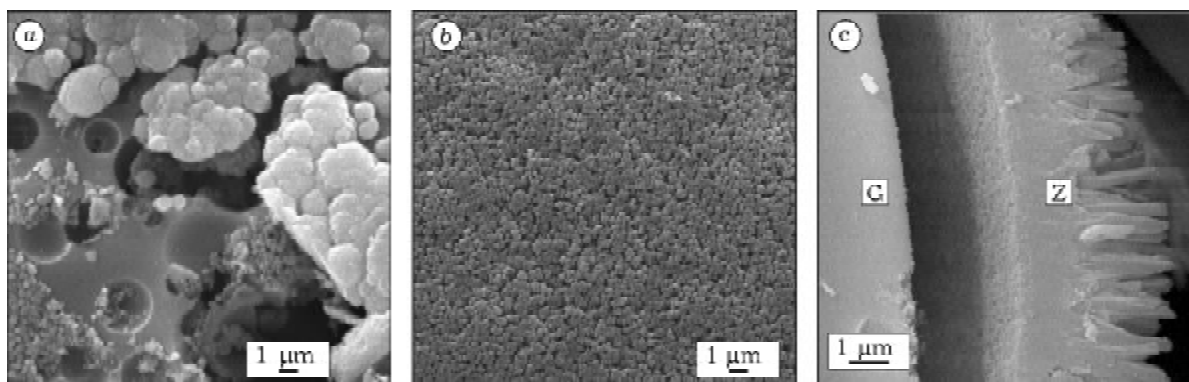


Fig. 5. Electron micrograph images for samples K-100-1.5-6 (a) and K-100-1.5-12 (b); general view of a partly destroyed zeolitized cenosphere from sample K-100-1.5-24 (c). G – glass, Z – zeolite layer.

as the dependence of the synthetic [20] and natural [21] lomontite crystal shape the solution supersaturation level.

The main stages of the zeolite layer formation one could trace by the example of the transformation of cenospheres in 1.5 M NaOH solution at 100 °C. During the first moments after the reagents mixed there is a non-selective dissolution observed for a part of silica-alumina material of cenospheres as well as silicate ions occurring in the solution, which is accompanied by a decrease in the overall concentration of alkali. After 6 h of the reaction occurrence, all the external surface of cenospheres is uniformly covered with a layer formed without visible structure, whose mass amounts to ~16 % of the cenosphere mass (Fig. 5, a; the layer in the picture is artificially destroyed in order to determine its thickness). Simultaneously, the specific surface area of the sample increases more than by an order of magnitude

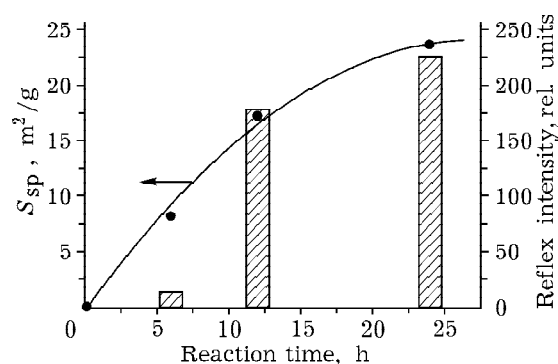


Fig. 6. Plot of the specific surface area and the reflex intensity at $d = 3.18 \text{ \AA}$ (hkl 310 for zeolite NaP1 cubic modification) against the duration of cenosphere processing in 1.5 M NaOH solution at 100 °C.

(for the initial and processed samples $S_{sp} = 0.2$ and $8.2 \text{ m}^2/\text{g}$, respectively) (Fig. 6). However, these changes are not accompanied with the occurrence of additional reflexes in the X-ray diffraction profile of the sample processed. Thus, at the first stage of the zeolitization process a semistructured layer (most likely, silica-alumina one) on the surface of cenospheres is formed with a highly developed surface, wherein an XRD amorphous component is prevailing.

