Modern techniques to process Eastern Transbaikalia zeolite-bearing rock

KK Razmakhina\textsuperscript{a,b,*} and AN Khatkova\textsuperscript{b,**}

\textsuperscript{a}Chinakal Institute of Mining, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia
\textsuperscript{b}Transbaikal State University, Chita, Russia

E-mail: *constantin-const@mail.ru; **alisa1965.65@mail.ru

Abstract. Technological research results are used to substantiate the selection of an optimal technique to process zeolite-bearing rocks of Eastern Transbaikalia origin. The feasibility is established to improve appreciably a grade of zeolite-bearing materials by employing the target-action physical, physicochemical and energy techniques.

1. Introduction

In the opinion of most professionals the natural zeolites are acquiring top position in terms of market demand among nonmetal minerals. The 1970s are ranked as an entry of mankind into “zeolite epoch” in view of global actuality of public health and environment protection and high performance of zeolite in concerned applications [1, 2, 3, 4].

Zeolites are aqueous aluminosilicates of mostly calcium, sodium, rarer barium, strontium, and potassium. Mineral species differ from each other in cation ratio, in content of alkali and silicic acid as well as water amount. In the general form the anion radicals constitute a carcass of aluminosilico-oxygen tetrahedrons, differing by abundance of channels, pores of strictly definite size from other similar carcass kinds. The porous structure of zeolites constitutes a huge internal surface reaching up to 47 \%, which is quite accessible for penetration of molecules from 2.6 to 7.4 Å in size exclusively. In general, specific structure and properties of zeolites induce individual physicochemical effects governing their consumer characteristics and a wide practical utilization scope [5, 6, 7].

Wide application of zeolites is restrained by a poor grade of the primary raw materials, so zeolite-bearing rocks as well as conventional raw materials should be subjected to beneficiation, including gravity, magnetic, and electric separation, specific physicochemical modification and activation.

2. Zeolite-bearing rocks processing

Methodical principles of processing flowsheets depend on further application of zeolite-bearing rocks. Considering the well-known [5] and established by the present researchers regularities in zeolite-bearing rocks, the following sequence of their processing is recommended: crushing, grinding, drying, screening, dedusting, magnetic and electrostatic separation, and dumping of waste tailings.

The pretreatment operations are crushing, grinding, ultrasonic pretreatment, drying, screening, and dedusting.

Special physicochemical operations introduced into the flowsheet for zeolite-bearing rocks processing are treatment of feed with salicylic or benzoic acid vapor in order to intensify electrostatic separation, probable hydrochemical techniques and high-power electromagnetic pulse effects.
It is important to point out that application of the above physicochemical treatment is compulsory in the case given that a specific physicochemical modification of zeolite properties is required in compliance with specificity of their application.

Basic principles to be realized in new-developed technical procedures for zeolite-bearing material modification rest on introduction of the following processing:
— mechanochemical (mechanodeformation) effects;
— ultrasonic treatment before screening of the material;
— deep cleaning from ferruginous impurities;
— electrostatic separation to remove non-magnetic impurities;
— high-power electromagnetic pulse effects.

The processing flowsheets for zeolite-bearing rock can be expanded by optional stages in both pretreatment and basic processing circuits.

Pretreatment circuit involves such processes as crushing and grinding to gain the maximum liberation of mineral grains. The rotor impact crushers can be recommended to crush zeolite-bearing tuffs with a minimized yield of unacceptable-shape grains. The preferable spherical shape of ground zeolite grains can be produced at ball mills.

When designing technological flowsheets for processing of zeolite-bearing rocks, the preliminary screening in a closed cycle with crushing should be provided in order to diminish the fine-size fraction yield and to increase a higher-value coarse-size yield. It is important to mention that efficient screening can be gained at material moisture of 0-3 % for Shivyrtuy clinoptilolite-zeolite-bearing rocks (Transbaikalia) and at W=0-8 % for Talan-Gozagorsky chabasite-bearing and esite-basalts (Transbaikalia).

