DOI https://doi.org/10.32782/geotech2022.35.04
UDC 54.05+54.058 +54.027+549.73

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DETRITIZATION OF AQUEOUS SOLUTIONS USING HIBSITE

Abstract. *An important task in protecting the environment from tritium pollution is to find effective, simple, affordable, low-cost and low-energy methods for extracting tritium from large volumes of low- and intermediate-level aqueous solutions. The article presents new data on the influence of the octahedral component of the structure of layered silicates on the extraction of tritium from aqueous solutions obtained using research on an experimental stationary system on the example of the natural mineral hibsite. The possibility of using hibsite as a natural adsorbent of tritium is considered. The degree of adsorption of tritium from an aqueous solution and the effect of fractionation of hydrogen isotopes in the stationary system "HTO-hibsite" were estimated. The mechanism of tritium retention in the structure of the natural adsorbent is explained. Tritium extracted from tritiated water is distributed in the mineral matter between different structural positions – with the lowest binding energy in the HTO molecular form in surface adsorbed moisture (1 fraction), with slightly higher – in -OT ionic form in the structural positions of the mineral adsorbent (2 and 3 factions). Up to 39% of the total amount of tritium extracted from the aqueous solution is retained in hibsite in a surface adsorbed form. The predominant retention of polarized HTO molecules, compared to H_2O molecules, near the mineral surface due to dynamic adsorption-desorption processes causes the effect of fractionation of hydrogen isotopes (α = 1.14). The exchange between the OH groups of the structural Al-hydroxyl layers of the mineral and the OT groups of tritiated water leads to the fixation of up to 55% of tritium in this form. New scientific results on the influence of structural and physicochemical properties of the studied mineral adsorbent on its ability to extract tritium from aqueous solutions and new data on the peculiarities of the mechanism of interfacial isotope-hydrogen exchange in a water-mineral system provide, together with the results of our previous studies, more effective development of methods for detritization of aqueous solutions.*

Key words: *tritium, hydrogen, heavy hydrogen isotopes, hibsite, adsorption, fractionation.*

Introduction.

According to IAEA estimates, with the growth of nuclear energy, the accumulation of tritium in the environment, especially in the surface hydrosphere, biosphere and groundwater, will increase. In conditions of insufficient protection of aquifers, a significant increase in the concentration of tritium in groundwater can occur due to infiltration from surface water basins in man-made accidents at nuclear power plants and in case of depressurization of radwaste storage facilities. During long-term storage of radwaste, tritium can be released from it, forming in the presence of condensing moisture tritium water "HTO". Volatile forms of tritium can diffuse through storage concrete, metals and polymeric materials [1] and thus enter the environment. The adoption of a special research program Euratom NFRP-14 "Cross-cutting support for improved knowledge on tritium management in fission and fusion facilities" by the European Commission indicates the urgent need for research to prevent the spread of tritium in natural and man-made biogeosystems. An important task in protecting the environment from tritium pollution is to find effective, simple, affordable, low-cost and low-energy methods for extracting tritium from aqueous solutions.

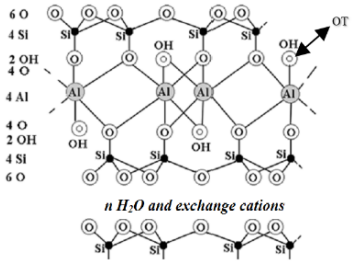


Fig. 1. Scheme of protium-tritium exchange in the structure of montmorillonite. [7]

Analysis of previous research

As our previous studies have shown, in HTO, which is filtered through clay rocks or composites formed on the basis of clay minerals, the specific activity of tritium is significantly reduced [9, 10, 12, 13]. It was also found that quite effective extractors of tritium from aqueous solutions are minerals from the class of phyllosilicates [5, 4, 11] which are based on two main structural compositions – tetrahedral silicon-oxygen and octahedral Al^{3+} (Mg^{2+}) – oxygen-hydroxyl network [14.]. The type of combination of these structural components determines the difference in the properties of different minerals of layered structure (може краще просто layered minerals).

Montmorillonite plays a special role among the minerals of layered structure. The mineral belongs to the group of layered silicates of structural type 2: 1, ie between two hexagonal grids of aluminum-silicon-oxygen tetrahedra is one octahedral aluminum-oxygen-hydroxyl mesh. Tetrahedra in a silicon-oxygen network are connected by the vertices of their bases into hexagonal rings. In an octahedral grid, octahedra are connected by their edges in such a way that their centers also form a hexagonal structure, and the hydroxyl groups occupy edge positions in the octahedral layer. It is believed [4, 5] that the octahedral layer provides the strongest retainment of tritium extracted from an aqueous solution in the structure of layered silicates (Fig. 1).

