

Analcime-Bearing Rocks of the Middle Timan Region

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Abstract—Specific features of the mineral composition, physicochemical parameters, and technological properties of analcime-bearing rocks developed in the Middle Timan region are discussed. Based on the study of dressability of these rocks, a technology for their concentrating is proposed. Possibility of the application of analcime-bearing rocks from the Middle Timan region in different fields of human activity is shown.

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Zeolites have attracted no less attention of scientists and industry than gold and diamonds. More than 90 varieties of natural zeolites are known to date (*Recommended...*, 1997; Pekov et al., 2004). Their diverse (absorption, ion-exchange, catalytic, and molecular-screening) properties provide basis for application in different areas of industry, agriculture, medicine, construction, and ecology. In the Komi Republic, potential of zeolites as a mineral raw material and prospects of its utilization are insufficiently studied. Resource strategy of the republic is oriented on the formation of its own zeolite resource base, which would allow the republic to outline new prospective directions in geology and create modern geological technologies.

Zeolite-bearing rocks are rather widespread in the Timan and adjacent regions. However, it is not easy to transform natural resources into blessing. Solution of such tasks depends significantly on results of studies in different fields of science. Achievements in this field are accumulated in technological mineralogy of zeolite-bearing rocks. Among many varieties of raw zeolite material, analcime-bearing rocks represent the most complicated but prospective object in terms of both geological and technological issues.

Among others, the following factors hamper the practical utilization of analcime-bearing rocks: (1) insufficient knowledge of correlation between their physicochemical properties and composition; (2) low dressability due to their polymineral composition and intergrowths of finely dispersed minerals with similar separation properties.

Therefore, study of physicochemical and technological properties of analcime-bearing rocks, as well as development of technologies for their dressing, have both scientific and applied significance.

MATERIALS AND METHODS

The Timan zeolite-bearing province was outlined in the Komi Republic in the second half of the 20th century (Ostashchenko, 1984). The Koin zeolite-bearing field is best studied in the region (Fig. 1). We studied analcime-bearing rocks from the Veslyana group of occurrences (Fig. 1, occurrences 7–10). The investigation was focused on Upper Permian rocks exposed in several areas and recovered by mining works. The bed-by-bed description of rock was mainly carried out by E.A. Malysheva with the participation of authors of the present communication and A.N. Ignat'ev, a geologist from the Komigeologiya Geological Association. We also investigated the collection of samples from outcrops and bulk samples taken from two prospect holes at the Veslyana analcime occurrence (Malysheva et al., 2000, 2002). We carried out detailed macroscopic and microscopic examination of rocks, performed the X-ray diffraction, semiquantitative spectral, complete silicate, and carbonate analyses of their mineral composition.

The density of analcime and other minerals was determined by the volumetric method. The microhardness was measured with a PMT-3M semiautomatic device; the specific magnetic susceptibility, with a Kapabridge KLY-2 equipment; the specific surface, by the chromatographic method based on argon desorption; and the ion-exchange capacity of magnesium, by the Bobko–Askinazi–Aleshin method. Gravitational concentration was carried out in heavy liquids with a VS-300 screw separator. Magnetic separation was performed with an electromagnetic mineral separator of the SIM-1 type. The ultrasonic treatment of rocks was accomplished with a UZDN-2T disperser.

