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Abstract

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V. V. RACHINSKII, L. A. LENSKII

ISOTOPE-EXCHANGE SORPTION OF TRITIUM FROM AQUEOUS SOLUTIONS UNDER DYNAMIC CONDITIONS

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The study of the dynamics of tritium sorption in porous media is of theoretical importance for the physical chemistry of isotopes, and also of practical importance for radiochemistry, sorption technology, chromatography, hydrogeology, and soil science when tritium is used as a radioactive tracer. In the present work, theoretical questions concerning the dynamics of tritium sorption in porous media and the results of a study of isotope-exchange sorption of tritium in soils are considered. Although soils were taken as the object of study, the results obtained are of general significance for any porous media.

Let there be a column of a hydrogen-containing porous medium. Consider three cases: a medium completely saturated with water; a dry medium; partial saturation of the medium with water.

In the first case, as tritiated water enters the column, isotope-exchange displacement of inactive (unlabeled) hydrogen takes place, with its replacement by hydrogen labeled with tritium. In the second case, part of the water introduced is molecularly sorbed by the medium, while part, in the form of free water, fills the pores, displacing the air. In the final result, as in the first case, all unlabeled hydrogen from the solid phase must be displaced by isotope exchange and replaced by hydrogen labeled with tritium. In the last case, the moisture present in the column of porous medium may be greater or less than the maximum molecular moisture capacity. If the moisture content of the medium in the column is less than the moisture content corresponding to the maximum molecular moisture capacity, then the solid phase becomes additionally saturated with tritiated water, with isotope-exchange displacement of all unlabeled hydrogen. In the other case, isotope-exchange displacement of unlabeled hydrogen and filling of the pores with tritiated water take place. Hydrogen present in various forms of bonding in the solid phase will conventionally be called old, and the hydrogen of the water introduced into the column during filtration will be called new. The theory of isotope exchange of hydrogen under dynamic con-

ditions can be developed on the basis of the general theory of sorption dynamics (^1). All the main aspects of this process can be revealed by considering the equilibrium regime in the absence of any spreading (kinetic and hydrodynamic) factors. Suppose that equilibrium is established instantaneously and that the factors causing spreading of the sorption-dynamics front are absent. According to the theory of sorption dynamics (^1), the front of the zone of new hydrogen in a column of porous medium should move with the velocity:

$$v_{\mathrm{H}} = uh_{\mathrm{H}}/(1 + h_{\mathrm{H}}), \tag{1}$$

where u is the mean linear velocity of the water flow in the pores of the column; h_{H} is the distribution ratio for new hydrogen, numerically equal to the ratio of the equilibrium amount of hydrogen in the free mobile water m_1 to the sum of the equilibrium amounts of hydrogen in the molecularly sorbed

water m_2 and chemically bound isotope-exchange hydrogen m_3, i.e.

$$h_H = m_1/(m_2 + m_3). \tag{2}$$

The distribution ratio for tritium will be somewhat larger than for stable hydrogen, since tritium is concentrated more in free water than in bound water and other chemical compounds:

$$h_T = \alpha h_H, \tag{3}$$

where α is the effective distribution coefficient of tritium.

It follows from equality (3) that the tritium front (the tracer) will somewhat precede the front of new stable hydrogen. The velocity of motion of the tritium front will be

$$v_T = uh_T/(1 + h_T). \tag{4}$$

By measuring the activity of separate water samples at the outlet of the column, one can obtain the frontal breakthrough curve. Under real conditions, kinetic and hydrodynamic factors of front spreading will act. However, proceeding from the law of conservation of matter, the effective boundary of the tritium front can be established from the experimental breakthrough curve.

Fig. 1. Schematic breakthrough chromatogram for the case of displacement of old hydrogen by new hydrogen from a soil column previously completely saturated with water

Let a column of porous medium with complete moisture saturation be taken for the experiment. In this case, during filtration of tritium-labeled water, free old water will first be displaced from the column. Its volume is

Schematic breakthrough chromatogram for the case of displacement of old hydrogen by new hydrogen from a soil column previously completely saturated with water

Figure 1: Schematic breakthrough chromatogram for the case of displacement of old hydrogen by new hydrogen from a soil column previously completely saturated with water

$$V_0 = LQ, \tag{5}$$

where L is the height of the layer of porous medium, Q is the cross-sectional area of filtration.

