

NATURAL ANALCIME AS A RAW MATERIAL FOR ION EXCHANGERS

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Analcime is rather widespread among the zeolites known on the territory of Georgia [1]: an abundance of analcime connected with volcanic-sedimentary rocks is observable in the Middle-Eocene rock masses of the Achara-Trialeti folded system, beginning with Mtskheta district, including the Borjomi valley and westward in Bagdadi and Vani districts; analcime-containing stratified rocks are known in Western Georgia in the deposits of Jurassic carbonaceous and colored suites of Kutaisi area, as well as analcime from a basaltic geode (environs of Tbilisi), analcime crystallized in the chemical way (sedimentary rocks from Kutaisi environs), and analcime of diagenetic origin in volcanic-sedimentary rocks from the Akhaltsikhe deposit, along with other zeolites (phillipsite, laumontite, mordenite, etc.).

Analcime belongs to minerals of tectosilicate group with zeolitic structure (crystal chemical data $[\text{Na}_{16}(\text{H}_2\text{O})_{16}] [\text{Al}_{16}\text{Si}_{32}\text{O}_{96}]$ -ANA, cubic, $Ia\bar{3}d$, $a=13.73 \text{ \AA}$ [2]) with high framework density of $18.5T/1000 \text{ \AA}^3$ ($T = \text{Si}$ or Al). The analcime framework (Figure 1) consists of singly-connected 4-rings, irregular channels are formed by highly distorted eight-membered rings (8mR, Figure 2) and have small entrance windows of approx. 2.6 \AA , and regular channels are formed by six-membered rings (6mR) along the [111] direction of the cubic lattice.

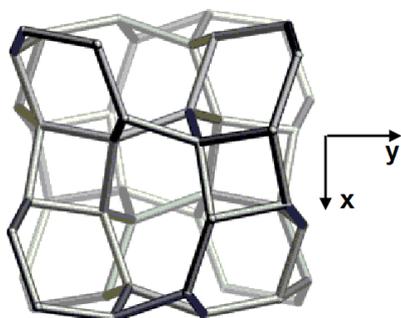


Figure 1. Analcime framework viewed along [001].

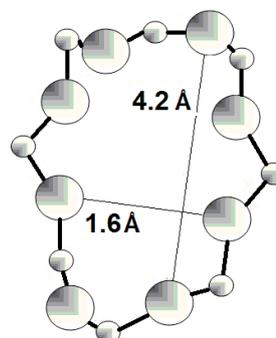


Figure 2. Distorted 8mR viewed along [110].

The compact structure of analcime also prevents the adsorption and diffusion of molecules in the cages and channels, therefore its use as an adsorbent or molecular sieve is limited. However, analcime has a scientific weight ion exchange capacity of 5.1 meq/g, and it was supposed to use natural analcime as an ion-exchanger for the nuclear wastewater treatment [3], but nothing is known about the practical implementation of this project.

The goal of our study was to demonstrate possibility to carry out synthesis of zeolite with high ion-exchange capacity by hydrothermal recrystallization of natural analcime and production of materials with different sizes of crystallites and suitable system of pores and channels.

Preparation of synthetic zeolite material was carried out using greenish-grey analcime-containing rock from the Chachubeti plot of the Tedzami deposit having high zeolite phase content (up to 95%) with chemical composition $(\text{Na}_{9.25}\text{K}_{2.25}\text{Ca}_{1.25}\text{Mg}_{0.95})\text{Me}_{0.30}[\text{Al}_{16.2}\text{Si}_{32.0}\text{O}_{96}]18.4\text{H}_2\text{O}$ (Me – impurity metals such as Fe, Cu, etc.), characterized by the X-ray diffraction pattern, IR spectrum, thermal analysis data, and ion exchange properties [4].