To confirm this position, an experimental study of the interaction of the natural mineral hibsite ($Al(OH)_3$), which can be considered as a natural analogue of the octahedral component of layered silicates, with tritiated water was performed.

The aim of the article is to determine the mechanism of tritium extraction from aqueous solution by the octahedral component of layered silicates on the example of the natural mineral hibsite.

Materials and methods

The main structural unit of hibsite is a layer of Al ions located between two layers of oxygen [3]. In the structure of hibsite, Al cations occupy only 2/3 of the octahedral positions, and the layers formed by Al-hydroxyl octahedra are placed in such a way that the lower oxygen atoms of one octahedral layer are placed directly above the upper oxygen atoms of another octahedral layer (Fig. 2).

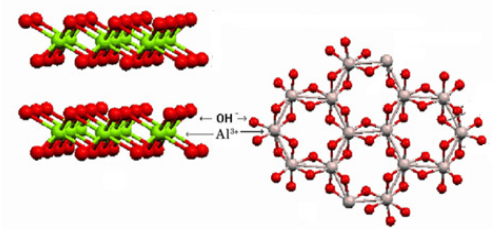


Fig. 2. Structure of hibsite [15]

One elementary cell of hibsite consists of two such layers, contains 8 Al-hydroxyl groups and has parameters along the axes "a" ≈ 8.64 Å, "b" ≈ 5.07 Å and "c" ≈ 9.72 Å.

It is believed that in contact with tritiated water, gibbon due to the large number of hydroxyl groups is able to effectively adsorb tritium from aqueous solution.

In order to identify and assess the degree of detritization of an aqueous solution, a model system with a mineral weight of 100 g and a volume of HTO of 300 dm^3 was created. To do this, the mineral mass, ground to a powder with a dry density of 1.08 g/cm^3 was placed in a glass vessel. Then it was filled with tritiated water and tightly closed (Fig. 3). The duration of the experiments was about 300 days.

Obtaining balance estimates of the distribution of tritium between the mineral and liquid phases was ensured by the closed and stationary experimental systems. The specific activity of tritium in the aqueous residue and in the mineral environment was determined. After decantation of the residual solution and weighing of the mineral substance, the moisture fractions corresponding to different structural positions in the studied mineral were isolated. Determination of tritium distribution between different structural positions of hibsite was performed using special equipment for separation of the moisture fractions from the mineral mass in the appropriate temperature ranges (Fig. 4).

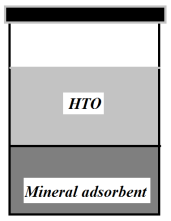


Fig. 3. Scheme of a stationary experimental system

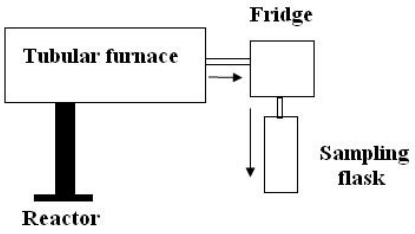


Fig. 4. Block diagram of equipment for thermogravimetric dehumidification from mineral samples.

The essence of this method is the use of sealed metal containers and a heating device with a controlled heating mode of fixed samples of mineral mass before and after the experiments.

At the end of the experiment, samples were taken from the moisture fractions extracted from the mineral sample. Then preparations were prepared for further measurement of the specific activity of tritium in them. Samples of residual solution and extracted moisture fractions were filtered and purified from organic impurities by oxidation by adding $K_2Cr_2O_7$ to the solution. After distillation, a portion of 8 ml samples was mixed with an 8:12 Hi Sife 3 Wallac scintillator. The content of tritium in the emulsions prepared in this way was determined using a liquid scintillation β-spectrometer Quantulus 1220 LKW Wallac (certificate of state metrological certification N 6961 of 17.11.2009). The relative measurement error was ± 5%.

