A METHOD OF COMMINUTING NATURAL ZEOLITE FOR THE PRODUCTION OF BIOLOGICALLY ACTIVE ADDITIVES

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This article describes a method of grinding a solid mineral material (zeolite), which can be used in medical applications, for the preparation of starting components for biologically active additives. Our method of preparing a solid natural material includes mechanical grinding, ultrasound comminution, and grading of natural zeolite. It differs from previously described methods in that material already ground mechanically to particle sizes of 5 – 20 mm is subjected to comminution and this process continues until particles of 1 – 2 to 10 μm are obtained. Zeolite particles obtained after processing in the homogenizer have greater roundness and smaller sizes than those obtained by mechanical crushing. Furthermore, our ultrasound method of comminuting zeolites also reduces the comminution process time by factors of 1.5 – 12.

Key words: Zeolites, ultrasound comminution, clinoptilolite.

Various aspects of zeolites have been studied in great detail in recent years, from technical specialties [1, 2] to biomedical uses [3 – 11]. Throughout the world, including Russia, a number of biologically active additives and sorbents based on zeolites are produced, such as Megamin, Lithovit, Litoplast, Zeosorb, and Bactistatin. As natural zeolites are quite hard aluminosilicate materials, we are presented with the unusually important technical problem of comminution, which is required to increase the working surface.

Zeolites are non-stoichiometric compounds whose composition varies over a wide range, forming series of solid solutions. More than 40 mineral forms of natural zeolites are known. The most common are:

Analcime $Na[AlSi_2O_6] \cdot H_2O$;
Heulandite $Ca_4[Al_8Si_{28}O_{72}] \cdot 24H_2O$
Clinoptilolite $Na_6[Al_6Si_{30}O_{72}] \cdot 20H_2O$
Laumontite $Ca_4[Al_8Si_{16}O_{48}] \cdot 16H_2O$
Mordenite $Na_8[Al_8Si_{40}O_{96}] \cdot 28H_2O$
Phillipsite $(0.5\ Ca, Na, K)_6[Al_6Si_{10}O_{32}] \cdot 12H_2O$
Faujasite $Na_{13}Ca_{12}Mg_{11}[Al_{59}Si_{133}O_{384}] \cdot 235H_2O$
Chabazite $Ca_2[A_4Si_8O_{24}] \cdot 12H_2O$
Erionite $(K_2, Ca, Mg, Na)4.5[Al_8Si_{27}O_{72}] \cdot 28H_2O$

One reported method for comminuting zeolite includes fragmentation of the material to a particle size of 5 – 10 mm and drying in a flow of air with a temperature of no greater than 70°C. This is followed by repeated comminution of the material to a mean particle size of 0.1 mm and repeated drying in a flow of air at the same temperature, mixing of the product with a ferromagnetic powder with a particle size of 1.0 – 50.0 μm at ratios of 1:1 to 2:1, followed by comminution of the product in a jet mill in the presence of the ferromagnetic powder to form an ultradisperse material with a particle size of 0.1 – 30 μm and a moisture content of no more than 2% by weight, followed by removal of the ferromagnetic powder from the mixture using a constant magnetic field and packaging of the resulting powder material in a vacuum pack [12]. However, this technology is quite complex and involves a large number of operations; it reduces the quality of the final product because it is virtually impossible to obtain complete removal of the ferromagnetic particles, the residues contaminating the final product. In addition, there are some losses of the ultradisperse powder when the ferromagnetic powder is removed, as particles of the material stick to them. The quality of the ultradisperse powder de-

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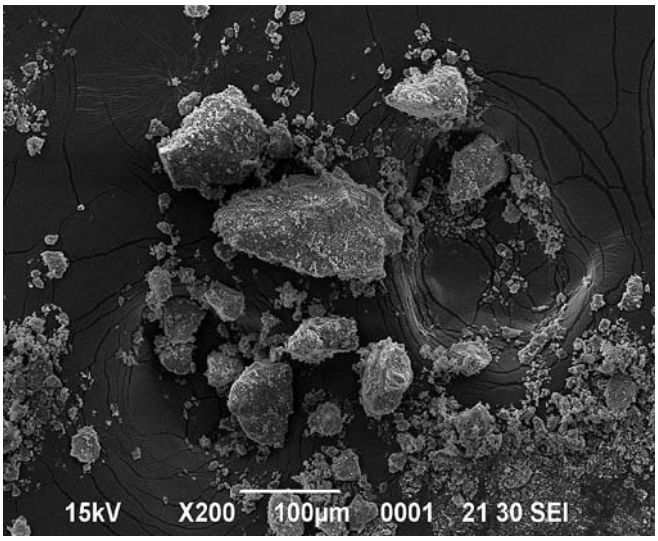

Fig. 1. Electron micrograph of clinoptilolite crystals, Magnification ×200.

