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GEOCHEMICAL FEATURES OF ADSORPTION OF TRITIUM FROM WATER SOLUTIONS BY CLINOPTILOLITE

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To study the mechanism of tritium extraction from aqueous solutions of the zeolite, two similar in composition closed stationary experimental systems based on clinoptilolite from the Sokirnytsky deposit (Ukraine) were created. In the first experiment, unchanged natural clinoptilolite was used; in the second, the mineral was thermally treated at 110 °C. The duration of the experiments was about 10 months. Measurements of the specific activity of tritium in the aqueous residue and in the mineral medium made it possible to determine the redistribution of tritium between the solid and liquid phases, as well as between the various structural positions in clinoptilolite. The adsorbed moisture present in the mineral during the interaction of the mineral and aqueous phases initially leads to a partial decrease in the concentration of the tritium indicator in the "HTO". In the future, this moisture provides the possibility of transit penetration of HTO molecules into clinoptilolite channels due to diffuse molecular exchange of HTO ↔ H_2O between the water and mineral phases. Heat treatment reduces the possibility of partial dilution of tritiated water, which interacts with the mineral. Thermal activation of adsorption centers in the mineral mass provides more efficient removal of tritium from the aqueous phase. After heat treatment, the pore space and the surface of the mineral particles are freed from the adsorbed water present in the mineral, and their surface is thermally activated. This leads to a relatively more intensive surface adsorption, where up to 68.5% of tritium absorbed by the mineral accumulates. The interaction of tritiated water with thermally activated surface of mineral particles was accompanied by dynamic adsorption-desorption processes, electrokinetic phenomena in the surface electric layer, which caused the fractionation of hydrogen isotopes with a coefficient $\alpha = 1.17$. The presence in a heat-treated clinoptilolite of the partial filling of the coordination spheres of alkaline cations, which is similar to the original mineral, made it possible to fractionate hydrogen isotopes in the mineral channels with a coefficient $\alpha = 1.16$. The heat treatment of clinoptilolite changed the ratio of hydrogen isotopes to hydroxyl groups, where the fractionation coefficient α increased accordingly to 1.06.

Keywords: *clinoptilolite, mineral adsorbent, tritium, tritiated water, thermal processing, fractionation of hydrogen isotopes.*

1. Introduction

One of the aspects of nuclear power engineering is the production of techno-geneal tritium, a radioactive isotope of hydrogen. By its chemical properties, tritium is identical to the main isotope of hydrogen - protium. Its main part (about 90%) is in the form of HTO molecules in connection with which, all the processes of migration of tritium are determined, first of all, by its aqueous form. It is partially absorbed by the geological environment of the aeration zone, but mainly enters surface water bodies and underground aquifers. Partially, the aqueous form of tritium is present in the gaseous state in an atmosphere where it is transformed into an organic substance.

The development of nuclear energy prompts the European community to pay more attention to the radioactive isotope of hydrogen. While discharges of most radio nuclides from nuclear facilities are reduced as a result of the application of new techniques for inoculating sewage, tritium discharges are increased through the use of new regimes for the use of nuclear fuel. In addition, there are problems associated with the lack of acceptable methods of detritization of industrial wastewater. The adoption at the level of the European Commission of a special research program "Cross-cutting support to improved knowledge on tritium management in fission and fusion facilities" indicates the extreme need for research to prevent the entry of tritium into the biosphere [10].

Previously, we carried out research on the feasibility of using mineral adsorbents to extract tritium from aqueous solutions [14; 13; 7.]. It was shown that the interaction with clay minerals in tritiated water decreases the concentration of tritium. Among mineral adsorbents an important place is occupied also by zeolites belonging to the group of framework silicates. A unique feature of these minerals is the presence of ion-exchange properties. Zeolites are very widely used in the purification of various industrial effluents. At the same time, there are no studies concerning the possibility of using zeolites to extract tritium from aqueous solutions, and the contribution of zeolites to the mechanisms of tritium extraction from aqueous solutions has not previously been studied. To solve this problem, a series of experiments was performed, the results of which are set forth in the following article.

2.Materials and methods.

2.1 Materials.

Zeolite used in the experiments presented by clinoptilolite (Sokyrnytsky deposit, Ukraine). Mineral refers to the class of microporous framework sodium potassium aluminosilicate. Clinoptilolite crystal lattice consists of rings stacked tetrahedras SiO_4 and AlO_4 (Fig. 1).