Additional exposing the sample to NaOH solution during 6 h results in doubling the specific surface as well as in occurring the diffraction reflexes inherent in zeolite NaP1 whose intensity increases with raising the S_{sp} . There-with the further dissolution of the vitrocry-stalline base of cenospheres and the formation of a crystalline zeolite phase occurs on the external surface of the particles in the form of a compact layer of randomly oriented submicron-sized crystals (see Fig. 5, b). The increase in the duration of the reaction results in a progres-sive formation of columnar crystals on the sur-face those are aligned mainly normally to the surface (see Fig. 5, c). One could suppose that the crystals of zeolite on the external surface of cenospheres are formed in a similar manner as in the case of the absence of reaction mixture stirring, namely, owing to a “remote” mass transfer across the solution. Inasmuch as this process requires for the diffusion controlled flow of the silica-alumina precursor from a dissolv-ing wall to the external surface across the layer formed one could consider a more likely process wherewith the crystals of zeolite are formed due to the crystallization of an amorphous layer formed on its external surface un-

der contacting the latter with NaOH solution, whereas the dissolution of the cenosphere wall occurs at the contact point with a non-structured silica-alumina layer formed.

Thus, it has been established that in order to carry out the process of vitrocrySTALLINE cenosphere zeolitization conserving the morphology of the precursor one should provide an optimum character of the circulation of the reaction solution above the surface. The formation of the zeolite layer proceeds through several stages, namely, *via* the formation of a semistructured silica-alumina coating on the surface which coating further represents a basis for the crystallization of a certain kind of the zeolite structure.

CONCLUSION

For the first time, adding no seeding agent and no structure-forming components, microspheric zeolite sorbents have been obtained from the vitrocrySTALLINE cenospheres of thermal power station ashes which sorbents contain individual zeolites or a mixture of zeolite phases such as NaA, NaX, NaP1. Utilizing the narrow fractions of preliminary separated cenosphere products allows one to achieve reproducible results of transformation with the use of cenosphere concentrates from various thermal power stations as a raw material.

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REFERENCES

- 1 J. D. Sherman, *Proc. Natl. Acad. Sci. USA*, 96 (1999) 3471.
- 2 R. L. Virta, US Geological Survey Minerals Yearbook, 2002, p. 841.
- 3 X. Querol, A. Alastuey, J. L. Fernandez-Turiel and A. Lopez-Soler, *Fuel*, 74 (1995) 1226.
- 4 Shih Wei-Heng, Chang Hsiao-Lan, *Mater. Lett.*, 28 (1996) 263.
- 5 X. Querol, F. Plana, A. Alastuey and A. Lopez-Soler, *Fuel*, 76 (1997) 793.
- 6 X. Querol, A. Alastuey, A. Lopez-Soler *et al.*, *Env. Sci. Technol.*, 31 (1997) 2527.
- 7 N. Shigemoto, S. Shirakami, S. Hirano, H. Hayashi, *Nippon Kagaku Kaishi*, 5 (1992) 484.
- 8 X. Querol, N. Moreno, J. C. Umana *et al.*, *Int. J. Coal Geology*, 50 (2002) 413.
- 9 X. Querol, J. C. Umana, F. Plana *et al.*, *Fuel*, 80 (2001) 857.
- 10 S. N. Vereshchagin, N. N. Anshits, A. N. Salanov *et al.*, *Chem. Sust. Dev.*, 11 (2003) 303.
URL: <http://www.sibran.ru/English/csde.htm>
- 11 RU Pat. No. 2212176, 2003.
- 12 T. A. Vereshchagina, N. N. Anshits, I. D. Zykova *et al.*, *Khim. Ust. Razv.*, 9 (2001) 379.
- 13 D. Breck, *Zeolite Molecular Sieves*, John Wiley&Sons, New York *etc.*, 1974, p. 780.
- 14 D. J. Wang, Y. H. Zhang, A. G. Dong *et al.*, *Adv. Func. Materials*, 13 (2003) 563.
- 15 R. M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, New York, 1982.
- 16 *Spravochnik Khimika (Handbook)*, vol. 3, Khimiya, Moscow, 1964.
- 17 R. O. Gould, B. M. Lowe, N. A. MacGilp, *J. C. S. Chem. Commun.*, 17 (1974) 720.
- 18 N. Murayama, H. Yamamoto, J. Shibata, *Int. J. Miner. Proc.*, 64 (2002) 1.
- 19 M. Tassopoulos, R. W. Tompson, *Zeolites*, 7 (1987) 243.
- 20 H. Ghobarkar and O. Schäf, *Micr. Mesopor. Mater.*, 23 (1998) 55.
- 21 I. Kostov, *Kristall und Technik*, 12 (1977) K49.