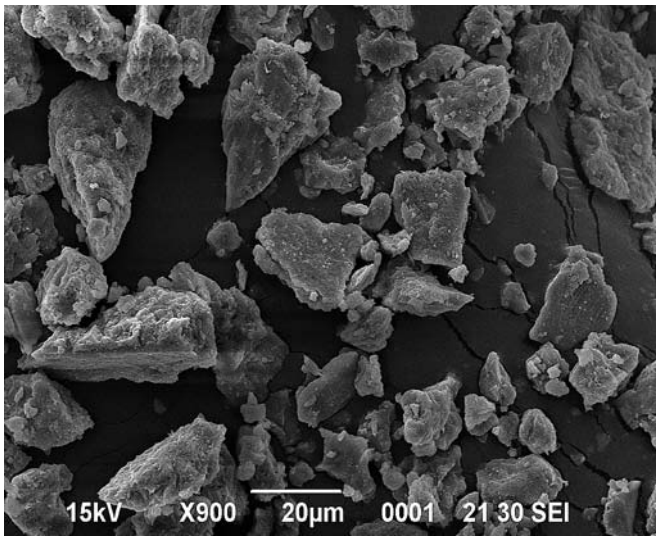

Fig. 3. Electron micrograph of clinoptilolite crystals, Magnification ×900.

creases because of partial oxidation on contact with the metallic powder, i.e., the ferromagnetic abrasive particles.

Methods of preparing solid natural material including fragmentation, comminution, and grading of the natural zeolite [13] are also known. A disadvantage of this solution is the production of comminuted material with angular particles, which complicates (and to some extent prevents) the introduction of this type of powdered material into the patient's body, due to side effects. Sharp-angled zeolite particles in powders are known to cause trauma to the gastric mucosa after oral administration. Preparation of finely dispersed material with particles of 1 – 2 to 5 – 10 µm by mechanical methods is also often impossible or requires comminution processes with high levels of energy and time expenditure.

The aim of the present work was to perform comminution to obtain finely disperse zeolite powder with particles as rounded as possible (priority patent application 2008116530, 25.04.2008).

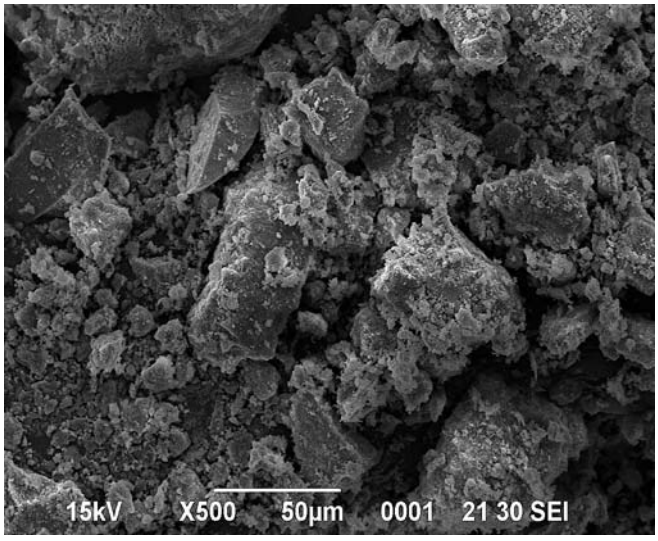

Fig. 2. Electron micrograph of clinoptilolite crystals, Magnification ×500.

MATERIALS AND METHODS

The zeolite used here was collected from the Vanginskii deposit in the Amur Region and was provided by M. G. Gamidov (Institute of Veterinary Medicine and Zootechnology, Far Eastern State Agrarian University, Blagoveshchensk). The natural zeolite was fragmented, ground, and graded. Mechanical fragmentation was performed using a VKMD6 cone mill (Vibrotekhnik). Ultrasound comminution was performed using a Bandelin Sonopulse 2070 ultrasound disintegrator (homogenizer), with a working frequency of 22 kHz and a power output of 100 W. Morphological studies and photography of samples were performed by I. Yu. Chekryzhov and P. P. Safronov using a JEOL JSM-6490LV scanning electron microscope at the Far Eastern Geological Institute, Far Eastern Division, Russian Academy of Sciences. Samples were initially sputtered with gold.

