

MECHANISM FOR TRITIUM WATER – CLAY BARRIER INTERACTION

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Abstract

Clayey rocks are well-known barriers for the radioactive waste protection. Different forms of water in the clays: porous, molecular-adsorbed and constitution water have been studied. Kaolinite and montmorillonite were used as investigation objects. These clays differ in molecular-adsorbed and constitution water content. Kaolinite contains 0.6% of molecular-adsorbed water and 13.8% constitution water and montmorillonite 8.6% and 4.2% accordingly. Experimental procedure bases on the clay wetting by the tritiated water during 1 hour – 6 month periods. Different forms of water were extracted from clays and analysed by β -counter. The experiments on tritium washing out from clays were also carried out. It was found that protium - tritium isotope exchange takes place in the all water forms of the clay minerals. Tritium activity in porous water did not change in course of time but it slightly increases in molecular-adsorbed and constitution water. Tritium washing out from clays shows that a 0.39% and 0.17% radioisotopes is remained in porous water of montmorillonite and kaolinite accordingly after 6 cycles of washing. Tritium retention effect has been observed in constitution water of clays. The obtained data must be taken into consideration at tritium waste storage disposal.

Introduction

A water state is one of the states of tritium inflow in an environment because of operation NPS and factories for regeneration of nuclear fuel. As a result of the tritium water (T_2O) dissolution in natural water (H_2O) the molecules HTO is formed. This tritium water takes part in usual water circulation. It is dangerous to human health and environmental. Therefore the study of tritium behaviour in the various systems is actual problem. Clayey rocks are well-known barriers for the radioactive waste protection. Previous investigations have shown the capacity of the clay minerals to tritium absorption (1). That is why mechanisms of the tritiated water – clay rock interactions were studied in this work. Clay rocks have the different forms of water: porous water, molecular-adsorbed water and constitution water (2). Porous water is that which locates between clay particles, i.e. in pores. It is loosely-coupled and it can be moved away up to $100^{\circ}C$. There are two types of molecular-adsorbed water in the clay minerals: interlayer water (locates in the interlayer space of clays) and water adsorbed on clays surface. They are moved away at $105-130^{\circ}C$ and $200-450^{\circ}C$ accordingly. Constitution (crystalline) water is the most closely coupled. In clays it is the water in form of hydroxyl OH-groups. Constitution water can be moved away at $450-700^{\circ}C$ when the chemical bonds are destroyed. As tritium is the constituent of

water it can penetrate into clays with the different forms of water. Thus, different isotope exchange reactions may take place in the different clay minerals: molecular HTO – H₂O exchange reaction, ionic T⁺ and OT⁻ isotope exchange reactions and both molecular and ionic reactions. On account of above-mentioned, porous, molecular-adsorbed and constitution waters were extracted from clays and studied. Tritium accumulation in clay minerals and the inverse process of tritium washing-out from the tritiated clays were estimated.

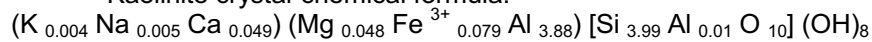
Methods

Clay minerals: Kaolinite and montmorillonite were the objects of investigation (Table 1).

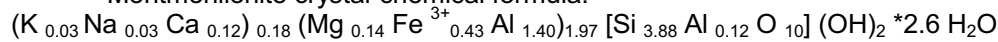
Table 1: Clays characterization

Clay	Origin	Particle form	Particle size (nm)	Particular surface (m ² /g)
Kaolinite	Ukrainian	Sheets	360X200X12	70
Montmorillonite (Askangel)	Georgian	Sheets	120X30X1.2	680 – 770

Kaolinite crystal-chemical formula:



Montmorillonite crystal-chemical formula:



Experimental procedure: Experiments have been fulfilled at the room temperature and atmospheric conditions. Initial clays were dried at 110°C during 5 hours for the porous water moving away. Dried clays were damped by HTO-water and saved on the different periods: 1 hour – 6 month. The mass ratio of tritiated water to clays was consist 1:1 for kaolinite and 2:1 for montmorillonite. This ratio depends on the mineral crystal features and sorption capacity of clays. Initial distilled tritiated water has got 1.04018 MBq/l tritium activity. Different forms of water were extracted from clays and analysed by β-spectrometry (LKB – 1219, Vallac). Water extraction has been done by the hydraulic pressing and, then, by the thermo-chemical water extraction. The evaporation of the different water forms from clays was realised in corresponding temperature intervals: up to 100°C for porous water, 105 – 450°C for molecular-adsorbed water and 450-700°C for constitution water. The experiences on tritium washing out from clays were also carried out. Dried clays have been treated by tritium water during 1 month and, then, the washing-clean procedure was applied. Six cycles of H₂O washing-outs have been done. Then, clays were exposed to thermo-chemical analysis as stated above.