Research results

The interaction of tritiated water with the mineral substance was accompanied by a decrease in the specific

Table 1. Decrease in specific activity of tritium in HTO in experimental systems

Adsorbent	Weight of mineral sample, g	Volume of HTO, dm^3	Specific activity of tritium in solution over mineral, $Bq \times dm^{-3}$		Reduction of specific activity of tritium in solution over mineral, %
			before the experiment	after the experiment	
Hibsite	100	300	2560	1568	38,7

activity of the HTO working solution and the accumulation of tritium in the mineral phase (table 1).

During the experiment, due to interfacial redistribution, tritium was extracted with hibsite, which led to a decrease in its specific activity in aqueous solution by 38.7%.

Tritium extracted from the aqueous solution was distributed between different structural positions in the mineral adsorbent. In this case, bonds of different energy are created. To break them, heating of the mineral substance is required. In the temperature range of 70 – 120°C, the removal of moisture adsorbed on the surface of mineral particles (1 fraction) is observed. According to Brindley and Nakahari [2], heating of hibsite to 140-200°C leads to partial loss of water with the formation of γ-Al_2O_3*H_2O+2H_2O. Further heating to 220-240°C causes its subsequent transformation into anhydrous alumina ($\gamma+\chi$)Al_2O_3+3H_2O (2 fraction of moisture). At a temperature over 300°C, final dehydration of the mineral (3 fractions of moisture) takes place.

Quantitative assessment of the distribution of tritium extracted from the HTO aqueous solution between different structural positions in the studied minerals was performed using the calculated indicator – the partition coefficient Kri (%), which is calculated according to the expression (1):

$$Kr_i = Qi \times Qm^{-1} \times 100 \quad (1)$$

where: Qm – tritium reserve in the mineral, Bq; Qi – the stock of tritium in the i-th fraction extracted within the corresponding temperature range, Bq.

In the distribution of tritium between different structural positions of minerals, manifestations of isotope-hydrogen fractionation were observed. Calculations of the fractionation coefficients of hydrogen isotopes during the interaction of tritiated water with a mineral adsorbent are performed according to the expression (2) [6]:

$$\alpha = T_m \times T_w^{-1} \quad (2)$$

where: α is the hydrogen isotope fractionation factor, Tm is the concentration of tritium atoms in the mineral mass, atom × ml^{-1}; Tw is the concentration of tritium atoms in the "HTO", atom × ml^{-1} after reaching the equilibrium state in the "mineral adsorbent – tritiated water" system.

The data obtained from the studies carried out in stationary systems made it possible to determine the patterns of tritium distribution between different structural positions of hibsite and to establish the presence of manifestations of the hydrogen isotope fractionation effect (Table 2, Fig. 5).

Part of the tritium extracted by hibsite from an aqueous solution is retained in the surface adsorbed form (Kri = 39.3, Table 2, Fig. 5, fraction 1) by the mechanism of molecular HTO → H_2O exchange. In this case, due to dynamic adsorption-desorption processes on the surface of mineral particles in the limiting layer, heavier HTO molecules are retained with a greater advantage than H_2O molecules. At the same time, the overwhelming retention of polarized HTO molecules at the surface of hibsite mineral particles causes the effect of hydrogen isotope fractionation (α = 1.14, fraction 1).

Table 2. Distribution of tritium between moisture fractions with different bond energies in the structure of hibisite

	Heating temperature, °C	Fraction volume, ml	Fraction specific activity, $Bq \times dm^{-3}$	Qi, Bq	Kr_i, %	Fractionation factor, α
1 fraction	120	10,8	1707	19,9	39,3	1,14
2 fraction	250	17,2	1491	27,7	54,7	0,99
3 fraction	700	27,95	100	3,0	6,0	0,07
Total:		55,95		50,5	100,0	

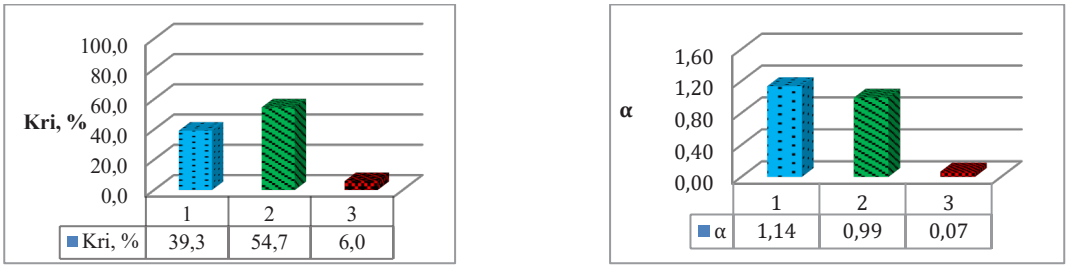


Fig. 5. Distribution of tritium between different structural positions of hibsite (Kr) and fractionation coefficients of hydrogen isotopes (α).

