Genesis and structure of natural zeolites and clay rocks

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DOI: https://doi.org/10.52340/building.2026.73.01.11

Abstract This paper presents the potential for the use of natural minerals, such as clay shales, bentonite clays, and zeolites, common in Georgia in modern construction. This paper provides their chemical and structural composition. Their use significantly reduces prime cost of concrete and plays an important role in the sustainable use of country's natural resources.

Keywords: zeolite, bentonite clay, clay shale, argillite, clinoptilolite, kaolinite, montmorillonite, thermal modification, microsilica.

Introduction

One of the ways to realize the concept of new generation concretes is to modify them with more advanced technological materials. These can be mixed compositions of traditional additives and new synthetic products. An example of this is complex modifiers characterized by high technological and technical efficiency. The mineral part of modifiers consists of microsilica, or a mixture of it and fly ash, while the organic component is represented by new generation superplasticizers. However, it should be noted that imported microsilica is expensive and increases the cost of one cubic meter of concrete by approximately GEL 70. Natural resources available in Georgia allow us to achieve results similar to those we would obtain using expensive microsilica through thermal processing. Minerals discussed in the article that are widespread in Georgia, can be used for this very purpose.

Figure 1. Clay shale

Figure 2. Argillite

Main Part

Natural zeolites are crystalline hydrated aluminosilicates; their skeletal crystal structure contains voids occupied by freely moving ions and water molecules. They are characterized by their ability to undergo molecular sieving and can actively participate in ion-exchange reactions.

The term "zeolite" is derived from the Greek words "zeo" meaning boiling and "lith" meaning stone. That is, "boiling stone". The mineral got this name because when heated to high temperatures, it loses water and creating the appearance of boiling.

Swedish mineralogist Axel F. Cronstedt was the first to discover zeolite in 1756 . Within a few years, dozens of different species were discovered and their crystal structures were determined. Natural zeolites are primarily of volcanic and volcanic-sedimentary origin

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Figure 3. Zeolitic tuff

The first type of zeolites is collected from basalts or monoclinic rocks. Such zeolites are not of great practical interest. The first report on zeolites of volcanic-sedimentary origin appeared in 1928. However, it attracted special attention of scientists relatively late. Currently, 43 types of natural zeolites are known. Due to their large reserves, these types of zeolites are mainly used for practical purposes.

The presence of zeolite minerals in the territory of Georgia has been noted since the 19th century. In this respect, the first zeolite mineral was heulandite, which in 1844 was found by Wilhelm Karl Haidinger in eocene volcanogenic rocks of Akhaltsikhe region. In the sedimentary and volcanogenic-sedimentary series of Georgia, zeolites such as analcime, laumontite, phillipsite, heulandite, clinoptilolite, and mordenite are very often found as rock-forming minerals, while authigenic minerals include halloysite, montmorillonite, calcite, and silica impurities.

The basic, or primary, building blocks of the zeolite framework are SiO_4 with Si and Al atoms. They are tetrahedrally coordinated to the oxygen atoms, which are located at the vertices of the tetrahedron.

In crystalline zeolites, the primary units are interconnected in such a way that they mainly form a three-dimensional framework, although a distinction is usually made between two-dimensional (lamellar) and one-dimensional (fibrous) zeolites.

Idealized chemical formula of zeolites is as follows:

$$Me_{x/n}[AI_xSi_yO_{2(x+y)}]\ z\ H_2O$$

Where Me = Na, K, Ca, Mg, Ba

n is the oxidation state of metal;

x is the number of monovalent cations and AI atoms;

Y is the number of silicon atoms;

Y/X determines the silicate modulus (Si/AI ratio);

z is the number of water molecules [8].

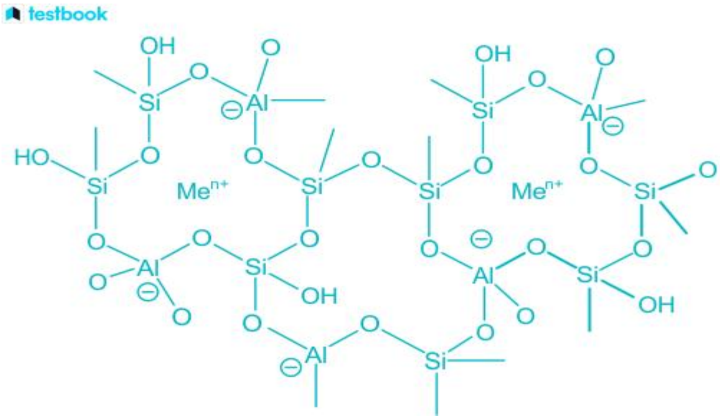


Figure. Structural pattern of zeolites.