Mineral belongs to the class of microporous framework silicates. The rings form a main crystal structure of silicon and aluminum ratio greater than 4: 1. The dominant exchangeable cations in the clinoptilolite are Na^+ and K^+ [*1;2*; *15*]. In the structure of clinoptilolite there are three types of channels that form a two-dimensional system. Channels of the first type with a window size of 4.0-5.6 nm are located parallel to the ***a*** axis in 8-membered rings. Channels of the second type with a window size of 4.4-7.2 nm run parallel to the ***c*** axis in 10-membered rings. Channels of the third type with a window size of 4.1-4.7 nm are oriented at an angle of 50 ° to the axis ***a*** in 8-membered rings. On the walls of the channels are placed exchangeable cations with which coordinated water molecules that are in the clinoptilolite's channels. Sorption capacity of the mineral can be up to 10-15% of its weight. Crystal-chemical mineral properties are shown in Table 1.

Table 1. Crystal-chemical properties of clinoptilolite [1]
Табл. 1. Кристалохімічні властивості кліноптилоліту.

Empirical formula	$(NaK)_4\ CaAl_6\ Si_{30}\ O_{72} \times 24H_2O$
Cell dimensions	a = 1,769 nm, b = 1,798 nm, c = 0,742 nm
The size of the windows (holes) channels in the crystal lattice	0,4 nm
Ion-exchange capacity	1,5 mg-eq×g^{-1}
Sponginess	44%
Density	2,37 kg/m^3
Specific surface	50 – 65 m^2/g

Ion exchange and adsorption properties of the clinoptilolite depend on the composition of the exchange complex and the Si / Al-ratio. Number of exchange cations in the clinoptilolite (Sokyrnytsky field, Ukraine), which can be coordinated with water molecules are the number of aluminum atoms that are in tetrahedron frame. The residual charge value of unit frame formula [10], which makes possible interfacial proton exchange, is from -0.03 to -0.38. [1; 2].

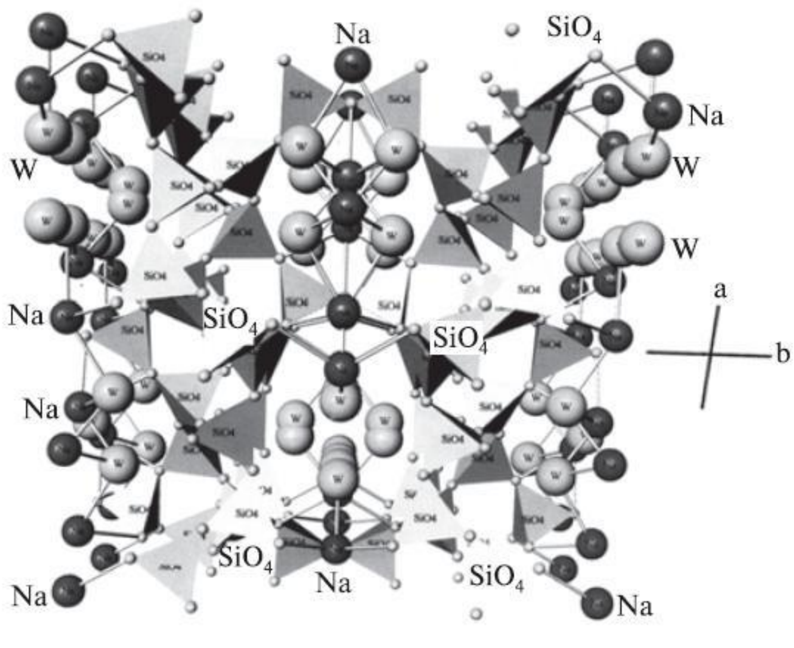

Fig. 1 Projection of the clinoptilolite structure on the ab plane. Dark blue circles show the position of Na cations in the channels of the structure, surrounded by water molecules W.

Рис.1 Проекція структури кліноптилоліту на площину ab. Показано положення катіонів Na в каналах структури, в оточенні молекул води W.