The presence of Al-hydroxyl layers in the hibsite structure determined the possibility of exchange between the OH groups of the mineral and the OT groups of tritiated water. As a result of this exchange, most of the tritium absorbed by the mineral from an aqueous solution was retained in the structural Al-hydroxyl layers of hibsite (Kri = 54.7, fraction 2). The removal of this form of tritium from the structure of gibbsite occurred in the temperature range of 140–240°C as a result of its transformation into anhydrous alumina $(\gamma+\chi)Al_2O_3+3H_2O$ (fraction 2) without the effect of fractionation ($\alpha = 0.99$).

The final and insignificant part of the tritium absorbed by hibsite (Kri = 6.0, fraction 3) is somewhat more strongly retained in its structure and is released from the mineral when it is completely dehydrated. In this form, the isotopic H↔T exchange between the mineral and the HTO solution does not occur.

The inclusion of gibbsite in experimental studies made it possible to obtain new data on the processes of tritium adsorption, which we observed in water-mineral systems during the interaction of clay minerals with tritiated water [7, 11, 12, 8]. It was also found that minerals of the phyllosilicate class are quite effective extractors of tritium from aqueous solutions [4, 5, 10, 13]. The possibility of using gibbsite as an adsorbent of tritium from aqueous solutions and the mechanism of accumulation of tritium in the structure of layered silicates, namely, in their octahedral component, were confirmed.

Conclusions

The use of stationary experimental water-mineral system confirmed the possibility of using hibsite as an adsorbent of tritium from aqueous solutions and provided new data to elucidate the mechanism of tritium accumulation in the structure of layered silicates, namely in their octahedral component.

When hibsite interacts with tritiated water in the stationary water-mineral system, the specific activity of tritiated water decreased due to the extraction of tritium by the mineral adsorbent from an aqueous solution. The ability of hibsite to extract tritium from an aqueous solution is 38.7%.

Up to 39% of tritium extracted from tritiated water (Kri = 39.3, fraction 1) is retained on the surface at the surface adsorbed form by the mechanism of molecular HTO → H_2O metabolism. Due to dynamic adsorption-desorption processes on the surface of mineral particles in the boundary layer, heavier HTO molecules are retained with a greater advantage than H_2O molecules, which causes the effect of fractionation of hydrogen isotopes $\alpha = 1.14$.

The presence of Al-hydroxyl layers in the structure of hibsite led to the possibility of exchange between the OH groups of the mineral and the OT groups of tritiated water. As a result of this exchange, most of the tritium absorbed by the mineral from the aqueous solution was retained in the structural Al-hydroxyl layers of hibsite (Kri = 54.7, fraction 2) without the effect of fractionation ($\alpha = 0.99$).

Experimental studies have determined the degree of influence of structural and physicochemical properties of hibsite on its ability to remove tritium from aqueous solutions and elucidated some aspects of the mechanism of interfacial isotope-hydrogen exchange in layered silicates. The obtained new scientific results together with the results of our previous research provide the opportunity to develop more effective methods of detritization of aqueous solutions.

