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PHYSICO-CHEMICAL STUDIES OF NATURAL ZEOLITE OF NAKHCHIVAN

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(Presented by Academician of ANAS A.M.Aliyev)

The studeid of physico-chemical properties of natural zeolite of Nakhchivan. On the basis of the data IR-spectroscopic, X-ray diffraction, elemental and derivatographic methods analysis it was found which group of zeolites include natural sample, its composition, the thermal stability, impact ion exchange on the thermal stability, the region of dehydration. The structure of zeolites defines an interior volume, that becomes available after dehydration. The dehydrated zeolite is a crystalline body, riddled with micropores. In the dehydrated state zeolites exhibit its maximum adsorption, molecular sieve and catalytic properties. The ion exchange capacity of zeolites - one of the main parameters that characterize their sorption and technological properties. Ion exchange on zeolites is possible to isolate ions, removing another method which is often of great complexity.

Keywords: *mordenite, zeolite, a natural minerale, X-ray diffraction analysis, IR-spectrum, thermal stability, ion exchange, dehydration field*

Knowledge of physical and chemical properties of natural zeolites it allows pre-set area of their application.

The zeolite sample was taken from the field Goydzheler, where its content is in the range 75 - 80%. From the comparison data diffractometry and chemical analysis with the published information on the structures of aluminosilicates-zeolites [1-3], we can conclude that the investigated by us belong to the natural zeolite to the class of zeolites mordenite.

We investigated a sample of natural zeolite Nakhchivan is characterized by the following chemical composition:SiO_2 - 65,70%, Al_2O_3 - 15,89%, Fe_2O_3 - 1,30%, CaO – 5,08%, MgO – 0,50%, TiO_2 – 0,05%, MnO – 0,07%, K_2O – 3,8%, Na_2O – 1,1%, P_2O_5 – 0,08%, H_2O – 7,5%; Σ 101,07.

The empirical formula of the mineral (according to the chemical composition)in the form:

$$Ca_2Na_2K_{2,8}Al_{8,8}Si_{39,2}O_{96}\cdot 34H_2O$$

It was calculated silicate module-SiO_2/Al_2O_3 the natural sample. According to calculations, it found that silicate module of natural zeolite Nakhchivan is 7, which is in good agreement with literature data silicate module of natural mordenite [4, 5].

To determine the degree of crystallinity of the natural sample is measured intensity of light flux which is proportional to the maximum value of transmittance the sample of zeolite in the 400-1200 cm^{-1}, measured intensity of the radiation is proportional to the minimum value of the transmittance of sample absorption bands of 776.24 cm^{-1} and determine the value of the optical density D_1.

The goal is achieved by additional measuring the intensity of flux proportional to the maximum value of transmittance of the sample in the 463.23 cm^{-1} and 1058.13 cm^{-1}, measured intensity of flux is proportional to the minimum value of transmittance of sample in the 797.53 cm^{-1} and determine magnitude optical densities D_1 and D_2 relative values of intensities of fluxes are proportional to the maximum and minimum transmittance.

According to the calculations of Nakhchivan zeolite it has high crystallinity, which varies between 85 - 93%.

Nakhchivan mordenite was investigated by X-ray diffraction (Fig. 1, Table 1), IR-spectroscopy (Fig. 2), thermogravimetric (Fig. 3) and elemental (Table 2) methods analysis.