The parameters of the unit cell of clinoptilolite depend directly on its chemical composition. Due to the inherent Si/Al ratio mineral, the configuration of the channels is somewhat distorted-

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[1] "О природных цеолитах Закарпатья Сокирницкого месторождения и возможностях их использования" //ГП "Сокирницкий цеолитовый завод" МЧС Украины.— Препр. — 8 с.

stretched in the direction of the ***a*** axis and compressed in the direction of the ***b*** axis, that is, the channels have an elliptical shape in the cut (Figure 1).

To create experimental systems clinoptilolite was crushed to fine-grained condition, with a particle size of less than 0.25 mm and a dry density of 1.197 g/cm^3.

2.2. Methods

The balance estimate reallocation tritium between aqueous and ceolite adsorbent was determined in a closed water-mineral system. For this, the mineral mass placed in glass containers was filled with tritiated water and tightly closed.

It should be noted, that mineral in air-dry condition is located the surface-adsorbed moisture, therefore in the early stages of tritium water interaction with zeolite there is a partial dilution. To determine the effect of surface-adsorbed water on the adsorption quality of the zeolite was created two identical types of experimental systems: using the original minerals and thermally treated at 110°C. The duration of the experiments was: to not dried mineral 311 days and 237 days for pre-dried clinoptilolite. For the experiment in closed systems established regime tritium - protium equilibrium interphase exchange.

Getting the balance estimates distribution of tritium between mineral and liquid phases ensured secrecy and stationary experimental systems. Under these conditions, all tritium was closed in the experimental system. The dimensions of specific activity of tritium in the water residue and mineral medium made possible to determine interfacial reallocation of tritium.

Additionally, distribution of tritium between different structural positions zeolite was researched. For this, after the experiment executed the allocation of mineral water phase fractions fixed temperature ranges (110ºC, 250-300ºC and 700-800ºC) according to the data of reference [3].

The essence of this method is the use of sealed metal containers and heating device with a controlled heating mode fixed mineral masses before and after the experiment (Fig. 2). With this device, it was determined the moisture content in different structural positions of the mineral before and after contact with tritiated water.

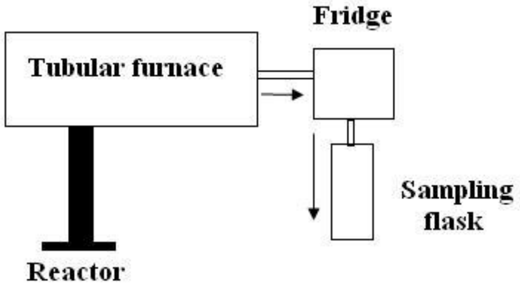

Figure 2. The flowchart thermographic equipment for removing moisture from mineral batches.

Рис. 2. Блок-схема устаткування для термогравиметричного видалення вологи з мінеральних наважок.

Samples of residual tritiated water and isolated aqueous fractions after purification of organic impurities (oxidation added to the solution of $K_2Cr_2O_7$) and distillation were mixed with scintillator HiSife 3 Wallac in the ratio 8:12. The content of tritium in this way prepared emulsions was determined in a liquid scintillation β - spectrometer Quantulus 1220 (LKW Wallac) with an accuracy of measuring not more than 5%.

3. The experimental results and discussion

3.1. Interphase reallocation of tritium.

Surface adsorbed water in the zeolite is weakly bound, kept its molecules on the surface of mineral particles due to the forces of intermolecular interaction with surface atoms of the mineral particles. This energy weakly bound water is removed from the mineral, according to differential thermal analysis (DTA) at a temperature of 110°C (Table 2).

Table 2. The content of surface-adsorbed water in the air-dry zeolite.
Табл 2. Вміст поверхнево-адсорбованної води у повітряно-сухому цеоліті.

Mineral	Temperature heating, °C	Weight before heat treatment, g	Weight after heating, g	Weight reduction, %
Clinoptilolite	110	100	93,1	6,9

Surface adsorbed moisture which contents in the zeolite is 6,9% (Table 2) provides transit HTO molecules in the channel space and further molecular HTO → H_2O exchange. However, the presence of adsorbed surface moisture making adjustments to the process of protium - tritium exchange. At the initial stage of the process starting surface adsorbed water reduces the specific activity of tritium in tritiated water due to its dilution in accordance to the expression (1).

$$D = W_0 / (Ws + W_0), \qquad (1)$$

where: D - dilution coefficient, W_0 - initial volume of tritiated water in the closed water - mineral system, ml, Ws - amount of surface adsorbed water in the mineral mass, ml.

