

CLAYEY BARRIERS FOR TRITIATED GROUNDWATER PROTECTION

V.P. Samodurov¹, P.F. Hach-Ali², J.H. Baker³, A.S. Lytovchenko⁴, A.V. Pushkarev⁴ and G.D. Kovalenko⁵

¹ Institute of Geological Sciences NAS Belarus,
Kuprevicha str.7, Minsk 220141, Belarus
e-mail: samod@ns.igs.ac.by

² Cristalografia y Mineralogia Departamento, Universidad de Granada
c/ Fuentenueva s/n, 18002 Granada, Espana
e-mail: pfenoll@goliat.uqr.es

³SELOR eeig, Amsterdam, Netherlands,
E-mail: selor@wish.net

⁴State Scientific Center of Environmental Radiogeochemistry, Palladina av. 34a., 252680 Kiev,
Ukraine
E-mail: science1@carrier.kiev.ua

⁵Ukrainian Scientific Research Institute for Ecological Problems, Bakulina st. 6, 310166
Kharkov, Ukraine
E-mail: kovalenk@kovalg.kharkov.ua

Abstract

Tritium groundwater pollution has been observed at Kiev and Kharkov radioactive repository sites (Ukraine). Water shows activity 1.5MBk/l, pH=7.15, Eh=+295mV, (Ca²⁺+Mg²⁺) - 10.1meq/l, Na⁺ - 0.41meq/l, K⁺ - 0.027meq/l, HCO₃⁻ - 6.84meq/l, SO₄²⁻ - 1.75meq/l. This water consists of the different protium-tritium forms: H₂O, H⁺, OH⁻, HTO, T⁺ and OT⁻. In spite of negligible Tritium concentration, the absolute HTO-molecule quantum is a very high (8.415·10¹² per ml) and dangerous for human health. Clayey barriers for the Tritium protection have been studied. Five groups may be declared within DANA mineral system: H-free, H-bearing, hydroxyl-bearing, H₂O-bearing and mixed (OH+H₂O) minerals. Different clay minerals are the OH-bearing and mixed minerals and they show the different adsorption effects. Kaolinite, montmorillonite, illite, palygorskite and sepiolite were studied. Temperature, pH-, Eh-parameter and pressure dependence has been defined and water chemical composition was under consideration as well. Tritium distribution coefficient K_d shows the small value in the all experiments, but it differs substantially for the different phyllosilicates. Protium-tritium exchange in the mineral matrixes has been studied. Tritium multi-formity in water is the reason of the tritiated groundwater mobility. It is the negative effect in ecology, but it may be used for Tritium labeling experiments in mineralogy, geochemistry and hydrology.

Introduction

There are more than 4000 minerals in the nature according Dana's mineral system (1). Phyllosilicate (layer silicate) mineral group contains about 200 mineral species and most of them are the clay minerals. Clayey geological barriers are widely used for the radioactive waste repository (RWR) construction, nevertheless the tritiated groundwater protection in RWR is the most intractable problem because of the great tritium mobility. Some radioactive accidents with tritium getting into groundwater have been marked around the world. There are five radioactive repositories in the Ukraine and two of them have got tritium blots in

groundwater (2). Kharkov and Kiev tritiated groundwater were studied within this research. The purpose of this work is the evaluation of tritium accumulation and retention effects in the different phyllosilicates for the best RWR geological barriers. Tritiated water – clay rock system is a very complex one because of the mineral matrix variety and different tritium molecular and ionic forms in water. Theoretical criteria of the hydrogen exchange effects and experimental data on the tritium accumulation and retention in the different phyllosilicates are under consideration in this work. Besides the RWR protection aspects, hydrogen isotopes (protium, deuterium and tritium) behavior in the “water – rock” system gives the base for the tritium labeling method in geology and geochemistry.