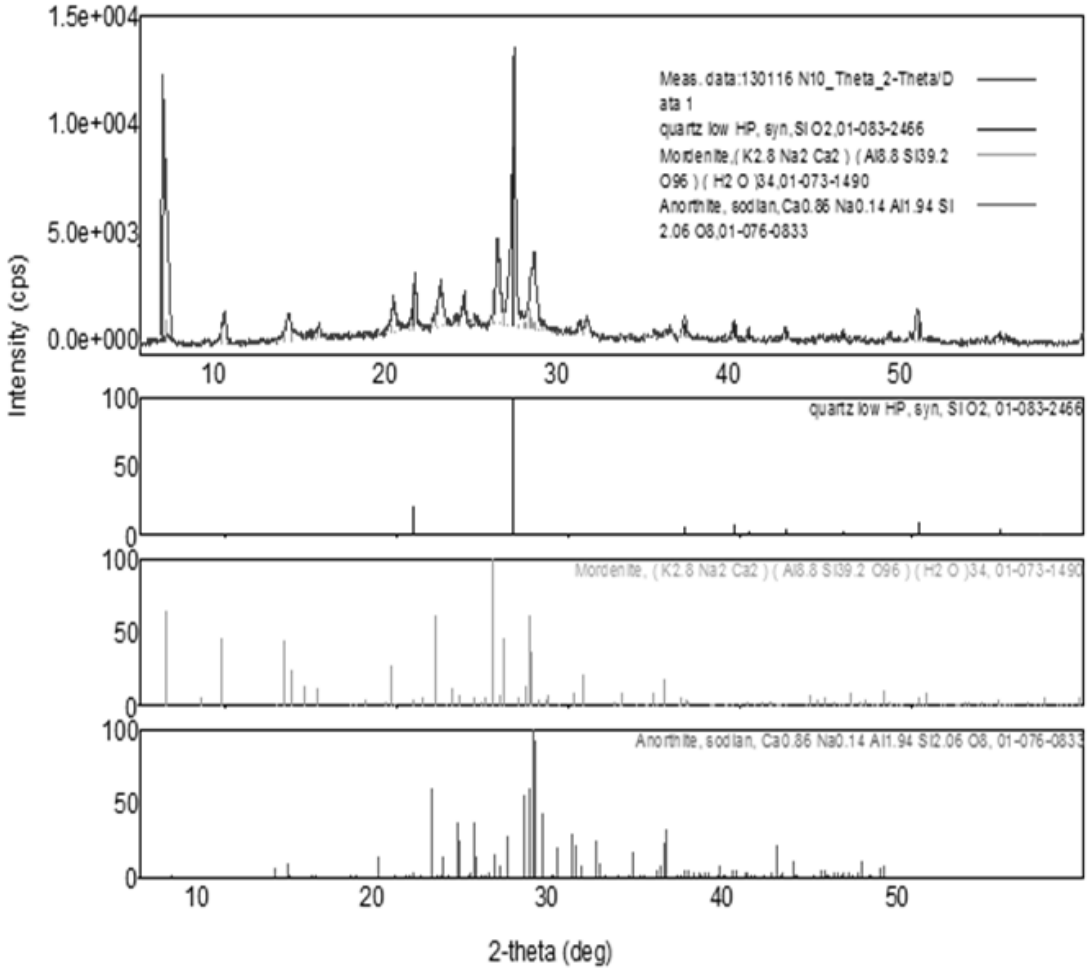

Fig. 1.The diffractogram of the sample of natural zeolite

Table 1

The results of X-ray diffraction carried out

The name of thesubstance	Formula	I/Ic DB	S-Q
Mordenite	$(K_{2,8}Na_2Ca_2)$ $(Al_{8,8}Si_{39,2}O_{96})\cdot(H_2O)_{34}$	0,900	78,5 %
Quartz	SiO_2	3,410	19,5 %
Anorthite	$Ca_{0,85}Na_{0,14}Al_{1,94}Si_{2,06}O_{8,01}$	3,670	2,00 %

Crystal system	Space group	a	b	c	Z	The unit cell volume, $Å^3$	Density, g/cm^3
Orthorhombic	Cmc21 (36)	18,094	20,516	7,524	1	2793,03	2,213
Hexagonal	P3221 (154)	4,91344		5,405	3	113,01	2,660