Mechanical (mechanodeformation) effects are more or less present in conventional preliminary fine grinding of the primary feed. When breaking particles with different imperfections and surface energy levels. Transition from one mill type and grinding modes to another ones (for example, from conventional ball to autogenous grinding) or to a higher-energy processes like centrifugal, vibration or disintegrating separation of particles lead to formation of mineral surfaces with different defect levels and physicochemical properties. Zeolites with specific porous structure are sensitive to mechanical effects [9].

It was established by X-ray diffraction technique that diffraction reflections, characteristic to clinoptilolite, are notably weakened because of enhanced crystalline defects and increased dispersion. At the same time intensity of quart reflexes is preserved unchangeable thanks to much higher strength of crystals.

The diffraction thermal analysis (DTA) curves were used to evaluate the effect of preliminary activation on reactive capacity of zeolite-bearing rocks in terms of a magnitude, accumulated under the mechanical energy influence, calculated considering variations in temperature of zeolite-water dehydration along with the molar water entropy in gaseous and crystalline states.

Some increase in mass loss is observed for mechanically activated specimens along with displacement of the endoeffect minimum in DTA curves to higher temperature range; it is caused by formation of appreciable amount of hydroxyl Si-OH and Al-OH groups, resulted from respective strain processes at spots of rupture of silico- and alumooxygen bonds (Si-O-Al) and exhibiting higher energy bonds with surface atoms as compared to water molecules present in zeolite channels.

Distinguished physicochemical properties of activated zeolite surface due to higher defectiveness level govern the efficiency of followed processing operations. The character of variations in capillary-porous structure is one of the most significant factors for understanding the processes running on zeolites or with zeolite participation. Characteristics of porous structure of mechano-activated zeolites are assessed based on the nitrogen vapor adsorption isotherms at 77 K°, by processing the experimental results for Brunauer, Emmett, Teller, and Langmuir equations. It is found that mechanical activation leads to a certain increase in specific surface area, summarized pore volume, mesopores volume, equivalent pore radius, conditioned by a plenty of inflections in zeolite rock grains
which are capable to provide access of sorbate molecules to never-before impenetrable structural channels.

Ultrasonic pretreatment of zeolite-bearing materials used to intensify zeolite separation from mineral impurities (feldspar, montmorillonite, quartz, plagioclase, etc), thus providing the best performance of magnetic and electrostatic separation. The use of ultrasonic field energy enhances dispersion effect thanks to spot erosion of hard surface at phase boundaries and accelerates zeolite concentration process. It is valid that the ultrasonic treatment of zeolite-bearing materials enables to gain a rather high clayey component removal. The experimentally justified frequency of ultrasonic treatment of zeolite-bearing materials is 22 kHz. This allows reduction in number of recleaning stages and higher zeolite content in the concentrate up to 85-95 %.

The analysis of IR-spectra of adsorption of primary, pretreated, and enriched without ultrasonic pretreatment of test specimens indicate variations in intensity of characteristic adsorption bands in range 3100–3700 cm⁻¹, 1640 cm⁻¹, related to oscillations of OH-bonds in associates of zeolite water molecules (3440 cm⁻¹), oscillations of OH-bonds in hydroxyl groups on surface of the carcass (3620 cm⁻¹), strain oscillations of OH-bonds of water molecules (1640 cm⁻¹), the increase in intensity of the above parameters proves higher zeolite content in technological products as a result of the ultrasonic treatment.

In the basic circuit of magnetic and electrostatic separation the iron-bearing impurities, quartz minerals and feldspars are removed actually completely from zeolite-bearing tuffs. The application of electrostatic separation is a rather efficient way to remove quartz minerals, mica, and feldspar, while application of salicylic and benzoic acids charging the contrast mineral surface for 30–60 min guarantees higher efficiency in removal of the above impurities from feed of -0.074+0.05 mm in size.

