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РЕСПУБЛИКИ КАЗАХСТАН

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OF THE REPUBLIC OF KAZAKHSTAN

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MAIN PROPERTIES OF ZEOLITES AND THEIR MULTIPURPOSE APPLICATION

Abstract. The study of the geological system of zeolite deposits in recent years in developed countries is becoming more profound, since zeolites are significant in a broad sense mineral objects. The scientific research in this field is carried out in many countries of the world, especially in European countries. Over the past century, the use of zeolites has been expanding more and more. This is explained by the valuable mineral composition and various chemical properties of zeolites. When carrying out geological studies on this project, zeolite deposits Birlik, Kainarbulak, Kainar will be thoroughly studied and the original origin in all areas of geology is revealed. In addition, laboratory work will be carried out with the appropriate kinds of analyzes required for studying the composition and properties of zeolites.

Key words: zeolite, minerals, geological system, chemical properties, purification, fertility.

After the discovery of catalytic properties of zeolites in the late 50's, intensive studies of their structure, properties and methods of production began. In nature, zeolites are formed as a result of hydrothermal synthesis. Effective ways of enriching the rocks do not exist, therefore in practice only rich deposits of zeolites are used.

Natural zeolites refer to the first group of natural materials on thermo-and acid-fastness (i.e. highly resistant). Zeolites have good regenerative abilities, withstand high temperatures (up to 600 ° C), are resistant to aggressive environment without visible traces of destruction. Zeolites are not toxic, no mutagenic actions have been detected, and the use of zeolites has no limitations in all areas of the economy.

Chemical composition of zeolite: $(Na, K)_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 8H_2O$. The total cationic capacity is 87 mg-equ/100 g of rock, the ion exchange capacity is 2.5 mg-equ/g. There is an adsorption capacity for H₂O (water), methanol, CO₂ (carbon dioxide), O₂ (oxygen), SO₂ (sulphurous gas), H₂S (hydrogen sulfide), NH₃ (ammonia), N₂ (nitrogen), large organic molecules (table 1).

Table 1 – Chemical composition of zeolite

| | | | |
|--------------------------------|-------------|-------------------|-----------|
| SiO | 69,0-74,0 % | CaO | 1,7-3,3 % |
| TiO | 0,08-0,16 % | MgO | 0,4-1,7 % |
| Al ₂ O ₃ | 11,4-14,0 % | K ₂ O | 4,0-5,5 % |
| Fe ₂ O ₃ | 0,60-1,8 % | Na ₂ O | 0,4-0,9 % |
| MnO | 0,02-0,05 | H ₂ O | до 10 % |

On an industrial scale, synthetic zeolites are mainly used. Although more than 30 natural zeolites are known, only 8 of them (analcime, chabasite, clinoptilolite, erionite, ferrierite, lomontite, mordenite and phillipsite), found mainly in sedimentary rocks, can be of industrial importance. Difficulties are associated with exploration, study and development of deposits [1]. In general, the world wide potential supply of zeolites suitable for use is sufficiently large (Figure 1).



Figure 1 – Application of zeolites in various industries

The level of modern industrial production of synthetic zeolites reaches several hundred thousand tons per year and is mainly determined by the needs of the petrochemical industry, where synthetic zeolites of some structural types find wide application as catalysts or their carriers. Also zeolites are widely used for drying, cleaning and separation of substances, as well as ion exchangers. The effectiveness of using Zeolite perfectly aerates the soil, promotes the development of the root system, the growth of the entire plant; keeps in the root zone a sufficient amount of water – 40-70% of its weight, works as a storage tank for fertilizers - nitrate, phosphates, potassium, nutrients, the most important components for plant health and its growth. Zeolite captures fertilizers in its branched structure, until the roots of the plants find them. Nitrogen, detained in Zeolite, is insoluble in water and is not washed out by rain for a long period of time. Zeolite saves fertilizer. Less fertilizers, especially nitrogen, fertilizers are washed into groundwater. It increases fertilization by 20-40%. Without the use of Zeolite, about 35% of the nitrogen is washed out of the root zone and enters groundwater and pollutes it with nitrates and nitrites.

The use of Zeolite can give positive results in almost all types of soil and according to some data it can increase the yield of many crops - potatoes, barley, winter wheat, clover, maize, etc. by 10-30%. After the application of Zeolite, increased yields can be observed for 3- 4 years and more. According to some researchers, even after 7 years from the introduction of zeolite into the soil, its adsorption and cation-exchange functions did not change. In plant cultivation, Zeolite is extremely useful because of the stimulation of crop yields. When zeolite is introduced into substrates in organic mineral mixtures of the earth, the quality of the soil will improve by the majority of its parameters.

