

TRITIUM ACCUMULATION AND PRESERVATION INTO CLAY MINERALS FOR ENVIRONMENTAL PROTECTION

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The comparative analysis of new and previously received data is represented, which allows us to estimate the influence of hydrodynamic conditions on tritium accumulation and retention in clay minerals. We have received time dependence of the tritium exchange process with the hydrogen of natural clay mineral matrix, long time half-cycle tritium capture by clay, the part of total tritium activity captured by clay for long time (more than 1 year). The received data and mathematical modeling let us determine the mineral component of natural clay, which more efficiently captures and retains tritium and is the best component for making barrier near radioactive tritium waste repository.

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1. INTRODUCTION

Tritium is one of the most hazardous β -emitters. Its large amounts are contained both in the cooling water of nuclear reactors and settling basins, radioactive waste repositories (RWR) and it can escape into the environment in the case of leakages. Tritium was identified in a study by the Nuclear Energy Agency of the Organization for Economic Co-operation and Development as one of four volatile radionuclides arising from the nuclear fuel cycle with potential long term radiological significance. The environmental behaviour of tritium was addressed in the symposium [1]. Tritium was registered in deep ground water at the areas affected by Nuclear Power Plants [2].

Tritium was detected in water sampled at groundwater-monitoring points located at the Kharkov and Kiev RWRs [3,4]. In [3,5,6] we investigated some aspects of Kharkov' accident.

Tritium exchanges with hydrogen of clay structure during its distribution through clay layers. This process can lead to decrease of tritium activity after such layers. The review of isotopic exchange of tritium with hydrogen in clay was published recently [7].

The isotopic exchange of tritium with hydrogen, included in free water, pore and interlayer water, was researched in laboratory experiments. These processes last 1...100 days. Investigation of an isotopic exchange of tritium with hydrogen, which is included in OH-groups of clay structure, is going on more than 1 year. We have studied this process as a leading result of tritium distribution in the environment after the radiation accident on Kharkov RWR since 1997.

The received data and mathematical modeling let us determine the mineral component of natural clay, which more efficiently captures and retains tritium, and is the

best component for making barrier near radioactive tritium waste repository.

2. GEOLOGICAL ENVIRONMENT PARAMETERS MEASUREMENTS

In immediate proximity from radioactive waste repositories of Kharkov RWR, from which there was a leakage of tritium, the borehole 31d was drilled and soil was sampled on different depths. As it was clarified after the mineralogical analysis, the underlayers mainly consist of loams containing much clay. The chemical and mineralogical composition of an aeration zone was defined.

2.1. Chemical composition of aeration zone soils

SiO₂ predominates in soils (72...76%), whereas compounds of aluminium and ferric oxides are ~10% and ~5% accordingly. The oxides of kalium, magnesium and calcium are contained in concentrations of about 1.5%. The rest elements are in minor impurities.

From data analysis it follows that the soil is introduced by an intermixture of quartz sand and clay minerals. Thus, hydromica (illite) cannot be a layer-making mineral in clay. So, the contents of kalium is low. Therefore heightened contents of potash feldspars in a sand fraction (up to 13% K₂O in potash feldspars) and illite (5...10 % K₂O) in a clay fraction are not registered. Another feature of clay minerals composition corresponds to the rather low content of aluminium, therefore kaolinite, in which one Al₂O₃ compounds are 39.5%, is an impurity, and does not predominate among clays.

2.2. Mineralogical composition of aeration zone soils

The sand fraction is presented by light (quartz) sand. Soils clayiness varies from 30 to 70%.

The quartz is determined on jerks 4.24, 3.34, 2.45 Å on diffractograms. The feldspar is registered in minor impurities and is revealed in the field of 3.2 Å. The calcite in samples is legibly seen on jerk 3.03 Å.

The quartz predominates in sand fraction composition. The minor impurity of feldspars is registered, and the impurity of a calcite is registered in samples. The percentage of a calcite is determined under the chemical analysis (5.7%).

Common soil type in a section is the following: the sand-clay materials predominate. Various parts of the section differ by essential common clayiness oscillations and by concentrations of separate clay components. Clayiness predominates (50...60%) in the upper part of the section (1...5 m). The essential clayiness oscillations (10...40%) are registered below in the section.

Three basic types of clay minerals are registered: montmorillonite, kaolinite and illite. Illite is registered only as impurities. The section can be divided into 3 parts: upper (1...9 m) and lower (12.5...20.1 m) with a dominance of montmorillonite, and middle (11...12.5 m) is essentially kaolinite.