The microporous system of zeolites—the cavities and through channels - contains water molecules and metal cations, as well as ammonium, hydroxonium and other multivalent ions, which are introduced into the zeolites through cation exchange. The micropore volume of zeolites accounts for 25–50% of its total volume.

More than 15 types of natural zeolites have been discovered in Georgia, with total reserves exceeding 300 million tons. Of these, six minerals—clinoptilolite, heulandite, mordenite, analcime, phillipsite and laumontite —are of industrial significance due to their large reserves and high quality. Therefore, the study of these minerals, their properties and subsequent practical application are priority development objectives for our country.

Minerals of the heulandite-clinoptilolite series are the most common zeolites in nature. Extensive deposits of clinoptilolite, developed in many countries around the world, its interesting properties and variety of applications have led to interest in this mineral and its intensive study. The composition of the idealized unit cell of clinoptilolite is expressed by the following formula;

$$\mathbf{Na_6[(AlO_2)6(SiO_2)30]\ 24\ H_2O}$$

The parameters of the monoclinic unit cell depend very little on the chemical composition of clinoptilolite:

$$a = 1.77 \text{ nm};\ b = 1.79 \text{ nm};\ c = 0.74 \text{ nm},\ \beta = 116^0$$

Crystal structure of clinoptilolite consists of sheets of tetrahedrons arranged in mirror planes that are connected to each other by oxygen atoms. Thickness of sheets is 0.9 nm and the lattice formed by them contains three channels A, B, C. Channels A and B are parallel to the "c" axis and contain 10- and 8-membered rings, respectively. The third channel C is parallel to the "a" axis and consists of 8-membered rings. Compensating cations are located in the channels, bound to oxygen atoms, and surrounded by water molecules. Cations and water molecules can be replaced or displaced by other cations or molecules without altering or disrupting the silica skeleton. Effective pore diameter of clinoptilolite is 0.35–0.454 nm.

However, in addition to these pores, like other natural zeolites, clinoptilolite has mesopores, the diameter of which can be four nanometers or more.

Bentonite clays

As a result of studies of chemical-mineralogical and physico-chemical properties of clays, it was revealed that they are mainly sedimentary mixtures of various porous minerals of very complex and unstable composition. Clays are natural aluminosilicates, the general formula of which is as follows:

$$\mathbf{Al_2O_3 \cdot nSiO_2 \cdot mH_2O,}$$

Where the molecular ratio of Al_2O_3/SiO_2 is in the range from 1:2 to 1:5.

Thus, clays provide polymineral systems consisting of several clay minerals and other impurities. Clays consisting of pure monominerals are rare. The clay type is determined by the predominance of clays over other clay minerals in its composition, whether kaolinite, montmorillonite, or others. Among clay minerals, bentonite clays are more important due to their diverse and valuable properties, which determine their application.

This clay was first discovered in America, on

Mount Benton, from which it was named. In nature, bentonite clays form the largest clay deposits of industrial value.

Many millions of years ago, the territory of Georgia was characterized by intense volcanic activity, as a result of which we obtained many significant deposits of bentonite clay. Trachyandesite clays are considered to be primary rocks that, through prolonged physical and chemical influences, transformed into bentonite clays.

Among the bentonite clays of Georgia, the Gumbrini and Askan deposits stand out due to their high quality and special properties, and they are of industrial significance.

The specific properties of bentonites are determined by the structure of clay minerals, among which the following should be noted: montmorillonite – $\mathbf{Al_2O_3 \cdot 4SiO_2 \cdot nH_2O}$, saponite – $\mathbf{Al_2O_3[MgO]4SiO_2 \cdot nH_2O}$, nontronite – $\mathbf{Al_2O_3[Fe_2O_3]\ 4SiO_2 \cdot nH_2O}$, beidellite – $\mathbf{Al_2O_3 \cdot 3SiO_2 \cdot nH_2O}$ and others. The water content varies in the range of 4-8 molecules. Since the main component of clay is montmorillonite, bentonite clays are also called montmorillonites, and the minerals they contain belong to the montmorillonite group.