According to the above expression values of the indicator degree of dilution tritiated water (D) in the original zeolite is 0.977, which reflects the degree of influence of pore and surface adsorbed water on the processes of isotope-hydrogen exchange.

Reducing the specific activity of tritium in the "HTO" during its interaction with the mineral phase results the accumulation of tritium in the adsorbent. For quantitative assessment effectiveness of this process it is advisable to use such parameter as the specific stock of tritium per unit of mineral mass. In the closed experimental systems, this value is calculated as the difference between the stock of tritium in tritiated water before and after its interaction with clinoptilolite, divided by the mass of adsorbent (2):

$$Q_m = (Q_w - Q_f) / m \qquad (2)$$

where: Q_m - specific stock of tritium in weight clinoptilolite, Bq×g^{-1}; Q_w and Q_f - stock of tritium in the "HTO" before and after the experiment, Bq, *m* - mass of adsorbent, g.

The indicator of the tritium specific stock allows calculating the adsorption capacity for various masses of mineral adsorbent in case it is used as a reacting substance for the purification of industrial discharges contaminated with tritium. At the same time, in such calculations there arises the need to take into account also the fact that the specific activity of tritium in "HTO" and its volumes that will be purified by clinoptilolitic adsorbent may be different. Therefore, in order to obtain an estimate of the relative efficiency of tritium extraction from a solution of "HTO" independent of these parameters, used of a tritium accumulation factor in the K_{ac} adsorbent, calculated in accordance with expression (3):

$$K_{ac} = Q_m * Q_w^{-1} * 100\% \qquad (3)$$

where: Q_m - stock of tritium in a mineral adsorbent, Bq, Q_w – stock of tritium in the volume of filtered «HTO», Bq.

Table 3. Indicators value for experimental systems C-1 and C-2.
Табл 3. Значення показників для експериментальних систем С-1 та С-2.

System	Specific stock of tritium in weight clinoptilolite, Bq×g^{-1}	Coefficient of accumulation of tritium in adsorbent, K_{ac}, %
C-1	4.03	43
C-2	6.9	30

Experimental data suggest the following. The adsorbed moisture in the clinoptilolite performs two functions. At the beginning of the interaction of «HTO» mineral mass with adsorbed in the clinoptilolite protium water (H_2O) reduced specific activity of tritium in the water phase by dilution with a coefficient of 0.977 (Tabl. 3, system C-1). At the same time, due to molecular diffusion HTO↔ H_2O exchange between water and mineral phases, there was a transit penetration of molecules HTO in clinoptilolite channels, resulting to a somewhat greater accumulation of tritium in the adsorbent (Tabl. 3, K_{ac} = 43%). Removal of surface adsorbed water from the mineral by heat treatment made transit HTO molecules in the channels of the clinoptilolite more difficult and therefore less accumulation of tritium in the adsorbent (K_{ac} = 30%).

3.2. The distribution of tritium in the structure of the zeolite.

3.2.1 Initial clinoptilolite.

HTO molecules that are included in the clinoptilolite feeds interact with components of the mineral structure. Thus, in the different structural mineral positions formed different energy ties, to break which energy impact is required in the respective temperature ranges. Such structural positions correspond to certain moisture fractions that are removed from the mineral in a fixed temperature interval using special equipment, the principal scheme of which is shown in Figure 3. Distribution of tritium that was in the mineral feeds between different structural positions of the mineral was accompanied by isotopic - hydrogen fractionation. The extent of this process assessed using fractionation factor [5] according to the expression (4).

$$\alpha = \frac{T_m}{H_m} / \frac{T_w}{H_w} \qquad (4)$$

where: α - hydrogen isotope fractionation factor, T_m, H_m - concentration of tritium and protium atoms in the mineral mass, atom*ml^{-1}; T_w , H_w - the concentration of tritium and protium atoms in the "HTO" , atom*ml^{-1} after reaching equilibrium in the "mineral adsorbent – tritiated water."