Results

Integral (common effect) parameters and differential (different components of common effect) parameters of tritium sorption were calculated. Partition (distribution) coefficient K_d is a common sorption indicator and it was determined by formula:

$$K_d = (A_i / A_e - 1) * V / P$$

where A_i – initial water activity, A_e – water activity after interaction with clay, V (ml) – water volume, P (g) – clay mass (3). Protium – tritium exchange in the porous, molecular-adsorbed and constitution water was evaluated by the relative (comparative) activity: A_{100} ($T = 100^\circ C$), A_{450} ($T = 450^\circ C$), A_{700} ($T = 700^\circ C$). The relative activity has been calculated as a ratio of water activity extracted at corresponding temperature interval to initial water activity. For example, $A_{700} = 0.021$ means that the constitution water activity (extracted at 700°C) has got 21.8 kBq/l in compare to the initial water activity 1040.1 kBq/l. This value shows that 2.1% of crystalline OH-groups have accepted tritium, therefore, the relative activity is an indicator of the specific exchange reaction.

The received data indicate that tritium is accumulated in the different water forms of montmorillonite more than in kaolinite. These clays differ in molecular-adsorbed and constitution water content. It was experimentally established by DTA method that 1g kaolinite contains 0.6% of molecular-adsorbed water and 13.8% constitution water and montmorillonite 8.6% and 4.2% accordingly. Although the constitution water content in kaolinite is lager than in montmorillonite but only 3% ($A_{700}=0.0320$) of it was exchanged on tritiated water in an initial stage (3 days). In montmorillonite about 30% ($A_{700}=0.3186$) of all constitution water was exchanged on tritiated water. The molecular-adsorbed water content in montmorillonite is much lager than in kaolinite. And the about half of it was exchanged on tritiated water. If it is calculated with allowance for clays mass: 0.004 g heavy constitution water and $1 \cdot 10^{-3}$ g heavy molecular-adsorbed water are contained in 1g of kaolinite. In 1g of montmorillonite

0.0126g heavy constitution water and 0.043g heavy molecular-adsorbed water are contained. Tritium exchange effect in OH-groups of kaolinite slowly increases from 3% to 13% during 5 months. Porous water activity saves its initial value (does not change) in the both minerals.

Tritium partition coefficient K_d is quite small in the all experiments, but differ for clays. It is much smaller for kaolinite ($K_d = 0.01 - 0.04$) than for montmorillonite ($K_d = 0.10 - 0.14$). These values show the negligible tritium sorption effect in the porous water.

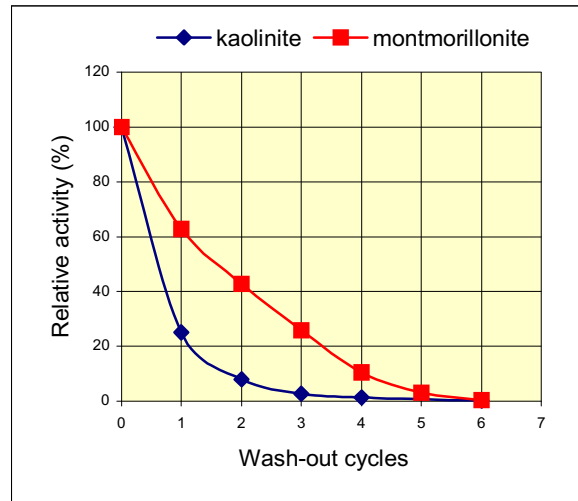


Fig. 1: Tritium wash-out from the porous water of the tritiated kaolinite and montmorillonite.

Tritium wash-out experiments have been fulfilled for the evaluation of tritium retention effect. Fig.1 and Tables 2 and 3 show the experimental results of tritium washing out from porous water of kaolinite and montmorillonite. Tritium washing out from clays shows that porous water has no tritium retention effect. Its activity is strictly in accordance with the dilution procedure. The final relative activity of porous water after 6 cycles of washing is 0.0017 for kaolinite and 0.0039 for montmorillonite.

Therefore, tritium retention effect takes place in the tritiated clay matrix for both clay minerals. Table 4 show that relative activity of constitution water is larger than porous water.

Table 2: Data on predicted and real porous water activity in “kaolinite – washing-out” experiment

Cycle	Kaolinite Weight (g)	Quantity of Added Water (g)	Quantity of Pressed Water (ml)	Relative Activity of Porous Water (predicted)	Relative Activity of Porous Water (experimental)
0	100	(+HTO) 100	62	1.0	1.0
1	120.3867	(+H ₂ O) 100	95	0.2753	0.2515
2	114.5924	(+H ₂ O) 60	65	0.1049	0.0807
3	110.3731	(+H ₂ O) 52	51	0.0340	0.0265
4	85.6971	(+H ₂ O) 74	71	0.0091	0.0133
5	No data	-	-	-	-
6	73.0874	(+H ₂ O) 35	35	-	0.0017

Table 3: Data on tritium washing-outs from the porous water in montmorillonite

Cycle	Montmorillonite Weight (g)	Quantity of Added Water (g)	Quantity of Pressed Water (ml)	Relative Activity of Porous Water (experimental)
1	139 g / 274 g HTO	(+H ₂ O) 200	122	0.6282
2	139	(+H ₂ O) 100	135	0.4284
3	139	(+H ₂ O) 150	179	0.2586
4	139	(+H ₂ O) 150	190	0.1045
5	139	(+H ₂ O) 150	178	0.0302
6	139	(+H ₂ O) 250	194	0.0039

Kaolinite constitution water activity shows 0.0030 value and porous water – 0.0017. Thus, tritium retention effect may be defined as:

$$K_r = A_{cr} / A_{por},$$

where A_{cr} – relative activity of constitution water and A_{por} – relative activity of porous water. So, tritium retention effect in kaolinite $K_r = 1.76$.