The weighted mean values of clay minerals (depths 1.2...20.1 m) are the following: clay – 34.2%; montmorillonite – 21.9%; illite – 3.2%; kaolinite-9.5%.

3. VOLUMETRIC TRITIUM ACTIVITY IN BOUND WATER ON VARIOUS DEPTHS

The differential-thermal analysis (DTA) was held for three samples. The intervals of temperatures, at which different types of water are separated, were defined. The measurements of volumetric tritium activity in water on different depths are held in four fractions: 1st fraction is the free water extracted at temperatures up to 105 °C; 2nd fraction is the bound water extracted at temperatures from 105 °C up to 250 °C; 3rd fraction is the bound water extracted at temperatures from 250 °C up to 400 °C; 4th fraction is the bound water extracted at temperatures from 400 °C up to 800 °C. The selection of free and bound water was carried out with two methods: the heating up selection method and the pressure method. Both methods have yielded similar results, showing that the heating up does not influence on the water activity in the different fractions.

The measurement results of tritium activity in all fractions are represented in Fig. 1. The figure represents the dependence of volumetric tritium activity in the indicated fractions from the depth in the borehole 31d.

Analyzing data, represented in Fig. 1, it is necessary to note, that on depths more than 6 m the volumetric tritium activity in all fractions is approximately equal within errors of measurement. On these depths the time of tritium interaction with clay minerals exceeds 10 years, therefore the volumetric activity in all fractions are equal due to the isotopic exchange. The exception from this one can see on the depths up to 6 m. The time of tritium interaction with clay minerals on these depths

was less than 2 years, therefore the volumetric tritium activity were not equal in all fractions due to the isotopic exchange. On these depths the maximum tritium activity is in free water, and the minimum is in crystalline water. In few years the maximum on depth 4 m will move deeper into the aeration zone, and the activity in all fractions will be aligned.

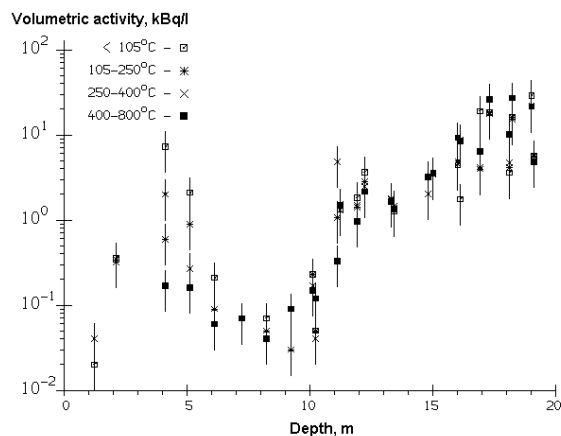


Fig. 1. Volumetric tritium activity vs depth

4. TRITIUM PROPAGATION THROUGH THE AERATION ZONE

The process of tritium propagation through aeration zone was studied theoretically as well as by environment measurements.

4.1. Model of tritium transport through an aeration zone

The calculated tritium activity in free water is found as the solution of the differential equation in particular derivatives, described the tritium transport process through the aeration zone [8]:

$$\begin{cases} n \cdot C_t = D_m \cdot (C_{xx} + C_{yy}) + D \cdot C_{zz} - v \cdot C_z - \\ \alpha \cdot n \cdot C - \beta \cdot n \cdot C + f(x, y, z, t) \end{cases} \quad (1)$$

$$C(x, y, z, 0) = 0$$

where x, y, z, t are the spatial coordinates and time, x, y are the plane ground coordinates, $z > 0$ is the depth, the coordinates' centre is arranged on the ground; $C(x, y, z, t)$ is the tritium volumetric activity in the point with coordinates x, y, z, t ; $C_t = \partial C / \partial t$ is the volumetric activity's derivative on time; $C_{xx} = \partial^2 C / \partial x^2$ is the volumetric activity's second derivative on x ; $C_{yy} = \partial^2 C / \partial y^2$ is the volumetric activity's second derivative on y ; $C_z, C_{zz} = \partial C / \partial z, \partial^2 C / \partial z^2$ are the volumetric activity's first and second derivative on z ; n is active soil porosity; D_m is the molecular diffusion coefficient in soil; D is the total molecular diffusion and hydrodynamics coefficient; v is the filtration velocity, directing along the vertical axis z ; α is the tritium radioactive decay constant; $f(x, y, z, t)$ is an external tritium source. The time dependence $f(x, y, z, t)$ consists of two components, relevant to two radioactive waste repositories (units №19, 20), with own time dependencies. The dependence from coordinates was set by polygon enveloping the total repositories

area. Total release from unit № 19 is 166 Ci, from unit № 20 is 944 Ci. We describe the tritium capture by clay structure by adding to the right part of the eq. (1) the term $-\beta \cdot n \cdot C$, similar to the term describing a radioactive decay. The coefficient β relates to the halftime (T) of tritium capture by clay structure as follows: $\beta = \delta \cdot \ln(2)/T$, where δ is the part of tritium, captured by clay structure.