An application of classic formula for the calculation of the hydrogen isotope fractionation demands some corrections. This is due to the fact that the concentration of protium and tritium in water of different experimental phases 14 orders. Therefore, the interaction of «HTO» and mineral adsorbent protium concentration varies on a very small amount, so the value Hm and Hw remain at 6.69 * 10^{22} atoms H*ml^{-1}. Given the above expression (4) was transformed into the expression (5):

$$\alpha = T_m * T_w^{-1} \qquad (5)$$

The specific activity of adsorbed moisture of the initial clinoptilolite does not exceed background values 5 Bg*dm^{-3} and for the beginning of the experiment all tritium in model systems was in the tritiated water. Redistribution of tritium in the system as a whole and in particular ceolite structure occurred in the process of interaction "HTO" and clinoptilolite adsorbent. To calculate the hydrogen isotope fractionation factor in the structure of the clinoptilolite during its interaction with tritiated water enough to take into account only the concentration of tritium in the mineral and "HTO" after establishing equilibrium between the water and the mineral phases, after the experiment (Table 4).

According to the given data, some clinoptilolite of tritium (18%) adsorbed on the surfaces of mineral particles (fraction 1, Table 4), but the largest amount delayed its channel space (fraction 2). This form of tritium is 73% of its total stock in the mineral. The entry of tritiated water in the channel space provides the opportunity to further cooperation HTO molecules with the structure of the clinoptilolite and create the most tightly bound to form OH groups, which may remove at 700°C (fraction 3).

Table 4. Distribution of T in the residual "HTO" and moisture fractions removed from the initial clinoptilolite after the completion of the experiment.

Табл. 4. Розподіл Т в залишковій «НТО» та фракціях вологи, видалених із вихідного кліноптилоліту після завершення експерименту.

The parameter	Residue «HTO»	Fractions removed from the zeolite			In general
		1	2	3	
Share of the tritium in the fraction (%)	-	18	73	9	100%
The specific number of atoms per unit of tritium volume in water	$8{,}8 \times 10^8$	$8{,}47 \times 10^8$	$9{,}24 \times 10^8$	$7{,}69 \times 10^8$	$8{,}93 \times 10^8$
Fractionation factor, α.	-	0,96	1,05	0,87	1,01

The results of the experiment revealed the real effect of the hydrogen isotopic fractionation, in a closed system "clinoptilolite – tritiated water" with the overall coefficient $\alpha = 1{,}07$. Getting heavier hydrogen isotope is fixed at the stage of adsorption of HTO molecules on the surface of mineral particles, where the rate of protium - tritium fractionation $\alpha = 1{,}01$ (Table 4).

The peculiarity of adsorption processes is their dynamic nature. Each adsorbed water molecule has a different strength bonds with the surface, which is determined by its delay adsorption surface, adsorption time τ [11] For physical adsorption, due to weak components of the surface energy, that time is very short and up to 10^{-13} seconds. Therefore, the value of adsorption, delayed particle surface, is kinetic factor which determines the ratio of adsorbed and desorbed molecules. The dynamic nature of adsorption - desorptiv processes create the conditions for the possibility of fractionating molecules with different molecular weight (HTO and H_2O) and priority detention on adsorption surface of mineral particles more inertial HTO molecules.

More meaningful was the fractionation of hydrogen isotopes in clinoptilolite channel structures ($\alpha = 1,\ 1$). Tritiated water molecules which penetrate into the channels of the mineral can linger for a while in them as a result of ellipsoid pores distortion. The possibility of this effect follows from the theory of the water existence not only as individual molecules, but also in water associates - clusters [15]. Under the proposed model to associate water molecules, hydrogen bonds in water continuously formed and broken. This process can lead to the formation in distorted ellipsoidal pores temporarily mineral molecules linked groups as defined by the authors as twinkle clusters. Prolonged time of water clusters in the channels of the mineral provides the ability to immobilize molecules HTO and ionic $T^+ \leftrightarrow H^+$ exchange between clinoptilolite and water molecules of tritium solution.

According to existing ideas in chemistry aqua complexes [4] full coordination sphere hydrated complexes of sodium and potassium in channels of clinoptilolite is respectively 6 and 7 coordination numbers. In air-dry in zeolites, as we identified (Table 2), are no more than 7% water. This leads to the formation of the state of instauration coordination areas of the alkali metals are immobilized on the walls of the zeolite channels (Fig. 7). Tritiated water inflow in the channels led to filling HTO molecules free bonds in the unsaturated coordination areas of the alkali metals and, consequently, prolonged immobilization tritium (Table 6).