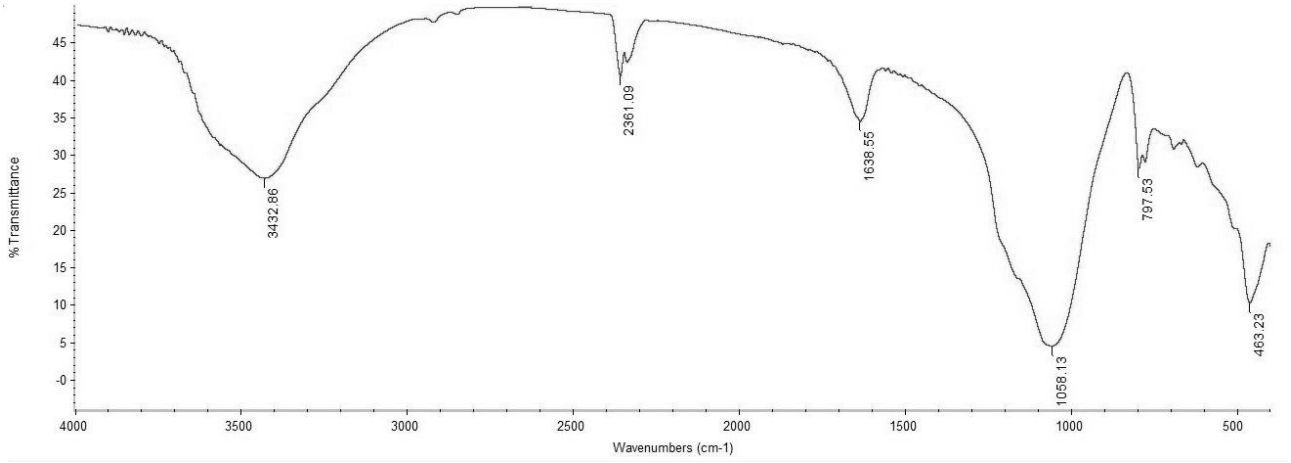

Fig. 2. IR-spectrum of the sample of natural zeolite

When compared the X-ray experimental data with published information, it determined that the sample under investigation is high silica zeolite - mordenite. Highs interference of phase characteristic of mordenite correspond to the bragg angle 2θ = 6,5; 9.8; 13.5; 14; 19.5; 22; 25.5; 26; 27; 28, etc.

Identification of phases in the sample confirmed, that the composition of the sample included 78.5% mordenite phase, 19.5% quartz and 2.00% anorthite phase.

Anorthite refers to a group of minerals feldspar (plagioclase). In terms of composition refers to aluminosilicates frame structure.

The relative intensity and the interatomic distances obtained experimentally correspond to the literature data (within experimental error), indicating, that the main phase of the sample is mordenite. The values of the interatomic distances (d) and the diffraction line intensities (İ), equal to d = 3,34Å (100), 2,45Å (30), 2,28Å (201) and 2,12 Å (20), suggest that in the composition of the sample is present of silicon dioxide, i.e. α-quartz. According diffractogram in the composition of the sample is also present of anorthite in small amounts.

According to the X-ray data of the natural sample crystallizes in orthorhombic crystal system with unit cell parameters a = 18,094 Å; b = 20,516 Å; c = 7,524 Å.

IR-spectrum of Nakhchivan zeolite is given in Figure 2.

The absorption bands in the frequency range 250−1400 cm^{-1} correspond to the major fluctuations in silico tetrahedral framework structure of zeolites.

Flaningen [6] investigated the absorption bands of various zeolite structure. The observed absorption bands are allocated to two types of vibrations:

1 –fluctuations, characterizing the primary structural units - TO_4, where T - cations Si^{4+}, $A1^{3+}$;

2 - fluctuations TO_4-tetrahedra on foreign relations.

Fluctuations in the first group is not sensitive to changes in the framework structure. The second type of fluctuations it depends on the nature of the articulation tetrahedral in secondary structural units and the features of the cavities of zeolites [7].

The first type are anti-symmetric, symmetrical and deformation fluctuation of T - O bonds in the region 1250-950, 720-650, 500-420 cm^{-1}.

The second type are anti-symmetric, symmetric fluctuations of external relations and the fluctuations of double chains in the region 1150-1050, 820-750, 650-500 cm^{-1}.

The most intense absorption band observed at 1058.13 cm^{-1} and responds the fluctuations of bonds Si - O - Si.

Zeolites have an absorption band in the 550-560 cm^{-1} related to fluctuations tetrahedra

on foreign affairs [SiO_4] and [AlO_4] frame, due to the presence of dual four-, five- and six-membered rings and defining a zeolite structure. The absorption band of 797.53 cm^{-1} related to the stretching vibrations of the Al - O, and 463.23 cm^{-1} - with deformation vibrations of Al - O_4.