RESULTS AND DISCUSSION

The zeolite crystalline structure is formed by $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ fragments joined at their vertices in a three-dimensional carcass pierced by cavities and channels (windows) of size 0.2 – 1.5 nm. The zeolite "windows" can contain H_2O molecules and cationic alkaline and alkaline earth metals, ammonia, alkylammonias, etc. Zeolites are known to

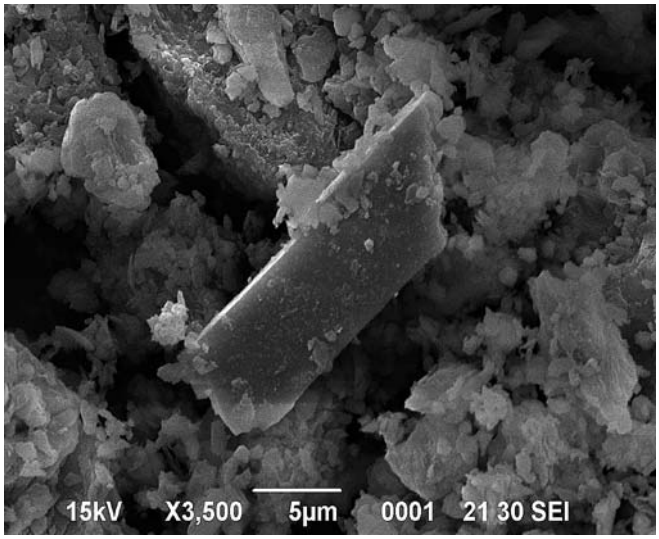

Fig. 4. Electron micrograph of clinoptilolite crystals, Magnification ×3500.

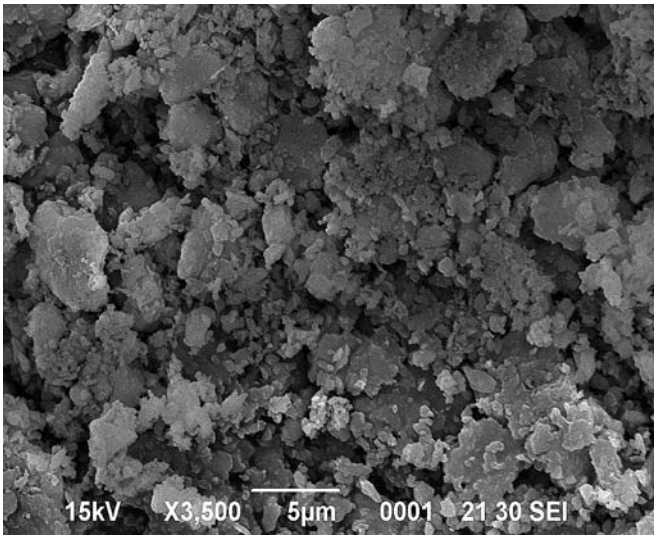

Fig. 6. Electron micrograph of clinoptilolite crystals, Magnification ×3500.

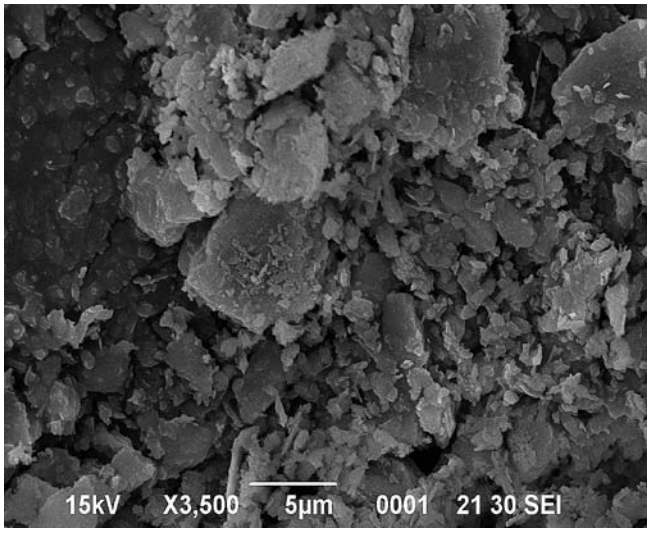

Fig. 5. Electron micrograph of clinoptilolite crystals, Magnification ×3500.