Zeolite-containing rock powder (0.063-0.1 mm), washed in distilled water (solid : liquid =1:20, 3-5 times) and dried at 100-110°C was treated at room temperature by HCl water solution under stirring, washed by water before the complete disappearance of Cl^- ions, and dried at 100-105°C; water suspension of homogeneous amorphous (XRD tested) material was prepared with the solid to liquid ratio of 1 : 3; suspension was treated at room temperature by NaOH water solution, solid to liquid ratio of 1 : 6; homogenization of produced gel takes approx. 30 minutes, its aging at room temperature – several days. Crystallization of aged gel was carried out in the Teflon flasks using temperature-controlled water bath (OLS26 Aqua Pro); the temperature (up to 95°C) and duration (up to 120 hours) have been adjusted to prepare crystals with average diameter of 5 μm ; separation of produced crystalline material was carried out by filtration of mother solution, solid material was cleaned by distilled water until pH 8.0-8.5, and dried at 90-100°C.

The analysis of the XRD pattern (Fig. 3) allows us to attribute the obtained material to the Linde Type A synthetic zeolite ($[\text{Na}_{12}(\text{H}_2\text{O})_{27}]_8 [\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]_8$ -LTA). Experimental XRD pattern has the same peculiarities mentioned in [5,6] for the LTA zeolites produced from kaolin considered as an ideal raw material for the preparation of this type of zeolites. However, materials obtained from kaolin contain quartz (strong peak at $2\Theta = 26.63^\circ$) and the SOD type zeolite (characteristic peaks at $2\Theta = 14.14^\circ$ (0.53), 24.62° (1.00), 31.96° (0.98), and

35.1° (0.78)) as impurities, not observed in XRD patterns of samples obtained by recrystallization of analcime.

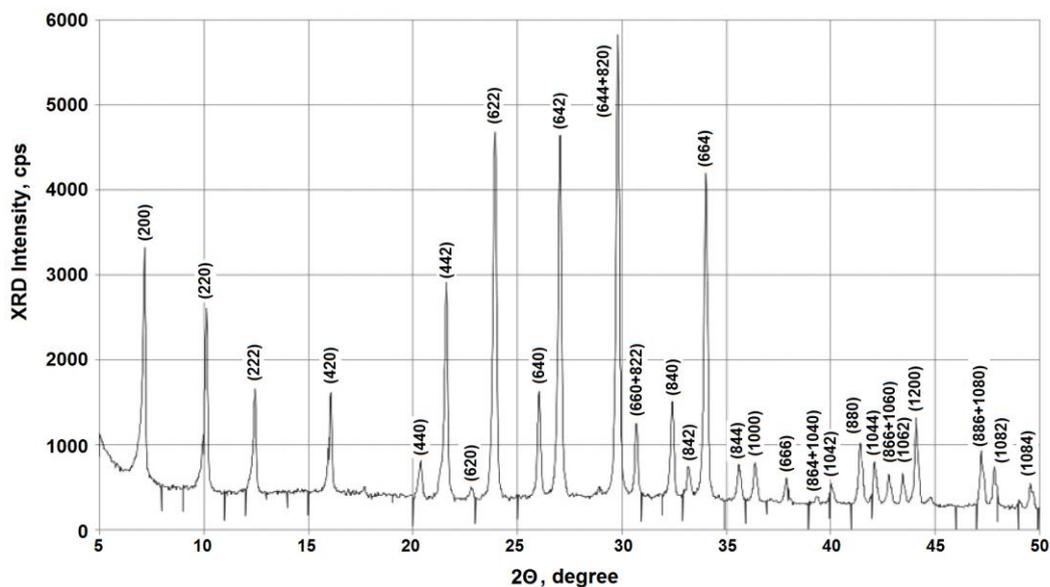


Figure 3. Powder XRD pattern of the material obtained by the recrystallization of analcime; numbers in parentheses are Miller indices (hkl)

Zeolites have been produced from the $3.4\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:1.1\text{SiO}_2$ reaction mixture, the chemical composition of prepared materials, $0.92\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:2.04\text{SiO}_2:3.00\text{H}_2\text{O}$, is in a good accordance with corresponding crystal chemical data for LTA. Developed zeolitic crystal microporous structure in synthesized samples is confirmed by high value (>13 mmole/g) of water adsorption capacity under static conditions at the “plateau” pressure $p/p_s=0.40$ and room temperature. Share of impurity metals in compensation of the negative charge is 8%, but in some cases this value reaches 15%. In general, recrystallization of analcime retains a greater amount of impurity metals than recrystallization of clinoptilolite [7], but the preparation of LTA zeolite from clinoptilolite is possible only in two stages, with the intermediate production of sodalite.