With the presence of the zeolite bound water absorption bands in the range 3100-3700 cm^{-1}, 1638.55 cm^{-1}– band of deformation vibrations of water molecules. Increasing the intensity of these fluctuations indicates higher content of zeolite in the rock. Absorption band in the range 2100 - 2500 cm^{-1} due to the presence of calcium and sodium carbonates.

The absence of the absorption band of 960 cm^{-1}, it shows the high crystallinity and the adsence in the composition of the zeolite of amorphous phase.

The absence of the absorption band of 3720-3740 cm^{-1} corresponding to the amorphous SiO_2, also indicates a high crystallinity and phase purity ofthe samples.

It will be appreciated that the exact frequency, where absorbs a particular group depends on the environment of this group and its physical condition.

The method of thermographic analysis is set of region dehydration, water content and thermal stability of the natural zeolite. Curves DTA (differential thermal analysis) and TG (thermal gravimetric analysis) are shown in Figure 3.

The DTA curve of natural zeolite is characterized by two endothermic and one exothermic effects. Dehydration mordenite occurs in two stages and in a wide temperature range of 120 - 650^0C. At all these stages the loss in weight is 11.14%. The first endothermic effect, characterized by a maximum 185^0C corresponds to the care of the water molecules in the cavities are structures. The second endothermic effect corresponds to the care of crystal water from the structure. Complete dehydration of the sample of natural zeolite ends at a temperature of 615^0C.

As shown by X-ray diffraction analysis of the natural zeolite structure is stable up to 960^0C temperature, i.e. zeolite Nakhchivan is stable at high temperatures. When the temperature rises above 960^0C, as shown by X-ray diffraction analysis of the natural zeolite structure is destroyed and the diffraction pattern a represent intensity of anorthite and quartz.

The elemental composition of the sample of natural zeolite is presented in Table 2.

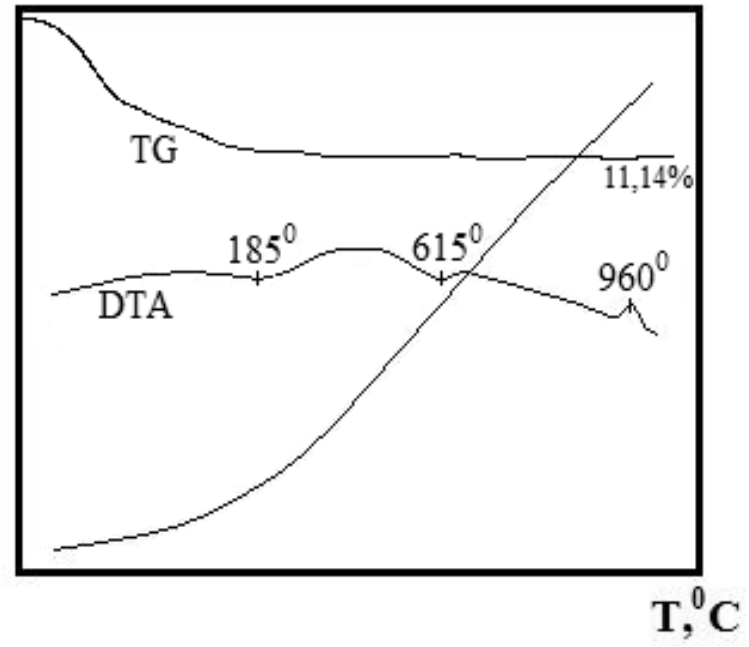

Fig. 3. DTA and TG curve of Nakhchivan zeolite

Table 2

The percentage of oxides and elements in the natural zeolite

Element	Weight %	Atomic %	Amount of oxides %	Formula
Na	0,42	0,37	0,56	Na_2O
Mg	0,38	0,32	0,63	MgO
Al	4,49	3,38	8,48	Al_2O_3
Si	40,53	29,33	86,71	SiO_2
K	0,75	0,39	0,90	K_2O
Ca	1,14	0,58	1,59	CaO
Fe	0,87	0,32	1,12	FeO
O	51,42	65,32		
Result	100,00			