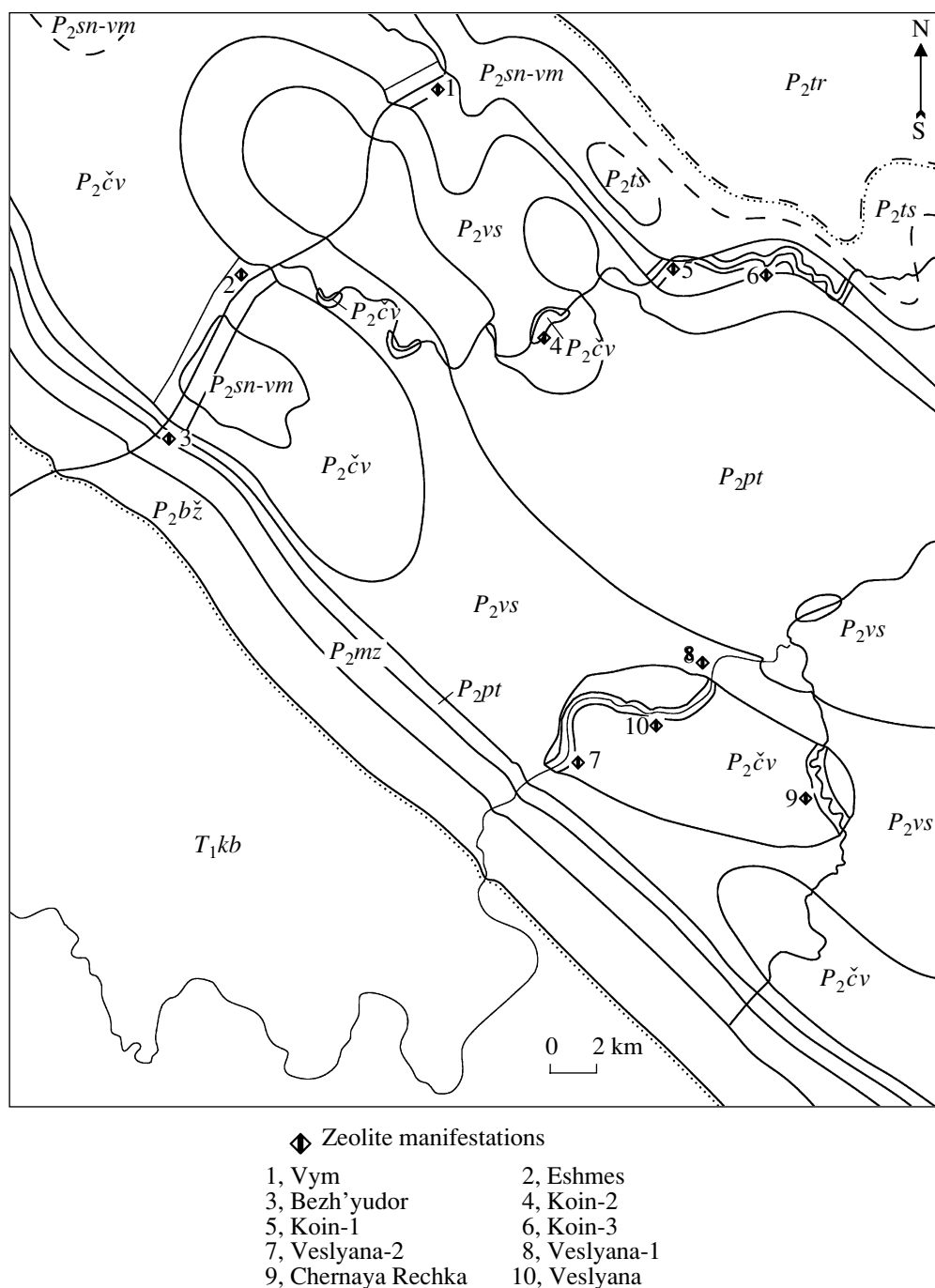


Fig. 1. The Koin zeolite-bearing area. Based on materials of V.M. Kapitanov, A.N. Ignat'ev, et al. from the Komigeologiya Geological Association (Shushkov et al., 2006).

MINERAL COMPOSITION OF ANALCIME-BEARING ROCKS

The analcime-bearing rocks are represented by Upper Permian siltstones, mudstones, and subordinate marls with cavities partly or entirely filled with analcime.