Table 4: Data on tritium retention in the clay matrix

Clay	Relative Activity				
	100°C	200°C	450°C	550°C	700°C
Kaolinite	0.0017	0.0019	0.0032	0.0033	0.0030
Montmorillonite	0.0039	0.0035	0.0090	0.0096	-----

Relative activity of the montmorillonite porous water shows 0.0039 value and the activity of the constitution water is 0.0096, thus, tritium retention coefficient in montmorillonite $K_r = 2.46$. The comparison tritium retention effects in kaolinite and montmorillonite shows the montmorillonite best characteristics.

Discussion

It is obvious from results that protium - tritium exchange takes place in all water forms of montmorillonite and kaolinite. Processes of tritium accumulation in clay minerals and tritium washing-out from the tritiated clays are differing for kaolinite and montmorillonite. The best tritium accumulation and retention effects have been observed in montmorillonite. This is the evidence of the structural characteristics which are defined the various opportunities for HTO molecules and T^+ ions access to localisation places in mineral structure. Kaolinite having (1:1) structure is the hydroxyl bearing mineral. Its structure consists of one tetrahedral and one octahedral layers (4). There are two different hydroxyl positions in its structure: internal and external (5). Internal hydroxyls locate at the border of tetrahedral and octahedral layers. External hydroxyls locate on surface of octahedral layer and interact with basal oxygen atoms of tetrahedral adjoining layer. Water in molecular form practically does not penetrate into interlayer space of kaolinite. Taking into account the peculiarities of kaolinite crystal lattice it is possible to assume that the protium – tritium exchange will take place mainly between OH-groups. Montmorillonite having (2:1) structure is the mixed (OH – H₂O) mineral. Its structure consists of two silicon-oxygen tetrahedral layer divided by the octahedral alumin-oxygen layer (4). There is only one species of hydroxyl positions in montmorillonite structure. It is so-called interlayer hydroxyl groups. They locate in the flat which is general for tetrahedral and octahedral layers. The distinctive feature of montmorillonite is the presence a lot of molecular-adsorbed water. Thus, it may be involved in both ionic and molecular tritium exchange processes.

Comparative quantity of the OH-groups in clay minerals with 1:1 structure (e.g. kaolinite) is more than in clays with 2:1 structure (montmorillonite). Therefore there are more H bonding positions that can be exchange to heavy isotopes in the first structure than in the second. But the availability of well developed paths for access of T^+ ions to structural OH-groups (constitution water) of montmorillonite ensures a possibility of more intensive tritium accumulation in these position of montmorillonite. The presence of water mobile molecules in montmorillonite interlayer space provides tritium diffusion to places of structural hydroxyl groups accommodations. The hampered access of T^+ ions to structural OH-groups, as it takes place in kaolinite, even at availability in its structure the great number of exchange position conducts to much smaller tritium sorption then in montmorillonite. So at the interaction of tritium water with clay minerals the different mechanisms of tritium isotope exchange reactions take place.

As tritium is a component of water molecules the quantitative characteristics of hydrogen contents in various types of water allocated in minerals are simultaneously the characteristics of their potential ability to tritium sorption in the appropriate structural positions. Potential sorption capacities of clay minerals are large to possible tritium concentration. The amount of tritium atoms in water used in the experiments with its specific activity 1,04 MBq/l was smaller in 10-12 orders than the amount of possible positions for replacement of protons. So the sorption potential of clay minerals is only partially realised under these conditions. But tritium accumulation and retention effect in the structure of kaolinite and montmorillonite occur even at such tritium water activity.

The ability of kaolinite and montmorillonite clays to tritium accumulation and especially to tritium retention allows to use them as natural barrier materials at the water protection from the receipt and distribution of tritium and also at tritium waste storage disposal. The use of montmorillonite-bearing geological beds is better for these aims.

Conclusions

Mechanisms of the tritiated water – clay rock interactions were studied in this work. Different water forms contained in kaolinite and montmorillonite: porous, molecular-adsorbed and constitution waters were taken into account. Tritium accumulation in clay minerals and the inverse process of tritium washing-out from the tritiated clays were estimated. The best tritium sorption effects have been observed in montmorillonite. Tritiated clays show tritium keeping effect in the OH-groups (constitution waters) after repeated dH₂O washing. Structural peculiarities of clay minerals determine their properties. Thus, tritium accumulation in montmorillonite occurs in both molecular-adsorbed and constitution waters. So montmorillonite may be involved in ionic and molecular mechanisms of tritium exchange processes. Kaolinite structure allows mainly the ionic tritium exchange processes. These data are important for the arrangement and realization of the nature protection measures using clays as sorption barriers.

Acknowledgments

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