Tritium forms in groundwater

Tritium differs from the other radionuclides by their behavior in water. The most of the other radionuclides present in water by cationic or anionic forms only and the selective ion exchange reactions prevail in these systems. Tritium fits into molecular HTO, cationic T^+ and anionic OT^- forms. Some other forms (TCO_3^- , gaseous, organics) may be tritium-bearing as well. The main tritium T-forms and the hydrogen H-forms may be defined in the tritiated groundwater on the base of the water activity, pH-parameter and the water temperature. The tritium nuclide quantity in the water may be calculated by the nuclear physics equations and the pH-parameter defines the H^+ and OH^- concentration in water at particular temperature (3). The real Ukrainian tritiated groundwater shows activity 1.5MBk/l, pH=7.15, Eh=+295mV, ($Ca^{2+}+Mg^{2+}$) - 10.1meq/l, Na^+ - 0.41meq/l, K^+ - 0.027meq/l, HCO_3^- - 6.84meq/l, SO_4^{2-} - 1.75meq/l. This water contains H_2O - 99.99%, H^+ - $1.79 \cdot 10^{-4}\%$, OH^- - $2.28 \cdot 10^{-4}\%$, HTO - $2.51 \cdot 10^{-9}\%$, T^+ - $2.26 \cdot 10^{-14}\%$ and OT^- - $2.87 \cdot 10^{-14}\%$. Tritium concentration in the groundwater is a negligible one but the absolute HTO-molecule quantum is a very high (HTO - $8.415 \cdot 10^{12}$ per ml) and dangerous for human health. Thus, the HTO-molecule quantity is less than H^+ , OH^- ions and T^+ , OT^- ions are in the least quantum. Tritium contains in the molecule HTO form mostly.

Mineral hydrogen exchange properties

There are more than 4000 minerals according Dana mineral classification in the nature. Five mineral types may be declared within Dana mineral classification (1) by hydrogen and tritium positions in their crystal structures:

1. H-free minerals
2. H-bearing minerals
3. Hydroxyl (OH) bearing minerals
4. H_2O bearing minerals
5. Both OH and H_2O bearing minerals

Native elements (119 minerals) and sulfides (193 minerals) are completely H-free mineral groups. These minerals may be involved in the tritium adsorption processes only by their surface reactivity, but the adsorption processes can not take place. The cationic (T^+) adsorption processes may be realized within H-bearing mineral group. The cationic and anionic (T^+ , OT^-) adsorption processes allowed in the hydroxyl bearing minerals. Molecular (HTO) adsorption processes prevail in the crystal hydrates. Different types adsorption processes (T^+ , OT^- , HTO) may run in the fifth group minerals. Thus, the defined mineral groups are in the correlation with the different tritium adsorption mechanisms.

Clays are phyllosilicates. Kaolinite-like (1:1) minerals are the hydroxyl bearing minerals, and most of the others are the mixed (OH- H_2O) minerals. Therefore, kaolinite mineral matrix allows the ionic (T^+ , OT^-) tritium adsorption processes and the other clays may be involved in ionic and molecular processes as well. There are two different hydroxyl positions in the kaolinite $2(Al_2Si_2O_5(OH)_4)$ structure. Two hydroxyls are in the internal structure sites and six hydroxyls are in the external surface position. There are $7.00 \cdot 10^{21}$ external $6(OH)$ hydroxyl sites per 1g and $2.334 \cdot 10^{21}$ internal positions in the kaolinite structure. The tritiated groundwater at its activity $15 \cdot 10^3$ Bq/g contains $7.565 \cdot 10^6$ tritium cations per 1g. Therefore, kaolinite has got the great hydroxyl position capacity and it may be used for the tritium-

protium ion exchange reactivity. The hydroxyl position evaluation in the other clay minerals shows the same order of $n \cdot 10^{21}$ sites per 1g. Nevertheless, the other clay minerals involve water in their structure interlayer space and molecular exchange process takes place in the tritium absorption mechanisms as well.

Methods

Two different approaches have been used in the clay barrier research. Study of an integral (common) tritium sorption effect and investigation of the differential (specific) effects. Common effect is an averaged clay rock characteristic and differential effects deal with the mineral specific characteristics.