Ion exchange of the original cations - sodium, potassiumand calcium performed cations of magnesium, strontium, cadmium, zinc and nickel. It was found that the values of the degrees of exchange cations K^+ (α_K), contained in the original zeoliteon cations Mg, Ni, Co, Zn, Cd is considerably lower than the values of the degree of exchange of the cations Na^+ (α_{Na}) at the same cations. It has been found that the natural zeolite and its cation-exchanged forms are characterized by its interplanar spacings almost identical, but differ from each other by the relative intensities of the diffraction lines. This indicates that the cationic part of substituted natural zeolite and its cation-exchanged forms is different, which greatly affects the intensity is the diffraction lines (Fig. 3). It is known, that changes in the relative intensities of the diffraction lines (I/I_0) is directly related to the nature of (the ionic radius, the ion charge, the atomic scattering factor - number) cations [8-10].

Ion exchange influences the thermal stability of zeolites. As seen in Figure 3, the initial sample dehydration occurs in the temperature range 150-650^{0}C. The structure maintained until 960^{0}C. After ion exchange dehydration occurs in the temperature range 180-600^{0}Cand structure remains of 1000^{0}C.

Conclusion

From the above it can be concluded that the natural sample Nakhchivan relates to high-silica zeolites – mordenite. Besides by mordenite apart composed of natural sample present quartz and mineral – anorthite. Nakhchivan zeolites is resistant to high temperatures (960^{0}C), after dehydration of the sample structure is preserved. Ion exchange has a positive effect on the thermal stability of the zeolite, i.e. the temperature stability is increased (1000^{0}C), complete dehydration occurs at a lower temperature.

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TƏBİİ NAXÇIVAN SEOLİTİNİN FİZİKİ-KİMYƏVİ TƏDQİQİ

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Məqalədə təbii Naxçıvan seolitinin fiziki-kimyəvi xassələri öyrənilmişdir. İQ-spektroskopiya, rentgen difraksiya, element və derivatoqrafik analiz metodlarının əsasında müəyyən olunmuşdur ki, Naxçıvan seoliti mordenit qrupuna aiddir. Nümunənin tərkibində zərərli komponentlər müşahidə olunmur. Mordenitdən əlavə təbii nümunənin tərkibində kvars və anortit mövcuddur. Təbii seolit yüksək temperatura davamlıdır (960^0C). Dehidratlaşma geniş temperatur intervalında ($120\text{-}650^0$C) baş verir. Seolitlərin ion-mübadilə tutumu onların sorbsiya və texnoloji xassələrini xarakterizə edən əsas parametrlərdən biridir. Müəyyən olunmuşdur ki, ion-mübadilədən sonra Naxçıvan seolitinin termiki davamlılığı 1000^0C-yə qədər artır.

Açar sözlər: *mordenit, seolit, təbii mineral, rentgenfaza analizi, İQ-spektr, termiki davamlılıq, ion-mübadilə, dehidratlaşma sahəsi*

ФИЗИКО-ХИМИЧЕСКИЕ ИССЛЕДОВАНИЯ ПРИРОДНОГО ЦЕОЛИТА НАХЧЫВАНА

Г.А.Мамедова, Н.А.Мамедова

В статье изучены физико-химические свойства природного цеолита Нахчывана. На основании данных ИК-спектроскопии, рентгеновской дифракции, элементного и дериватографического методов анализа установлено, что цеолит Нахчывана относится к морденитовой группе.В составе образца нет вредных компонентов. Помимо морденита в состав природного образца входит кварц и анортит. Природный цеолит устойчив к высоким температурам (960^0C). Дегидратация происходит в широком температурном интервале $120 - 650^0$C. Ионообменная емкость цеолитов – один из основных параметров, характеризующих их сорбционные и технологические свойства. Установлено, что после ионного обмена термическая устойчивость цеолита Нахчывана увеличивается до 1000^0C.

Ключевые слова: *морденит, цеолит, природный минерал, рентгенофазовый анализ, ИК-спектр, термическая устойчивость, ионный обмен, область дегидратации*