On the surface of the zeolite channels as a result of substitutions Al^{3+} / Si^{4+} exists polyanionic skeleton [9].Water moving through channels in the form of clusters, faced with uncompensated electric double layer surface tetrahedrons of clinoptilolite, accompanied by dissociation of the molecules of HTO and the formation of covalent bonds such as H-O-Si. In addition, the negative charge of alumino-silicate surface conditioned equilibrium dissociation process in aqueous solutions of surface OH groups of the scheme «OH ↔ O^{-}---H^{+}». This led to compensation for defects and surface electrostatic charge crystalline framework by positive ions - protons and tritons (H^{+}, T^{+}). Then there was a stepwise isotope exchange between protium and tritium at the interfacial boundary surface OH - groups of zeolite and molecular water clusters (Fig. 8). This process led to the formation of a strong energy ties and consolidates tritium ions in the surface hydroxyl groups.

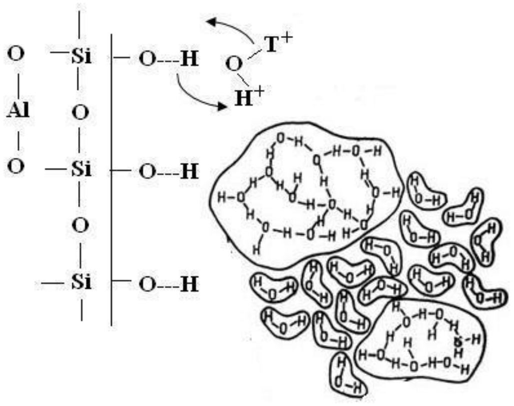

Fig. 8. Scheme ion T^{+}↔H^{+} exchange between clusters of molecules "HTO" and clinoptilolite channel surface.

Рис.8 Схема іонного T^{+}↔H^{+} обміну між кластерами молекул «НТО» та поверхнею каналу кліноптилоліту.

Thus, the presence in the original (unprocessed) clinoptilolite interstitial and adsorbed moisture on the initial stage of interaction the mineral adsorbent with tritiated water indication of partial dilution. Further molecular HTO began exchange with H_2O during the adsorption↔desorption processes on the surface of mineral particles. But the main contribution to the removal of tritium from water solution was provided processes taking place directly in the channels of the clinoptilolite. Molecules of HTO filled uncompensated focal areas of alkali metal cations, associated with structural walls of the channels in the clinoptilolite. Some tritium extracted from tritiated water is reinforced in the channels of the mineral by the ion triton → proton substitution. As a result, extracted from the «HTO» tritium was assigned largely in tightly bound forms.

3.2.1 Heat-treated clinoptilolite

The thermal treatment of the zeolite results in the removal of the pore and mineral mass surfactant adsorbed water. The surface of the mineral particles is activated and basal portions structures lose the associated polar water molecules but retain at this uncompensated charges on the surface. At the same time the mineral thermal treatment leads to increasing in the number of high-energy adsorption centers [8].

The process of molecular adsorption on interphase border "water - mineral particle" is accompanied by the formation of a boundary layer adsorption [6]. It usually develops within the electric double layer (EDL), which has the character of an electrical capacitor. Violations of electrical absorbent surfaces lead to the development in the EDL electrokinetic phenomena, the polarization and the attraction, close to the mineral particles of water molecules.

The interaction of tritium water with activated mineral particles was accompanied by dynamic adsorption↔desorption processes, as a result of electrokinetic phenomena in EDL, the manifestation of the effect of fractionation of hydrogen isotopes.

The quantitative characterization of the tritium distribution in the form of finding a different binding energy with the structure of clinoptilolite allocated from the mineral mass in the respective temperature ranges (fractions) given in Table 5.

Table 5. Distribution of T in the residual "HTO" and fractions removed from the heat-treated clinoptilolite after the completion of the experiment.
Табл. 5. Розподіл Т в залишковій «НТО» та фракціях, видалених із термічно-обробленого кліноптилоліту після завершення експерименту.