Oligomictic and polymictic siltstones are characterized by spotty or irregularly bedded structures related

to alternation of layers and nests of psammitic, silty, and pelitic material. The fine-grained material alternates with the coarse-grained one without any noticeable regularity in grain size. Silt-sized detrital particles are poorly rounded and sorted. Fragments of quartz, feldspar, and volcanics and flakes of muscovite are cemented by the clayey and clayey-carbonate material. The cement has a spotty appearance owing to the presence of inclusions of reworked brown organic material

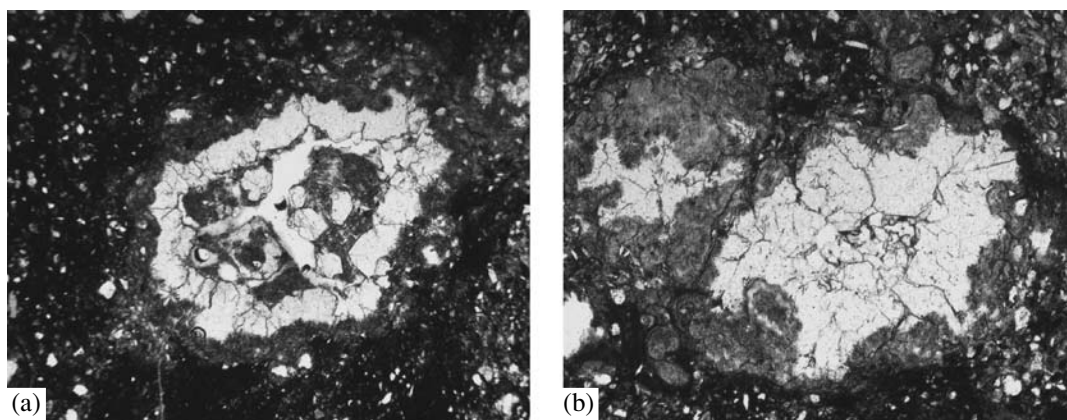


Fig. 2. Various stages of infilling of cavities with analcime-bearing aggregates. Images obtained with a Leica RD DM polarization microscope (VIMS, Moscow). Parallel nicols, magn. 200. (a) Cavity incrustation with analcime aggregates; (b) cavity completely filled with analcime aggregates.

of different tints. The cement has basal and contact-basal pattern. Authigenic minerals are represented by sericite, chlorite, and pyrite.

Mudstones also have spotty and irregularly bedded structure owing to the irregular development of ferrugination, on the one hand, and different thicknesses of layers of inequigranular (psammitic and silty) material. Coarse-grained particles are represented by quartz, feldspars, carbonates, and volcanics. Pyrite and iron hydroxides are also present.

Analcime aggregates encrust rounded and oval cavities and infill microfissures in rocks. Thin sections of analcime demonstrate distinctly different stages of its development in cavities ranging from insignificant encrusting to complete filling (Fig. 2). Both microcrystalline (crystals <0.01 mm in size) and medium-crystalline (~ 0.5 mm) aggregates are observed. The analcime content in rocks ranges from 1 to 30%.

TECHNOLOGICAL PROPERTIES OF ANALCIME-BEARING ROCKS

Analcime-bearing rocks of the middle Timan region are referred to an “unspecified raw material type” because of their insufficient investigation. Major issues in the investigation of analcime raw material are as follows: study of zeolites aimed at modification of their technological properties for the utilization in specific processes; development of complex technologies for the maximal extraction of analcime and other valuable components from analcime-bearing rocks.

Mechanical properties. Microhardness of minerals in analcime-bearing rocks is highly variable. The highest values are typical of quartz (1023–1236 kgf/mm²), feldspars (735–922 kgf/mm²), and goethite (532–580 kgf/mm²). The presence of structurally bonded water in minerals decreases their hardness. For example, microhardness of smectites and analcime is 50–76 and 329–377 kgf/mm², respectively.

The analcime-bearing rocks are characterized by high index of grindability and low indexes of vibration wear, abrasability, and mechanical crush resistance.

Gravitational properties of minerals are determined by their density. The density of minerals in analcime-bearing rocks varies from 2000 to 5500 kg/m³. All minerals (except goethite and hydrogoethite) are characterized by density ranging from 2000 to 3500 kg/m³. The density of the major minerals is as follows (kg/m³): quartz 2650–2660, feldspar 2540–3450, smectites 200–2330, analcime 2200–2300, and kaolinite 2500–2680. The density of goethite (hydrogoethite) varies from 3300 to 5500 kg/m³ (Shushkov, 2004).