Researchers in [10] estimated the performance of high-power electromagnetic pulse effects on processing (adsorption) properties of Eastern Transbaikalia zeolite-bearing rocks. Application of a nanosecond pulse series with frequency 125 Hz (~6*10⁴ imp) at voltage 44 kV enabled to reach a breakdown state of test rock surface with specific formation of fine defects, breakdown channels both nearby natural microfractures and zeolite–rock intergrowth boundaries and in areas, free of primary defects. As a consequence, the treatment altered texture-geometric parameters of rocks, caused growth of specific surface area, total cumulative volume of pores, equivalent pore radius and reduction in specific magnetic sensibility, as well as adsorption capacity of zeolite-bearing rocks.

The present research aim is comprehensive investigation into the effect of high power electromagnetic pulse effects on composition and physical properties of zeolite-bearing rocks of Eastern Transbaikalia origin by means of Mossbauer spectroscopy method. Zeolite-bearing rocks were treated at the test facility developed by Chanturia V.A. and co-researchers at IPKON RAS. Mossbauer spectroscopy of zeolite-bearing rocks originated from Shivyrtuisky, Kholinsky Badinsky, and Talan-Gozagorsky deposits revealed the presence of both normal and finely-dispersed hematite. It is essential that the pulse treatment influenced the content of normal and finely dispersed hematite with increase in proportional content of finely dispersed hematite and reduction in coarse-crystalline hematite in all the test specimens. Common for all Eastern Transbaikalia zeolite-bearing rocks was content of montmorillonite with specific non-equivalent peculiarities in its structure.

A magnitude of resonance effect being proportional to total iron content makes it possible to assess ferruginous content of montmorillonite by this parameter. The study results indicated that the pulse treatment led to higher iron content in test specimens. This effect can be explained by removal of volatile components in degritation and loosening of zeolite structure, thereto providing a better solubility.

By the research evidence the iron in zeolite-bearing rocks is present as a discrete impurity, rather than in zeolite cavities, where water molecules locate and have different bonds with zeolite carcass.

The experience in zeolite processing [5, 8] is summarized in Table 1 in terms of separation techniques applied.
As the associating minerals are mainly feldspars and micas, the other mineral species are of subordinate value, so it is reasonable to apply electromagnetic separation, electrostatic processing and heavy-media separation.

Given that mineral complexes contain zeolite of less than 50 µm, then the electrostatic separation should be conducted with the use of heating-electrization by salicylic and benzoic acids vapor, therewith ferruginous impurities are removed by electromagnetic separation. The integrated flowsheet with electromagnetic and electrostatic separation circuits enables to cut down appreciably associated mineral content and to upgrade zeolite content up to 80–90%.

Table 1. Basic zeolite processing techniques in terms of mineral composition of the feed.

| Target mineral      | Dominating mineral associates | Mineral processing techniques                                      |
|---------------------|-------------------------------|------------------------------------------------------------------|
| Zeolite, chabazite  | Feldspars, micas, > 50 µm     | Crushing in rotor mills and grinding in ball mills                |
|                     |                               | Ultrasonic treatment                                             |
|                     |                               | Magnetic separation at a separator with constant magnet system or |
|                     |                               | at electromagnetic separator with isodynamic field              |
|                     |                               | Electrostatic separation                                         |
|                     |                               | Ultrasonic treatment                                             |
|                     |                               | Magnetic separation                                              |
|                     | Clayey minerals < 50 µm       | Electrostatic separation with heating–electrization              |
|                     |                               | Crushing in rotor crushers, grinding in ball mills                |
|                     | Quarts minerals, clayey       | Ultrasonic treatment                                             |
|                     | minerals                      | Electrostatic separation                                         |

Selection and arrangement of processing flowsheets for zeolite-bearing rocks should be performed first of all considering fractional composition of raw materials, their physicochemical properties which characterize interrelation between separation attributes of host minerals and valuable content in the primary feed.