Parameter	Balance "HTO"	Fractions removed from the ceolite			Generally
		1	2	3	
Share of the tritium in the fraction (%)	-	68,5	24,8	6,7	100%
The specific number of atoms per unit volume of tritium in water (***T_w*** ,***T_m***), atom*ml^{-1}.	$2{,}36\times10^9$	$2{,}76\times10^9$	$2{,}74\times10^9$	$2{,}49\times10^9$	$2{,}74\times10^9$
Fractionation factor, α.	-	1,17	1,16	1,06	1,16

According to the given data in thermally processed clinoptilolite specific number of tritium atoms accumulated in its structure in order more than raw mineral (Tables 4, 5). The release of mineral mass of water molecules and the surface activated mineral particles led to more intense attraction and retention of HTO molecules due to adsorption↔desorption implementation processes dewatered substrate. Thus, in thermally processed clinoptilolite in interstitial and adsorbed form is up to 69% of tritium. At the same time electrokinetic phenomena in EDL caused fractionation of hydrogen isotopes with a coefficient α = 1,17 (Fraction 1, Table 5).

Relatively smaller amount of tritium delayed in channel space (fraction 2, Table 5). This form of tritium is relatively lower, ie up to 25% of its total stock in the mineral, but in absolute terms is higher than the untreated clinoptilolite (Tables 4, 5). Heating the mineral mass to 110°C does not lead to the removal of H_2O molecules from the coordination sphere of alkali cations in the clinoptilolite channels. Consequently, there was no increase in the absorptive capacity of the mineral structural position. However, the presence of a similar source with clinoptilolite incomplete occupancy coordination spheres alkali cations provided by the possibility of such hydrogen isotopes fractionation intensity by a factor $\alpha = 1{,}16$ (Fraction 2, Table 5).

Heat treatment of clinoptilolite does not changed ratio of hydrogen isotopes to hydroxyl groups where the fractionation factor $\alpha = 1{,}06$ (fraction 3, Table 5). Energy impact on the mineral mass during its heating to 110°C does not lead to the rupture of relations in the structural form of tritium finding.

Conclusions

The clinoptilolite of the Sokirnitsky deposit has the necessary properties for its use as an adsorbent of tritium from aqueous solutions and protection of the environment from tritium contamination. The complex of useful properties of clinoptilolite makes it possible to use it also for cleaning multicomponent industrial discharges containing tritium. Output thermally unprocessed clinoptilolite mainly delays absorbed from aqueous solutions of tritium in the channel structure of the mineral, that is, in a more energetically bound state than the surface adsorbed form. At the same time, capture of NTO molecules by coordination spheres of alkaline cations in the channel structures of clinoptilolite is accompanied by fractionation of hydrogen isotopes.

Thermal treatment of clinoptilolite at a temperature of 110 ° C led to the activation of the surface of mineral particles due to the conservation of uncompensated charges on such surfaces and an increase in the number of high-energy adsorption centers on these surfaces. When the thermally treated clinoptilolite interacts with tritiated water, the most intense is the capture of tritium from the aqueous solution in the adsorbed form as a result of dynamic adsorption-desorption processes. Simultaneously, the electrokinetic phenomena in the DEL on the surface of the mineral particles cause the fractionation of the hydrogen isotopes in this structural position of the mineral. The interests of tritium in the coordination spheres of alkaline cations in clinoptilolite canals occur according to a mechanism analogous to that inherent in a thermally untreated mineral. In general, thermal treatment of clinoptilolite leads to an increase in the specific number of tritium atoms in all structural positions of the mineral at close values of the fractionation factor of hydrogen isotopes.

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ГЕОХІМІЧНІ ОСОБЛИВОСТІ АДСОРБЦІЇ ТРИТІЮ З ВОДНИХ РОЗЧИНІВ КЛІНОПТИЛОЛІТОМ