It should be noted that mechanical, gravitational, and other properties were determined for technological assays without the consideration of different varieties of analcime and other minerals. It was necessary to estimate the variation range of hardness, density, and other parameters for technological processes (hydroseparation and concentration).

Magnetic properties. The magnetic susceptibility was used for estimating magnetic properties. The specific magnetic susceptibility of analcime (0.87×10^{-8} m³/kg) is substantially lower than that of other minerals, such as quartz $15\text{--}60 \times 10^{-8}$, feldspars $5\text{--}10 \times 10^{-8}$, smectite $15\text{--}60 \times 10^{-8}$, and goethite (hydrogoethite), $30\text{--}45 \times 10^{-8}$ m³/kg (Shushkov, 2004).

Sorption properties. The Ar-based specific surface of analcime-bearing rocks, values vary from 9.08 to 21.37 m²/g (table). The specific surface of the analcime-bearing rock calcined at 500°C for 1 h was 24.7 m²/g. The Ar-based specific surface of pure analcime is 1.5 m²/g. This difference is explained by the fact that analcime is a low-porous zeolite with inlet diameter of 0.26 nm, while the critical diameter of Ar molecule is 0.384 nm. Results of the investigation revealed that the specific surface value depends most likely on the content of clay minerals and does not correlate with

Specific surface and ion exchange capacity of analcime-bearing rocks

Ore occurrence	Sample no.	Analcime content in rock, %	Ar-based specific surface, m ² /g	Mg-based ion exchange capacity, mg-equiv/100 g
Veslyana-2	50201	5	13.66	34.2
	502010	7	n.d.	55.7
Veslyana	551	25	21.37	63.4
	55201	9	16.77	28.7
	58901	10–12	n.d.	120
Veslyana-1	56401	10	n.d.	47.0
	56402	11	n.d.	195
	56403	14–18	9.08	51.9
Chernaya Rechka	58601	15–18	10.46	47.3
	58602	18–20	16.72	58.0
	58603	18–20	12.67	83.6
analcime monofraction			1.5	21.5

Note: (n.d) Not determined.

the analcime content in rocks. This method of the determination of specific surface is more suitable for macro- and mesoporous objects and their mixed types. Therefore, the specific surface determined in the considered case is probably related to rock-forming minerals, i.e., secondary porosity. The primary porosity (microporosity), which depends of zeolite nature, should likely be determined by other methods (Shushkov et al., 2004).

The analcime-bearing rocks are characterized by low values of the benzol-based pore volume, toluene-based specific surface, water vapor-based limit sorption capacity, and medium porosity values.

Ion-exchange properties. The magnesium-based ion-exchange capacity (IEC) of analcime-bearing rocks ranges from 28.7 to 196 mg equiv/100 g. The IEC of analcime (21.5 mg equiv/100 g) appeared to be lower than that of the analcime-bearing rocks (table). Probably, the IEC value depends more on the content of clay minerals than on the content of analcime.

It was established that the ion-exchange capacity of analcime-bearing rocks depends on the grain size of components. The highest IEC value is registered in grain-size classes -0.05 and $+0.05-0.1$ mm (62.6 and 61.8 mg equiv/100 g, respectively). If the grain-size class increases to $-0.16+0.1$ and $-0.25+0.16$ mm, the IEC value decreases approximately by 25–33% (46.7 and 46.1 mg equiv/100 g, respectively). The IEC value of rocks is 25.1 mg equiv/100 g for the grain-size class $-0.5+0.25$ mm. The value is 3.4 times lower (18.6 mg equiv/100 g) in rocks of the grain-size class $-1.0+0.5$ mm and 5.6 times lower (11.1 mg equiv/100 g) in the grain-size class $-3.0+1.0$ mm. In coarser fractions ($+5.0$ and $-5.0+3.0$ mm), the IEC value (5.74 mg equiv/100 g) is 10.9 times lower than the maximal IEC value.