Methodology for development and selection of technological flowsheets for zeolite-bearing rocks and arrangement of the machinery for their realization is based on the use of optimality criteria: safety, maximum recovery of a valuable component and rational utilization of mineral resources.

It is reasonable to state that the object-oriented modification of mineral properties is ranked as a promptly advancing field of zeolite rock processing industry with a perfect opportunity to develop innovative techniques and ecologically safe approaches to processing of non-traditional raw mineral materials exhibiting close separation properties in view that available processes are not efficient so far. In terms of the problems to be solved the surface and near-surface strata of the mineral or even mineral volume are subjected to structural and chemical modifications resulting in a better contrast ratio and a gradient of properties or one of minerals undergo fundamental phase transformation. Selective transformation of surface properties permits to intensify dressability of raw mineral materials by using conventional classical processing techniques: magnetic, electrical separation, flotation, and gravity separation [5, 6, 8].

3. Conclusions
1. It is established that the most efficient processing of Eastern Transbaikalia zeolite-bearing rocks are magnetic and electrostatic separation in combination with target-oriented effects on raw mineral materials.
2. The target-oriented modification of physicochemical characteristics makes it possible to develop techniques to process a zeolite-bearing material distinguished for a low contrast ratio in properties to be separated, provided that performance of traditional techniques is not sufficient from the economic point of view.
3. The main principles realized in innovative technologies concerning modification of zeolite-bearing materials rest on introduction of operations which permit to produce zeolite products meeting the
consumer’s requirements: mechanical-and-chemical (mechanodeformation) processes including ultrasonic pretreatment before screening, deep removal of ferruginous impurities, electrostatic separation to remove non-magnetic impurities, high-power electromagnetic pulse effects.

Acknowledgements
The study was supported in the framework of the Basic Research Program, Project No AAAA-A17-117092750073-6.

References
[1] Coombs DC 1971 Present status of zeolites facies Molecular Sieve zeolites. J. Amer Chem. Soc. Wash DC pp 317–327
[2] Mikhailov AS, Distanov UG 1999 Mineral Raw Materials Zeolites: Reference Book Moscow: ZAO Geoinformmark (in Russian)
[3] Pavlenko YuV 2000 Zeolite Deposits of the Eastern Transbaikalia Chita: ChitGU (in Russian)
[4] Pavlenko YuV 1986 Natural Zeolites Are New Mineral Raw Materials for Large-Scale Use. Prospects of the Chita Region, Problems and Immediate Tasks: Review Chita: Chita TsNTI (in Russian)
[5] Khatkova AN 2006 Mineralogical and Technological Assessment of Zeolite-bearing Rocks of the Eastern Transbaikalia Chita: ChitGU (in Russian)
[6] Chelishchev NF, Berenshtein BG, and Volodin VF 1987 Zeolites–A New Type of Mineral Raw Materials Moscow: Nedra (in Russian)
[7] Chelishchev NF Ion-Exchange Properties of Natural High-Silicon Zeolites Moscow: Nauka (in Russian)
[8] Yusupov TS 1985 Methods of Concentration and Isolation of Zeolites from Rocks Methods for Diagnosis and Quantification of the Content of Zeolites in Mountain Rocks Novosibirsk: I GiG SO RAN SSSR pp 161–168 (in Russian)
[9] Yusupov TS and Koroleva SM 1995 Influence of mechanical activation on quartz depression during flotation Physico-Technical Problems of Mining No 6 pp 92–95
[10] Chanturia VA, Bunin IZh, Ivanova TA, and Khatkova AN 2004 Influence of powerful electromagnetic impulse actions on technological properties of zeolite-containing rocks GIAB No 10 pp 311–314
[11] Revnivtsev VI 1980 Enrichment of Feldspar Moscow: Nedra (in Russian)