The resulting material has a fairly high ion exchange capacity, 4.5 meq/g, and can be used as a builder in detergent powders and tablets for water softening.

Ratio of water molecules per compensating ion ($\text{H}_2\text{O}:\text{Na}$) in ideal LTA structure is 9:4, in synthetic samples it depends on conditions of crystallization: hydrated materials ($\text{H}_2\text{O}:\text{Na}=9:5.5$) are produced at low temperature, high temperature results in dehydration. Increasing basicity of reaction mixture results in creation of LTA structure with high aluminium content ($\text{Si}/\text{Al}\approx 1$), rapid crystallization gives nanoscale crystals and aggregates,

while slow crystallization at comparatively low temperatures gives micrometric crystallites (Fig. 4).

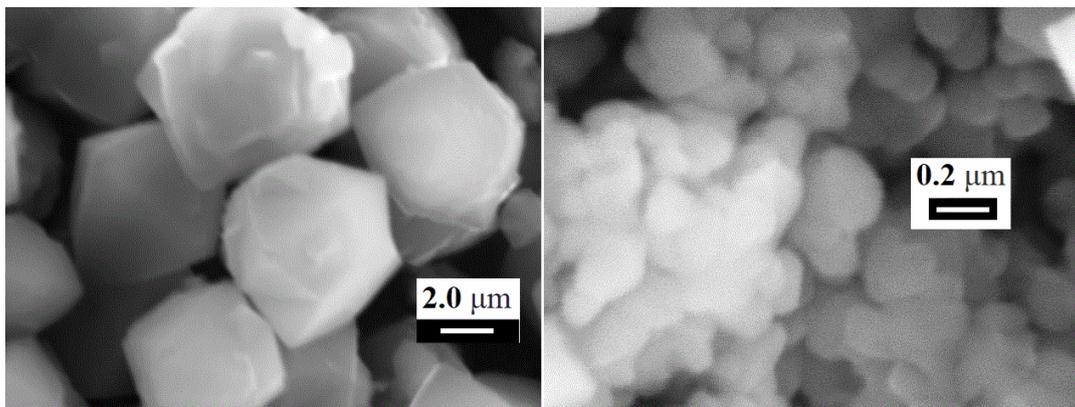


Figure 4. SEM images of micrometric (left, x5,500) and nano (right, x55,000) crystals of LTA zeolites recrystallized from analcime

The proposed method for preparation of the LTA zeolites is based on the use of natural silica-alumina raw materials and inexpensive reagents (HCl, NaOH), it is characterized by the relative rapidity and low energy expenditures.

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REFERENCES

- [1] N. Skhirtladze. Genetic groups of Georgian zeolites, their main deposits and manifestations, Tbilisi State University, Tbilisi, 1997, p. 16.
- [2] Ch. Baerlocher, L.B. McCusker, D.H. Olson, Atlas of zeolite framework types, 6th revised edition, Elsevier, Amsterdam, 2007, p. 46.
- [3] M.H. Mallah, H. Soorchi, T.F. Jooybari, Annals of Nuclear Energy, 47, 2012, pp. 140-145.
- [4] V. Tsitsishvili, N. Dolaberidze, S. Urotadze, M. Alelishvili, N. Mirdzveli, M. Nijaradze, Chemistry Journal of Moldova, 12, 2017, pp. 95-101.
- [5] A. Shoumkova, V. Stoyanova. Journal of Porous Materials, 20, 2013, pp. 249-255.
- [6] M. Gougazeh, J.-Ch. Buhl, Journal of the Association of Arab Universities for Basic and Applied Sciences, 15, 2014, pp. 35-42.
- [7] V. Tsitsishvili, N. Dolaberidze, M. Alelishvili, M. Nijaradze, N. Mirdzveli, Proc. Georgian Nat. Acad. Sci., chem. ser., 42, 2016, pp. 133-137.