Integral effects have been defined by the clay sample flooding experiments. The experiment bases on the clay sample damping by tritium water during 1 hour – 6 months and, then, water extraction by the hydraulic pressing. Clay samples had been dried in advance. Different clay mass (100 – 300 g) and water volumes (100 – 600 ml) were used because of the different crystalline water contents and the interlayer water presents. Tritium partition (distribution) coefficient K_d was used (4) for the integral effect evaluation:

$$K_d = (A_i / A_e - 1) \cdot V / P \quad (1)$$

Where A_i – initial water activity, A_e – water activity at the end of experiment, V (ml) –water volume, P (mg) – clay mass. Initial distilled tritiated water showed 1.04018 MBq/l tritium activity and it was used in the all experiments. Porous waters after experiment completing were extracted by the hydraulic pressing and, then, distilled for the prevention of the ionic influence. There is no tritium absorption in phyllosilicates at $K_d = 0$. The selective absorption takes place at $K_d > 0$ and tritium concentrates in the solid matter.

Differential effects show the different component influence within common effect. Differential effects have been studied by the thermo-chemical water extraction experiments. Capillary and interlayer water has been extracted at 105 °C, surface water was distilled in the temperature range 105 – 350°C and crystalline water – at 450 – 700°C. It was shown in our previous work (5) that tritium may penetrates into the mineral matrix, therefore, mineral surface and crystalline waters have been studied more detailed in the range of physical–chemical conditions (P , T , pH , Eh , pressure). Differential effects of protium – tritium exchange in the porous, surface and crystalline water was evaluated by the relative (comparative) activity. For example, $A_{600} = 0.021$ means that the crystalline water activity (extracted at 600 °C) has got 21.8 kBq/l in compare to the initial water activity 1040.18 kBq/l. This value shows that 2.1% of crystalline OH-groups have accepted tritium.

Samples. Ukrainian kaolinite, montmorillonite and palygorskite, Belarus illite and Spanish sepiolite were used for the experiments in this study.

Spectrometry. Beta-spectrometer LKB – 1219 Vallac has been used for tritium activity analysis in the water samples.

Results

Integral clay rocks parameters. Distribution coefficients K_d are quite small in the all experiments, but differ substantially. Distribution coefficient values present in the table 1.

Table 1.

Tritium distribution coefficient K_d in clays.

Kaolinite	Illite	Montmorillonite	Palygorskite	Sepiolite
0.02	0.09	0.13	0.15	0.16

Montmorillonite, palygorskite and sepiolite show the noticeable K_d increasing because the interlayer space and channeled structure blocks present in their mineral matrixes, therefore, these minerals have got the great surface reactivity. Annealed modified clays reveal the further K_d increasing. Calcinated kaolinite (meta-kaoline) shows $K_d = 0.17$ and the distribution

coefficient in the calcinated montmorillonite grows up to 0.27 because mineral matrixes have been destroyed at high temperature (500 – 800°C). Influence of the different physical-chemical parameters on K_d coefficient has been studied. Variations of temperature (3 – 70°C), pressure (50 – 300 atm), pH (3 – 10), Eh (-70 - +770 mV) and different water chemical compositions have been used in the experimental series. Some conditions show weak influence upon the integral tritium absorption effect, but there are no great K_d changes in this experimental series. Therefore, physical-chemical variation does not affect substantially on the common tritium sorption in the clayey geological barrier.

Differential parameters. Clay rock porous water, mineral surface water, phyllosilicate interlayer water and crystalline (mineral matrix) water have been investigated. Rock porous water and phyllosilicate interlayer water prevails in the common water volume and they make the main contributions into the integral tritium sorption parameter K_d . Crystalline water behavior in the mineral matrix – tritium water system differs substantially and this system was mostly under consideration in the differential parameter study. Crystalline water value differs in the different clay minerals. For example, kaolinite $Al_4(OH)_8[Si_4O_{10}]$ contains 13.8% H_2O and muskovite $KAl_2(OH)_2[AlSi_3O_{10}]$ contains 4.5% crystalline water. Crystalline water may be involved in the protium – tritium exchange partly according to the table 2 (period of experiments – 2 weeks).