To define some dynamic parameters of tritium distribution in the aeration zone we have drilled two boreholes 31H and 31d. The tritium activity was defined in free water in samples selected on different depths. The borehole 31d was drilled 3.5 years after borehole 31H on distance approximately 1 m from it.

4.2. Measurement results

The measurement results of the volumetric tritium activity in the aeration zone in boreholes 31H and 31d are displayed in Fig. 2. Calculated curves 1 and 2 in Fig. 2 represent the dependence of activity from depth for these boreholes accordingly.

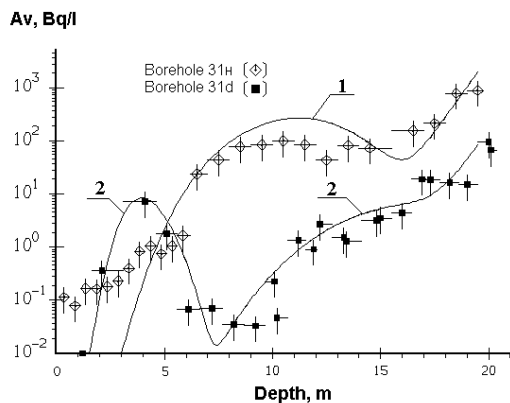


Fig. 2. Tritium activity depth dependence in free water for boreholes 31H and 31d

Curve 2 is gauged in 3.5 years after curve 1. For these years the central maximum at 11.5 m was shifted to the depth of 16 m, and the quantity in the maximum has decreased. The measured quantities are shown with measurement errors. The influence of activity capillary lift from aquifer we describe by the function:

$$F(z) = A_0 \cdot \exp(1.3 \cdot (z - z_0)), \quad z < z_0 \quad (2)$$

Where A_0 is the tritium volumetric activity in aquifer; z is the depth; z_0 is the depth of the aquifer surface; 1.3 is empirical coefficient. This function is added to solution of Eq. (1) to describe the capillary lift on depths beneath 17 m. We show the necessity of introducing this function in [5]. The activity in aquifer (A_0 coefficient in Eq. (2)) is decreased in time not only due to radioactive decay, but also due to activity flow into aquiclude. Curve 2 shows activity peak on depths 2...7 m with maximum on 4 m. This peak was found in measurements and is described by the solution of eq. (1) with the additional tritium leakage in time 2...3 years prior to measurements. The quantity of leakage is selected to get coincidence of measured and calculated values. This maximum it is not visible on curve 1 for borehole 31H. Obviously, the tritium leakage has taken place after sampling from borehole 31H. The solution of

Eq. (1) for the borehole 31H was normalized on the measurement values. This normalization was utilized for depth-dependence calculations of tritium activity in the close located borehole 31d for later time. In calculations for the borehole 31d the unknown parameters δ and T from Eq. (1) were used only. By the selection of these parameters we have described the depth dependence of tritium activity in the borehole 31d very well. It has appeared, that the value of activity, which is captured by clay structure for long time due to the isotopic exchange for our conditions, is equal to 7% (parameter $\delta=0.07$). And the halftime of tritium capture T is equal to 2 years.

5. TIME DEPENDENCE PROCESSES OF TRITIUM CAPTURE BY CLAY STRUCTURE

As the velocity of tritiated water in the aeration zone approximately is equal to 1 m/year and the width of a maximum is about 5 m, the interaction time of tritiated water with clay is about 5 years. At this time, as a result of an ion exchange, tritium substitutes hydrogen in clay mineral structure, including the closely coupled crystalline water, get free at high heat from OH-groups of clay minerals [7]. In vivo measurements demonstrate, that at that interaction time small tritium activity is captured by clay with halftime period of capture approximately equal to 2 years. Our laboratory measurements demonstrate, that the large tritium activity is captured and is held by structure about 10 days.