The results of numerous studies conducted in more than 20 scientific and research institutions in Ukraine show that the introduction of 4-10 tons / ha of zeolite fraction of 0-1 mm against a background of full mineral and organic fertilizer provides an increase in the yield of the main agricultural crops, reduces the consumption of nitrogen fertilizers (Table 2). Due to adsorption of gaseous and water-soluble nitrogen compounds, the coefficient of their use increases by 20-25%. Simultaneously, when zeolite is introduced in the calcareous soils, the content of exchangeable potassium increases by 20-45%.

Table 2 – Efficacy of using zeolites as a fertilizer

| Crop | Dose t/ha | Efficiency of application | |
|---------------------------------|-----------|---------------------------|--|
| | | Yield increase | Other indicators |
| Cereal crops wheat barley | 4-10 | 10% 20% | The duration of the action is 4-5 years, the improvement of the nitrogen nutrition regime, the reduction of heavy metals, radionuclides. |
| Potato | 4-10 | 32% | Decrease in the content of nitrates, heavy metals, radionuclides, decrease in nitrogen washability by 5 times. |

The effective use of zeolite in the feed of agricultural poultry was unmatched. The use of natural zeolites in poultry farming began with the replacement of gravel chips, traditionally used in poultry feeding as a physiological and mechanical factor. However, as it turned out, zeolite crumb helps to accelerate the growth rate of broiler chickens in comparison with ordinary gravel. Now a lot of experience has been acquired on the use of zeolites in poultry feeding, as evidenced by a number of methodological and practical recommendations. In the wild nature (established on the basis of research and observations), chicken (grouse, hazel grouse), inhabiting the area of zeolite deposits, gastroliths prefer this mineral in selection. In addition to mechanical functions, gastroliths also participate in the chemical processes of digestion.

On the basis of available data, it can be said that the use of zeolite additives in feeding all types of agricultural poultry, in amounts of 3 to 6% of the composition of feed increases the body weight, reduces the cost of feed, protein and exchange energy per 1 kg of growth by 3-19%, and in adult poultry increases the incubatory quality of eggs and the strength of the shell (Table 3). As in ruminants and other animal species, the chemical composition of the carcass meat of the control and experimental groups was practically the same.

Table 3 – Change in live weight of experimental chickens

| Groups | At the beginning of the experiment | After 7 days | At the end of the experiment |
|-------------------------------|------------------------------------|-------------------------------|-------------------------------|
| Average weight of one chicken | Average weight of one chicken | Average weight of one chicken | Average weight of one chicken |
| year | /% | year/ | % |
| I | 553,7 /100,0 | 681,3 /123,0 | 795,6 /147,7 |
| II | 540,7 /100,0 | 672,3 /124,0 | 778,0 /143,0 |
| III | 559,7 /100,0 | 684,3 /126,6 | 796,0 /143,0 |
| IV | 556,5 /100,0 | 680,7 /122,3 | 789,3 /141,2 |

In addition to the use of zeolites as a mineral additive in rations of farm animals and poultry, as well as the use in the production of mixed fodders and premixes, the use of natural zeolites as a mineral hygienic litter and deodorant for livestock and poultry houses is highly effective.

Natural Zeolite eliminates unpleasant odor due to enhanced adsorption and the ability to ion exchange. In addition, Zeolite adsorbs water well and is used as an excellent desiccant.

When applying Zeolite on the floor of poultry houses in the amount of 150-200 g per m², the unpleasant odor disappears within 15 minutes. The systematic application of this amount of Zeolite with an interval of 2-3 days is sufficient for almost complete deodorization of air.

Adding 200 g of Zeolite to 1 kg of chicken manure completely destroys the unpleasant odor, while the time that is required to reduce the humidity of the litter to 25% when dried in the sun is reduced to two days, whereas without zeolite, it takes 4 days.

The use of Zeolite provides a litter with a large content of fine particles, which increases its value when used as fertilizer.

At the same time, zeolites themselves are interesting objects for scientific research: they are porous bodies characterized by a specific skeleton structure and regular pore geometry (intracrystalline cavities and channels). An important feature of zeolites is the possibility of varying the chemical composition of crystals and the geometric parameters (shapes and sizes) of intracrystalline pores, i.e., the possibility of their structural and chemical modification, which can be carried out either by varying the conditions for

direct zeolite synthesis, or by changing the chemical composition of zeolite crystals of one and the same structural type. Due to the comparative ease of chemical modification of zeolites, there are ample opportunities for implementing controlled changes in the structure and properties of crystals. This circumstance makes zeolites very convenient objects for studying adsorption equilibria, the nature of adsorption interactions, the mechanism and kinetics of catalytic reactions, molecular sieve effects and diffusion of molecules in thin pores of controlled sizes.

When considering the chemical and catalytic properties of zeolites, a phenomenological description is often enough, but one can really understand these phenomena only by studying in detail the crystalline structure of zeolites.