References

1. Belovodskyy L.F., Haevoy V.K., Hryshmanovskyy V.Y. Trytyy. Moskva: Enerhoatom, 1985. 247 p.
2. Brindley G. W. and Nakahira M. (1959). Zeitschrift fur Kristallographie, Bd. 112. 136-149. https://doi.org/10.1524/zkri.1959.112.jg.136
3. Deer W.A., Zusman J., Howie R.A. Rock-forming minerals. Mir, Moscow, 1965, T. 5, Nesilikatnye minera., 404 p.
4. Lopez-Galindo A., Hach-Ali P. F., Pushkarev A.V., Lytovchenko A.S., Baker J.H., Pushkarova R.A. (2008). Applied Clay Science, v.39, p. 151–159.
5. Lytovchenko A.S., Pushkarev A.V., Samodurov V.P., Baker J.H., Hach-Ali P. F, Lopez-Galindo A., (2005). Mineralogical Journal. N 2. p. 59-65.
6. Nesmeyanov A.N. Radiochemistry. Moscow: Chemistry, 1972. 591 p. [in Russian
7. Pushkarev O.V., Dolin V.V., Pryymachenko V.M., Bobkov V.M., Pushkareva R.A. (2007). Zbirnyk naukovykh prats′ Instytutu heokhimiyi navkolyshn′oho seredovyshcha. Vyp.15. pp.27-36
8. Pushkarov O. V., Rudenko I. M., Dolin V. V. (mol.), Pryjmachenko V. M. Sepiolit-ceolitovi kompozyty jak potencijni vodopronykni reakcijni bar'jery. Zbirnyk naukovyh prac'. Instytut geohimii' navkolyshn'ogo seredovyshha. Kyi'v, 23, 98 -107. (2014)
9. Pushkarov O.V., Lytovchenko A. S., Pushkar'ova R. O., Jakovljev E. O. (2000). Mineral'ni resursy Ukrainy. Kyi'v, 3, 42-45.
10. Pushkarov O.V., Pryjmachenko V. M. (2010). Zbirnyk naukovyh prac', Instytut geohimii' navkolyshn'ogo seredovyshha. Kyi'v, 18, 149-156 pp.
11. Pushkarov O.V., Pryjmachenko V. M. (2010). Zbirnyk naukovyh prac'. Instytut geohimii' navkolyshn'ogo seredovyshha. Kyi'v, 18, 140-148.
12. Pushkarov O.V., Pryjmachenko V. M., Zolkin I. O. (2012). Zbirnyk naukovyh prac'. Instytut geohimii' navkolyshn'ogo seredovyshha. Kyi'v, 20, 98 -108.
13. Pushkarov, O.V., Rudenko, I.M, Skrypkin, V. V. (2016). Visnyk of Taras Shevchenko National University of Kyiv. Geology, 71, 43-48. https://doi.org/10.17721/1728-2713.71.07
14. Tarasevich Ju.I. (1988). Kyiv, Naukova Dumka, 248 p.
15. Wypych Fernando (2009). VII – caulinita e haloisita. Available at: https://www.researchgate.net/figure/Figura-4-Figura-4-Estrutura do-tipo-brucita-A-e-do-tipo-gibbsita-B-com-vista_fig2_292726910

ДЕТРИТІЗАЦІЯ ВОДНИХ РОЗЧИНІВ З ВИКОРИСТАННЯМ ГІБСИТУ

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Анотація. *Важливим завданням щодо захисту навколишнього середовища від тритієвого забруднення є пошук ефективних, простих, доступних, недороговартісних і низькоенергозатратних методів вилучення тритію з великих об'ємів низько- та середньоактивних водних розчинів. В статті з використанням досліджень на експериментальній стаціонарній системі на прикладі природного мінералу гібситу отримано нові дані щодо впливу октаедричної складової структури шаруватих силікатів на вилучення тритію із водних розчинів та визначена можливість використання гібситу в якості природного адсорбента тритію. Оцінена ступінь адсорбції тритію з водного розчину та ефект фракціонування ізотопів водню у стаціонарній системі «НТО-гібсит». Пояснений механізм затримки тритію в структурі природного адсорбенту. Тритій, вилучений із тритійованої води розподіляється у мінеральній речовині між різними структурними позиціями – з найменшою енергією зв'язку у молекулярній формі НТО в поверхнево-адсорбованій волозі (1 фракція), із дещо більшою – в іонній формі –ОТ у структурних позиціях мінерального адсорбенту (2 і 3 фракції). В гібситі у поверхнево адсорбованій формі затримується до 39% від загальної кількості тритію, вилученого із водного розчину. Переважна затримка біля мінеральної поверхні поляризованих молекул НТО ніж молекул* H_2O *внаслідок динамічних адсорбційно-десорбційних процесів обумовлює ефект фракціонування ізотопів водню (α = 1,14). Обмін між ОН-групами структурних Al-гідроксильних шарів мінералу і ОТ-групами тритійованої води призводить до закріплення у цій формі до 55% тритію. Отримані нові наукові результати, щодо впливу структурних і фізико-хімічних властивостей мінерального адсорбенту на його здатність вилучати тритій із водних розчинів та нові дані, щодо особливостей механізму міжфазового ізотопно-водневого обміну у водно-мінеральній системі. Це забезпечує, із залученням результатів наших попередніх досліджень, можливість розробки більш ефективних методів детритізації водних розчинів.*

Ключові слова: *тритій, водень, важкі ізотопи водню, гібсит, адсорбція, фракціонування.*