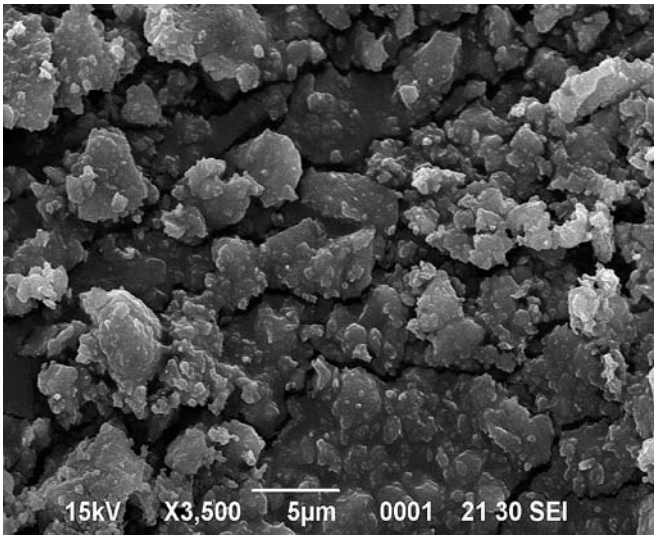

Fig. 7. Electron micrograph of clinoptilolite crystals, Magnification ×3500.

have large internal channels (up to 4.4 × 7.2 Å for a cation exchange capacity of the order of 200 mg-eq. ions per 100 g of zeolite). In normal conditions, they are filled with cations and water molecules, which have a significant level of free movement. We believe that the effect of acoustic treatment of zeolite particles is to produce cavitation in the liquid-filled pores, degrading the minerals as a result of sharp increases in the pressure within the pores. The intensive "mutual abrasion" of the particle surfaces (the bulk of the material is in the state of a "boiling layer") produces rounding of the particle surfaces, preventing the powder particles from being sharp-pointed.

During preparation of the solid natural material, the natural zeolite from the mine is fragmented to obtain material with particle sizes of 5 – 20 mm using a fragmenter. This material is then subjected to comminution with an ultrasound disintegrator to obtain a fraction with a particle size of 1 – 2 to 10 μm.

Comparison of results obtained using the mechanical and ultrasound methods for comminuting the material as the main preparation process is illustrated by scanning electron microscope photographs of the powder. Imaging parameters are shown at the bottom of each illustration (from left to right: acceleration voltage, magnification, scale bar, reference number, time).

Figure 1 shows the result of mechanical comminution of zeolites for 1 h. At a magnification of ×200, this shows the large range of particle sizes (from 150 to 5 μm), the proportion by volume of large particles (from 150 to 20 μm) constituting 65 – 80% of the total material.

Figure 2 shows the result of mechanical comminution of zeolites for 2 h. Here, the small, lighter particles on the background of zeolite crystals are montmorillonite. At a magnification of ×500, this photograph shows that the range of zeolite particle sizes was smaller, i.e., 20 – 50 μm, and that angular sides were clearly apparent on the zeolite particles.

Figure 3 shows the result of mechanical comminution of zeolites for 3 h. At a magnification of ×900, this shows that the range of particle sizes decreased but remained quite wide (from 5 – 10 to 20 – 30 μm) and that the zeolite particles again had sharp edges.

Figure 4 shows the result of mechanical comminution of zeolites for 4 h. Here, the small, lighter particles on the background of zeolite crystals were montmorillonite. At a magnification of ×3500, this photograph shows that the range of zeolite particle sizes decreased and was from 5 – 10 to 20 – 30 μm.

Increases in the duration of comminution did not increase the extent of the dispersity of the material, as the presence of a clay fraction promotes the aggregation of fine particles into "granules" with sizes of the order of 5 – 6 μm.

Figure 5 shows the results of ultrasound comminution of zeolites for 20 min. Here, the small, lighter particles on the background of zeolite crystals are montmorillonite. At a magnification of ×3500, this photograph shows that the range of zeolite particle sizes is not large, from 2 – 3 to 10 μm, and that the zeolite particles were rounded fragments.

Figure 6 shows the results of ultrasound comminution of zeolites for 30 min. The small, lighter particles on the background of zeolite crystals are again montmorillonite. At a magnification of ×3500, this photograph shows that the range of zeolite particle sizes was small, ranging from 2 – 3 to 10 μm, and that the zeolite particles were rounded fragments.

Figure 7 shows the results of ultrasound comminution of zeolites for 40 min. At a magnification of x3500, this photograph shows that the range of zeolite particle sizes was from 1 to 5 μm, and that the zeolite particles were rounded fragments.

Apart from the increase in roundedness and the decrease in the particle size of the material, our method of comminuting zeolites is also less time-consuming by factors of 1.5 – 12.

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