Therefore time dependence process of tritium capture by clay structure is possible to describe mathematically by two exponential dependences, for 7% of activity half-period of capture approximately equals to 2 years, and for 93% of activity it is about 10 day, see Fig. 3.

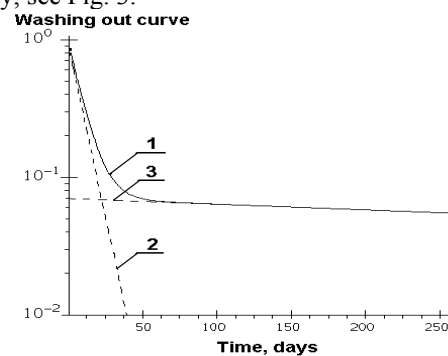


Fig. 3. Time parameters of washing out curve for natural clays of Kharkov radioactive waste repository

Curve 1 in Fig. 3 describes common time dependence of tritium activity decrease in clay during outwashing by distilled water, curve 2 is the component of outwashing with the small period, and curve 3 is the component with large period. In 50 days of outwashing by distilled water in laboratory there is approximately 7% of activity remained. We assume that times for both processes of capture and washing out are equal. The part of activity with large period of capture in our conditions approximately equals to 7%. From our point of view,

this process is determined by "deep" tritium capture by OH-groups (crystalline water). The crystalline water in relation to free water for our clays makes up about 15%. And on our data 7% of crystalline water is captured and is preserved about 2 years. From this data it is clear, that about half of crystalline water is captured and held tritium due to the isotopic exchange on prolonged time.

If to consider, that the part of crystalline water that capture and held tritium on time ~2 years in kaolinite and montmorillonite approximately equal, then for creation of a clay barrier on path of tritium penetration into an environment most preferential is such combination of clay materials, in which crystalline water is more, and, in particular, therefore kaolinite clay layer is much more preferential then montmorillonite one.

6. CLAY TYPE INFLUENCE ON TRITIUM PASSING THROUGH AERATION ZONE

As defined above the average content of montmorillonite in the natural clays in region of Kharkov radioactive waste repository is equal to 21.9%, and kaolinite is equal to 9.5%. Accepting, that montmorillonite contains 3% of crystalline water, and kaolinite contains 14%, we obtain, that the average crystalline water contents in the aeration zone near Kharkov RWR is equal to 11.7%. And on our model estimations from this crystalline water 7% are captured and held for ~2 years.

If to consider, that the parts of crystalline water that captures and holds tritium on time ~2 years in kaolinite and montmorillonite are approximately equal, then we can suppose, that if all clay has only montmorillonite, then it captures and holds 3.3% of crystal water for ~2 years, and if all clay has only kaolinite, this part would be 15.4%.

Thus, for the parameter δ in Eq. (1) we have three values: $\delta=0.07$ for natural clay near Kharkov RWR; $\delta=0.033$ for hypothetical clay from pure montmorillonite; $\delta=0.154$ for hypothetical clay from pure kaolinite. Solving Eq. (1) for different values δ and calculating the tritium flow on boundary of clays, we obtain different time dependences of common tritium activity, which it is going out from the aeration zone (thickness of natural clays ~17 m). This tritium is accumulated in the aquifer and the aquifuge. The results of calculations are displayed in Fig. 4. In this figure three calculated curves and measurement points with errors of measurements are displayed. The measurement values are obtained as a volume integral on all stratum of aquifer and an aquifuge on boundary of which volumetric activity of tritium decreased on 3-4 degree as compared to maximum values. Volumetric tritium activity is measured in water of 23 boreholes. The details of calculations see in [5].

The calculations demonstrate, what total tritium activity after the layer with width 17 m, consisted of natural clays in vicinity of Kharkov RWR will be. The curve 1 demonstrates how tritium is passing through a barrier of natural clays. Curve 2 demonstrates how tritium will pass through hypothetical pure

montmorillonite clay layer and curve 3 demonstrates similar results for hypothetical pure kaolinite clay layer.