Table 2.
Crystalline water relative activity.

Kaolinite	Illite	Montmorillonite	Palygorskite	Sepiolite
0.032	0.217	0.319	0.261	0.270

Therefore, 3% of kaolinite crystalline water involves in protium – tritium exchange and montmorillonite shows 30% effect. Montmorillonite clay rocks are the most effective geological barriers for the tritiated groundwater protection.

Physical-chemical parameter changes (temperature 3 – 70°C, pressure 50 – 300 atm, pH 3 – 10, Eh -70 - +770 mV and different water chemical compositions) show some variations of tritium absorption effect. For example, crystalline water relative activity in montmorillonite grows from 0.2 to 0.5 in the temperature range 3°C – 70°C. Nevertheless, the variations of these parameters do not affect greatly on the tritium sorption in the mineral matrixes.

Experimental study of tritium partition in the watery clay by the freezing has been fulfilled. Kaolinite and montmorillonite watery samples were frozen by liquid nitrogen. Tritium activities in the icy and liquid parts of the samples were compared. There are no effects of tritium partition by the freezing. Therefore, clayey barrier could not change the tritium distribution within barrier at freezing in winter.

Tritium retention effects in the different clayey rocks have been evaluated. Tritiated kaolinite and montmorillonite samples were studied by the washing-out experiments. Six cycles of the washouts by dH_2O have been applied in the each sample. At the end of experiment, kaolinite crystalline water activity shows 0.0030 value and porous water – 0.0017. Thus, Tritium retention effect may be defined as:

$$K_r = A_{cr} / A_{por}, \quad (2)$$

Where A_{cr} – relative crystalline water activity and A_{por} – relative porous water activity. Tritium retention effect in kaolinite $K_r = 1.76$. Relative activity of the montmorillonite porous water shows 0.0039 value and the activity of the crystalline 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

Some important properties of the clayey barriers for the tritiated groundwater protection have been studied. Common clay rock parameters and individual mineral matrix parameters were under consideration.

Integral rock parameters show the low values of the tritium K_d distribution coefficients because of the great tritium mobility in groundwater. Tritium multi-formity and the prevailing of the molecular water forms are the reasons of the tritium mobility. The other radionuclides present in water by ionic forms mostly and the ionic exchange and sorption increase the effectiveness of the nuclide uptake in the barriers. It was defined that the physical-chemical parameter variations, ionic water composition and freezing could not affect greatly on the tritium behavior. Nevertheless, different phyllosilicates show the noticeable differences of the common tritium effect. The reasons of these differences may be defined by the differential parameter study.

Differential parameters show the great differences for porous, surface, interlayer and mineral matrix waters. The main object of the study was the mineral matrix (crystalline) water behavior. Tritium uptake varies in the range 3 – 30% in the different phyllosilicate matrix and shows some variations in the different physical-chemical conditions. Crystalline water value varies from 3 to 14%, therefore, the contribution of the crystalline water effect in the common tritium sorption effect is a quite small one, but the mineral matrix effects may be used as a ballast (dead) volume of the RWR clayey barrier. Different clay minerals show the different tritium retention effect in the washout experiments. The evaluation of the different common and differential parameters of phyllosilicates demonstrates the best properties for the montmorillonite clay. This clay mineral shows the best distribution coefficient, mineral matrix uptake and tritium retention effect.

Conclusions

Tritium mobility in groundwater is a very negative effect in ecology, but a very useful one in the tritium labeling methodological approach in geochemistry and mineralogy. Mineral surface reactivity, interlayer space reactions and mineral matrix hydrogen diffusion may be studied by this approach for the “water-mineral” system. This system is of high interest for soil science, hydrology and mineralogy.

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