DRESSING OF ANALCIME-BEARING ROCKS

Irregular distribution and low content of analcime (1–30%) in the analcime-bearing rocks of the middle Timan region hampers their wider utilization, because some technologies, such as dehydration of gas and non-aqueous liquids, oil cracking, catalysis, and medicine, require a high zeolite content in rocks (75–95%). Therefore, we investigated the dressability of analcime-bearing rocks for their utilization in different spheres of human activity.

Gravitation dressing of analcime-bearing rocks was carried out using a BS-300 screw separator and the method of separation in heavy liquids (bromoform and alcohol mixture).

Since concentration by the screw separator was inefficient, the separation in heavy liquids was subsequently used. Dressing of rocks with the analcime content of 20% (grain-size class $-0.2+0.1$ mm) in heavy liquids with a density of 2250 and 2300 kg/m³ produced a concentrate with the analcime content of 52–55%. The degree of extraction and yield were equal to 45–53 and 22–28%, respectively (Shushkov, 2004).

Magnetic separation of analcime-bearing rocks with the grain-size class $-0.16+0.1$ mm was conducted by the dry method using a SIM-1 separator. The initial analcime content in the rock was 16%. The application of this method provided concentrate with the analcime content of 58–62%. The degree of extraction and yield were equal to ~30 and 6%, respectively (Shushkov, 2004).

Gravitational and magnetic separation technologies are insufficiently efficient for obtaining the high-quality zeolite concentrate. Therefore, combination of different methods is needed for dressing analcime-bearing rocks. Application of various methods of the modification of

physicochemical properties of zeolite raw material seems promising as well.

The *ultrasonic treatment* of rocks represents an efficient method for separating intergrowths along their boundaries and obtaining free analcime aggregates. We investigated rock of the grain-size class $-0.5+0.25$ mm (analcime 18%). After the ultrasonic treatment, dressability of the rock was examined with a SIM-1 magnetic separator. The analcime content in the concentrate was ~95% (degree of extraction 83%, yield 15%).

Based on results obtained, we propose the following technological dressing scheme: crushing of the analcime-bearing rock; separation of the grain-size class $-0.5+0.25$ mm; ultrasonic treatment; decantation of water suspension; and extraction of analcime from the concentrate using the magnetic separation method.

APPLICATION OF ANALCIME-BEARING ROCKS

There is a high demand for zeolites due to their specific physicochemical properties. In the Komi Republic, analcime-bearing rocks are utilized in agriculture. They are also used for domestic needs (e.g., as biotoilets for domestic animals) and the solution of ecological problems (regeneration of soil polluted by oil). We have conducted experiments with the purification of potable and technical water by the analcime-bearing rock subjected to thermal treatment. The experiments made it possible to decrease water coloration by 20%; turbidity, by 79%; permanganate oxidation, by 30%; and total iron content, by 70%.

CONCLUSIONS

Analcime-bearing rocks of the middle Timan region are represented by Upper Permian siltstones, mudstones, and subordinate marls with cavities partly or entirely filled with analcime.

The analcime-bearing rocks have the following mineral composition (%): clayey components (50–70%), quartz (10–30%), analcime (1–30%), and feldspars (2–5%). Carbonates, iron hydroxides, and altered pyroclastic material are rare.

The analcime-bearing rocks have a low specific surface, which can be increased by the initiation of defects. Ion-exchange properties of this raw material can be used efficiently for the solution of agricultural and ecological problems. Modification of physicochemical properties of these rocks widens significantly the scope of their application and represents a prospective direction in the study of zeolites and associated minerals.

Analcime-bearing rocks of the middle Timan region are characterized by low dressability. Preliminary ultrasonic treatment of the analcime-bearing rocks is efficient for the destruction of intergrowths along their boundaries and the production of free analcime aggregates. The proposed dressing procedure yields 95% analcime concentrate and, thus, offers opportunities for a wider application of this raw material. However, economic efficiency of the proposed technology has not been calculated so far.

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