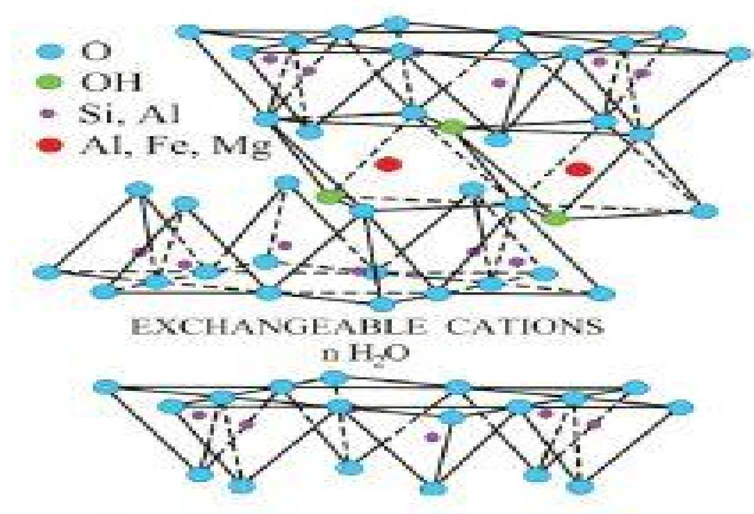


Figure 4. Structural pattern of bentonite clay

Mineral's structural framework, unlike kaolinite, consists primarily of two structural elements and, like karst, comprises three layers. One structural element consists of two outer tetrahedral silica lattices with silicon atoms at the center. The silicon tetrahedrons are arranged in an infinitely repeating hexagonal lattice.

The second structural element of the montmorillonite skeleton consists of closely spaced oxygen or hydroxyl groups, between which lie octahedrally coordinated aluminum atoms. The aluminum-oxygen octahedral lattice is located between two layers of silicon-oxygen tetrahedra.

Two tetrahedral and one octahedral lattices form a large continuous layer oriented in the direction of the a and b axes.

Since water molecules and cations are located on the edge side of silicon dioxide tetrahedra, the distance in the direction of the c-axis varies from 9,6 A^0 to 30 A^0. In some cases, it coincides with the material distance between the layers.

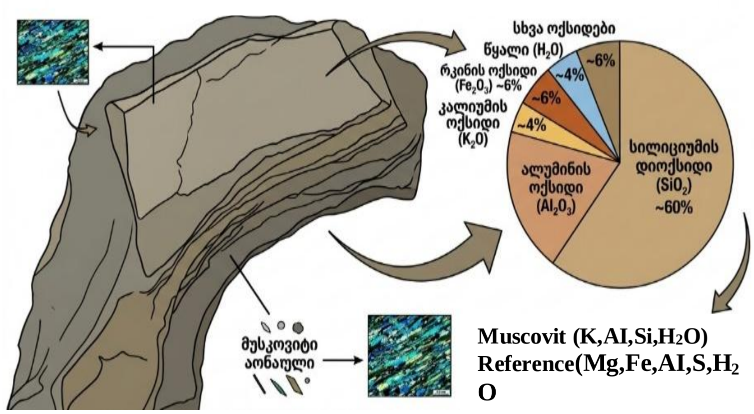
Clay shales

Clay shales are mainly blackish-grey metamorphosed fine-grained rocks with a slate-like texture and dense structure with a porosity amounting 1-3%.

Figure 4. Meta-argillite

Clay shales are not monominerals. They are composed of various minerals, such as clays (kaolinite, montmorillonite), hydrokarsts, quartz, feldspars, sericite, chlorite and sometimes contain carbonaceous substances and carbonates.

Chemical analysis of clay shale



Muscovit (K,AI,Si,H_2O)
Reference(Mg,Fe,AI,S,H_2 O

Muscovite anisotropic

Other oxides
Water (H_2O)
Iron oxide ($Fe_2O_{3)}$ -6%
Potassium oxide (K_2O)
Aluminium oxide (Al_2O_3)

Silicon dioxide (SiO^2) ~ 60%

Figure 5. Chemical analysis of clay shale

Georgia is a country rich in clay shales. The clay shales are found on the southern slopes of the Caucasus Range in Kakheti, Imereti, Racha, Svaneti and Abkhazia regions.
The area of application of clay shales mainly includes construction, where it is used as a building material, and more recently in cement production technology, for the production of porous fillers and lightweight products.

Figure 6. Clay shale roofing

Conclusion

Thermal modification of these minerals and subsequent fine grinding allows for the production of a mineral additive with a microsilica effect, enabling the production of concrete with high performance properties.

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