Due to the complexity of the physical properties of the zeolites, it is difficult to give an accurate definition. Therefore, one of the authors [2] suggests to call zeolites as "aluminosilicates with a framework structure in which there are cavities occupied by large ions and water molecules, both of which are characterized by considerable mobility, which provides the possibility of ion exchange and reversible dehydration." The frame structure is constructed from tetrahedrons connected by peaks, in which small atoms (called as T-atoms) lie in the centers of tetrahedra while oxygen atoms at their vertices. The positions of T in natural zeolites are predominantly occupied by Al and Si atoms, but in synthetic zeolites they can be replaced by Ga, Ge, and P atoms close in nature. The role of large ions in the cavities of natural zeolites is performed by single- and double-charged cations as Na, Ca, K, Mg and Ba, the content of which depends on the geochemical composition of the mineral formation environment and the distribution of elements between the crystallizing minerals. Under laboratory conditions, a wide range of other cations can be introduced into the zeolite by ion exchange or direct synthesis. The general formula for zeolite is $M_pD_q [Al_p + 2qSi_rO_{2p} + 4q + 2r] ChsH_2O$. Since each vertex belongs to two tetrahedra, the oxygen atoms in the framework must be twice as large as the T-atoms. For the charge to be compensated, the number of triple-charged Al ions should be equal to the sum of p (the number of singly charged cations) and 2q (twice number of doubly charged cationions).

In addition, A. S. Shakora was engaged in studies of the properties of cement-zeolitic, ash-zeolitic and cement-ash-zeolite compositions for use in mortars, heavy and light concretes, non-autoclaved cellular aerated concrete, and overburden zeolitic rocks in the production of ceramic products. In his experimental work, the rocks were crushed in a ball mill to the fineness of grinding, characterized by a residue on a No. 008 sieve in an amount of 15 ... 20%. Then, compositions were made with the addition of zeolites from 10 to 40; (on the weight of cement and cement-ash binder) with a gradation of 5%.

As a result, it has been found that the addition of zeolite additives of 10 ... 15% makes it possible to reduce cement consumption and use an astringent optimum ratio in mortars and heavy concretes of class B15 ... B10 [3-4]. Samples were made from non-autoclaved aerated concrete of grades D500 ... D700, in which the siliceous component was completely replaced by ground zeolite-containing tuff, and cement-ash and cement-ash-zeolite compositions were used as a binder.

From overburden zeolite-containing rocks, a brick of grade 150 and expanded clay gravel with a bulk density of 400–600 kg/m³ was obtained.

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ЦЕОЛИТТЕРДІҢ НЕГІЗГІ ҚАСИЕТТЕРІ МЕН ОЛАРДЫҢ ӘРТҮРЛІ САЛАДА ҚОЛДАНЫЛУЫ

Аннотация. Цеолитті кенорындарының геологиялық жүйесін зерттеу соңғы жылдары дамыған елдерде тереңдетіліп зерделеуде, себебі цеолиттер кең мағынада аса маңызды минералды нысандар болып табылады. Бұл салада орындалатын ғылыми зерттеулер әлем бойынша көптеген елдерде орын алып жатыр, әсіресе Еуропа мемлекеттерінде. Соңғы жүзжылдықта цеолиттерді пайдалану салалары кеңінен таралуда. Бұл жағдай цеолиттердің бағалы минералды құрамымен және әртүрлі химиялық қасиеттерімен түсіндіріледі. Бұл жұмыс бойынша жүргізілген геологиялық зерттеулердің нәтижесінде Бірлік, Қайнарбұлақ, Қайнар цеолитті кенорындары алынған және геология бағытында олардың алғашқы түзілу үдерістері аталып кеткен. Сонымен қатар цеолиттердің құрамы мен қасиеттері бойынша бірқатар зертханалық жұмыстар сәйкесінше анализдер де жүргізілген.

Түйін сөздер: цеолит, минералдар, геологиялық жүйе, химиялық қасиеттер, тазалау, құнарлық.

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ОСНОВНЫЕ СВОЙСТВА ЦЕОЛИТОВ И ИХ МНОГОФУНКЦИОНАЛЬНОЕ ПРИМЕНЕНИЕ

Аннотация. Изучение геологической системы цеолитовых месторождений в последние годы в развитых странах становится все более глубоким, так как, цеолиты являются значимыми в широком смысле минеральными объектами. Осуществляемые научные исследования в этой области проводятся во многих странах мира, особенно в Европейских. За последнее столетие сферы использования цеолитов все больше и больше расширяются. Объясняется это ценным минеральным составом и различными химическими свойствами цеолитов. При проведении геологических исследований по данной работе всесторонне изучены цеолитовые месторождения Бирлик, Кайнарбулак, Кайнар и раскрыто изначальное происхождение по всем направлениям геологии. Проведены лабораторные работы с соответствующими видами анализов требуемых для изучения состава и свойств цеолитов.

Ключевые слова: цеолит, минералы, геологическая система, химические свойства, очистка, плодородие.

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