Total activity in aquifer and aquifuge

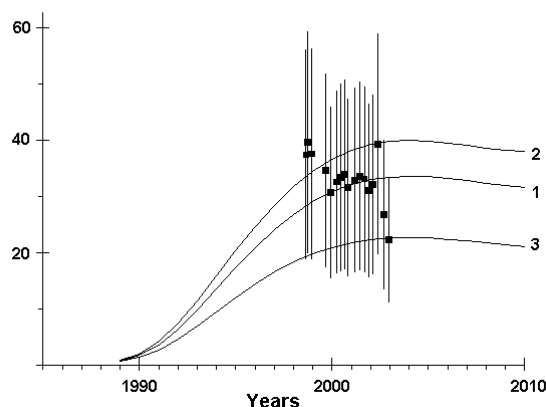


Fig. 4. Total tritium activity after aeration zone: 1-natural clay layer, 2-pure montmorillonite clay layer (hypothetic), 3-pure kaolinite clay layer(hypothetic)

The value in the maximum for a curve 2 is equal to 39.3 Ci, and that for the curve 3 is 22.2 Ci. As we see, behind the kaolinite clay layer maximum tritium activity approximately in 2 times less, than behind the similar montmorillonite clay layer. Taking into account, that the aeration zone contains only 34.2% of clays, the same results can be received for approximately three times less clay layer composed of pure clay.

As it follows from this data, the kaolinite clay is much more effective then montmorillonite clay as a barrier on tritium propagation into an environment. Therefore building the natural barriers on tritium propagation into an environment it is necessary to use the kaolinite clay. Capture and reduction of tritium activity due to a radioactive decay provide an effective barrier. These conclusions are related to a barrier, which tritium is passing more then 2 years for more effective isotopic exchange with hydrogen of crystalline water.

Creating the artificial barriers reducing tritium propagation into an environment it is necessary to provide presence in its clay structure strongly bound hydrogen groups and to provide small filtration velocity through such barriers. And the time of an isotopic exchange with such groups great enough and should be comparable to the period of tritium radioactive decay.

CONCLUSIONS

The data on tritium outwashing from natural clays by the distilled water and results of tritium distribution in the aeration zone let us obtain a time dependence of tritium capture in wide time range. We have found, that for natural clays near Kharkov RWR the value of common tritium activity captured by the clays on time about 2 years and more reaches 7%.

Is was shown, that for creation of a clay barrier on path of tritium penetration into an environment the most preferential is such combination of clay materials, in which it is more crystalline water, and, in particular,

therefore kaolinite clay layer is much more preferential than montmorillonite one.

Thus, the clay minerals as a result of tritium capture by OH-groups strengthen the protective characteristics of a barrier enclosing radioactive waste repository with tritium if passing times of tritium through them is more than 2 years. The efficiency of this protective barrier is more, when a barrier has more strongly bound OH-groups.

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НАКОПЛЕНИЕ И УДЕРЖАНИЕ ТРИТИЯ ГЛИНИСТЫМИ МИНЕРАЛАМИ ДЛЯ ЦЕЛЕЙ ОХРАНЫ ОКРУЖАЮЩЕЙ СРЕДЫ

В.В. Карташов, Г.Д. Коваленко, А.Н. Летучий, В.П. Самодуров, В.И. Витько

Представлен сравнительный анализ новых и ранее полученных данных, который позволил нам оценить влияние гидродинамических условий на накопление и удержание трития в глинистых минералах. Нами получена временная зависимость процесса обмена трития с водородом естественной матрицы глинистых минералов, оценен длительный полупериод захвата трития естественной глиной, часть полной активности трития, захватывающейся на длительное время (более 1 года). Полученные данные и математическое моделирование позволили нам определить минерал естественной глины, который наиболее эффективно захватывает и удерживает тритий, и является наилучшим материалом для создания барьера вокруг хранилищ радиоактивного трития.

НАГРОМАДЖЕННЯ ТА УТРИМАННЯ ТРИТІЮ ГЛИНИСТИМИ МІНЕРАЛАМИ З МЕТОЮ ОХОРОНИ НАВКОЛИШНЬОГО СЕРЕДОВИЩА

В.В. Карташов, Г.Д. Коваленко, О.М. Летучий, В.П. Самодуров, В.І. Витько

Представлено порівняльний аналіз нових і раніше отриманих даних, що дозволив нам оцінити вплив гідродинамічних умов на нагромадження й утримання тритію в глинистих мінералах. Нами отримано часову залежність процесу обміну тритію з воднем природної матриці глинистих мінералів, оцінено тривалий напівперіод захоплення тритію природною глиною, частина повної активності тритію, що захоплюється на тривалий час (більш 1 року). Отримані дані і математичне моделювання дозволили нам визначити мінерал природної глини, що найбільше ефективно захоплює й утримує тритій, і є найкращим матеріалом для створення бар'єра навколо сховищ радіоактивного тритію.