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Для вивчення механізму екстракції тритію з водних розчинів цеолітом були створені дві аналогічні за складом закриті стаціонарні експериментальні системи на основі клиноптилоліту Сокирницького родовища (Україна). У першому експерименті використовували незмінений природний клиноптилоліт, у другому - мінерал термічно оброблений при 110 °С. Тривалість експериментів становила близько 10 місяців. Виміри питомої активності тритію у водному залишку і у мінеральному середовищі дозволили визначити перерозподіл тритію між твердою і рідкою фазами, а також між різними структурними позиціями в клиноптилоліті. Наявна у клиноптилоліті адсорбована волога при взаємодії мінеральної і водної фаз на початку призводить до часткового зменшення концентрації тритієвого індикатора в «НТО». Надалі ця волога забезпечує можливість транзитного проникнення молекул НТО в канали клиноптилоліту внаслідок дифузійного молекулярного обміну НТО ↔ H_2O між водною та мінеральною фазами. Термічна обробка знижує можливість часткового розбавлення тритійованої води, що взаємодіє з мінералом. Термічна активація адсорбційних центрів в мінеральній масі забезпечує більш ефективне вилучення тритієвого індикатора з водної фази. Після термічної обробки поровий простір і поверхня мінеральних частинок звільняються від наявної в мінералі адсорбованої води, а їх поверхня термічно активується. Це призводить до відносно більш інтенсивної поверхневої адсорбції, де накопичується до 68,5% поглинутого мінералом тритієвого індикатора. Взаємодія тритійованої води з термічно активованою поверхнею мінеральних частинок супроводжувалася динамічними адсорбційно-десорбціоними процесами, електрокінетичними явищами в поверхневому електричному шарі, які обумовили фракціонування ізотопів водню з коефіцієнтом α = 1,17. Наявність у термічно обробленому клиноптилоліті аналогічної з вихідним мінералом часткової заповненості координаційних сфер лужних катіонів забезпечило можливість фракціонування ізотопів водню в каналах мінералу з коефіцієнтом α = 1,16. Термічна обробка клиноптилоліту змінила співвідношення ізотопів водню і в гідроксильних групах, де відповідно збільшився коефіцієнт фракціонування α до 1,06.

***Ключові слова**: тритій, клиноптилоліт, мінеральний адсорбент, тритійована вода, термічна обробка, фракціонування, ізотопи водню.*

ГЕОХИМИЧЕСКИЕ ОСОБЕННОСТИ АДСОРБЦИИ ТРИТИЯ ИЗ ВОДНЫХ РОСТВОРОВ КЛИНОПТИЛОЛИТОМ

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Для изучения механизма экстракции трития из водных растворов цеолитом были созданы две аналогичные по составу закрытые стационарные экспериментальные системы на основе клиноптилолита Сокирницкого месторождения (Украина). В первом эксперименте использовали

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неизмененный природный клиноптилолит, во втором - минерал термически обработанный при 110 °С. Продолжительность экспериментов составляла около 10 месяцев. Измерения удельной активности трития в водном остатка и в минеральной среде позволили определить перераспределение трития между твердой и жидкой фазами, а также между различными структурными позициями в клиноптилолите. Имеющаяся в минерале адсорбированная влага при взаимодействии минеральной и водной фаз вначале приводит к частичному уменьшению концентрации тритиевого индикатора в «НТО». В дальнейшем эта влага обеспечивает возможность транзитного проникновения молекул НТО в каналы клиноптилолита вследствие диффузного молекулярного обмена НТО ↔ H_2O *между водной и минеральной фазами. Термическая обработка снижает возможность частичного разбавления тритиированной воды, которая взаимодействует с минералом. Термическая активация адсорбционных центров в минеральной массе обеспечивает более эффективное изъятие трития с водной фазы. После термической обработки поровое пространство и поверхность минеральных частиц освобождаются от имеющейся в минерале адсорбированной воды, а их поверхность термически активируется. Это приводит к относительно более интенсивной поверхностной адсорбции, где накапливается до 68,5% поглощенного минералом трития. Взаимодействие тритиированной воды с термически активированной поверхностью минеральных частиц сопровождалась динамичными адсорбционно-десорбционимы процессами, электрокинетическими явлениями в поверхностном электрическом слое, которые обусловили фракционирование изотопов водорода с коэффициентом* $\alpha=1,17$*. Наличие в термически обработанном клиноптилолите аналогичной с исходным минералом частичной заполненности координационных сфер щелочных катионов обеспечило возможность фракционирования изотопов водорода в каналах минерала с коэффициентом* $\alpha=1,16$*. Термическая обработка клиноптилолита изменила соотношение изотопов водорода и в гидроксильных группах, где соответственно увеличился коэффициент фракционирования* α *до 1,06.*

Ключевые слова: *тритий, клиноптилолит, минеральный адсорбент, тритиированная вода, термическая обработка, фракционирования, изотопы водорода.*