Then water containing old isotope-exchange hydrogen will emerge. The filtrate volume at which the end of the emergence of the old isotope-exchange hydrogen will be recorded is determined on the basis of (1) and (5) by the formula

$$V_H = V_0(1 + h_H)/h_H. \tag{6}$$

Similarly, on the basis of (4) and (5), we obtain the value of the volume at which tritium will appear at the outlet of the column:

$$V_T = V_0(1 + h_T)/h_T. \tag{7}$$

The graph of water emergence from the column is shown schematically in Fig. 1. Since the volumes of water are proportional to their masses (the density of water is constant), from Fig. 1 we have

$$\frac{V_H - V_0}{V_T - V_0} = \frac{m_2 + m_3}{m_T - m_1}. \tag{8}$$

The coefficient α in (3) is determined by the formula

$$\alpha = (m_2 + m_3) \Big/ \left(\frac{m_2}{\alpha_{1,2}} + \frac{m_3}{\alpha_{1,3}} \right), \tag{9}$$

where $\alpha_{1,2}$, $\alpha_{1,3} = \alpha_{1,2}\alpha_{2,3}$ are the tritium distribution coefficients in the corresponding parts of the system. From formulas (6), (7), and (9) we obtain the calculation formula for determining m_3:

$$m_3 = \alpha_{1,3}(m_T - m_1) - \alpha_{2,3}m_2. \tag{10}$$

Let us introduce several additional notations: m_1^0 is the mass of old hydrogen in the free water of the initial moisture-saturated column of porous ···

Fig. 2. Experimental stepwise breakthrough curves for soil columns preliminarily saturated with water. 1 –for horizon A_1, 2 –for horizon A_2

Figure 2: Fig. 2. Experimental stepwise breakthrough curves for soil columns preliminarily saturated with water. 1 –for horizon A_1, 2 –for horizon A_2

medium; m_2^0 is the mass of old hydrogen in molecularly sorbed water; m_3^0 is the mass of old chemically bound hydrogen of the solid phase of the porous medium.

Then, for a dry column of porous medium, analogously to equality (10), one can obtain:

$$m_3^0 = \alpha_{1,3}(m_T + m_2) - \alpha_{1,3}m_2; \tag{11}$$

for a porous medium under-saturated to full molecular moisture capacity:

$$m_3^0 = \alpha_{1,3}(m_T + m_2 - m_2^0) - \alpha_{2,3}m_2; \tag{12}$$

for a column containing some amount of free pore moisture:

$$m_3^0 = \alpha_{1,3}(m_T - m_1^0) - \alpha_{2,3}m_2^0. \tag{13}$$

Fig. 2. Experimental stepwise breakthrough curves for soil columns preliminarily saturated with water. **1** –for horizon A_1, **2** –for horizon A_2

As an example illustrating the possibilities of applying the theory presented, we give the results of experiments with soil columns at their initial full moisture saturation with air-dry and absolutely dry soils. For the experiments a heavy loamy subsoil was chosen, taken in the vicinity of the Belyi Rast station, Moscow oblast, differentiated by horizons A_1, A_2, and B. The soil samples were first ground in a mortar and sieved through a 0.5 mm sieve. The soil columns were prepared in glass tubes about 10 mm in diameter and about 20 cm long. To collect portions of filtrates at the column outlet, a device with a graduated receiver was used. Filtrate samples of 0.5 ml were taken. The specific activity of tritium in the samples a_ϕ was measured on a liquid-scintillation radiometric setup described previously (2). Tritiated water was passed through the columns until, at the outlet, a constant specific activity of the filtrate was established, equal to the initial specific activity of the labeled water a_0. From the measurement results, stepwise breakthrough curves were constructed as the dependence of the relative specific activity of the sample a_ϕ/a_0 on the filtrate volume V. Figure 2 presents the stepwise curves obtained in this way for experiments with soils preliminarily fully saturated with water. Dashed lines mark the mean effective boundaries of the fronts: the front of old mechanically displaced water, the tritium front, and the front of new hydrogen.

The experimental results were used to determine the content of chemically bound isotope-exchangeable hydrogen in soils C, which was expressed in grams of hydrogen per 1 g of absolutely dry soil. The content of chemically bound isotope-exchangeable hydrogen without allowance for isotope effects, C', was also calculated, i.e., under the assumption that $\alpha_{1,2} = \alpha_{2,3} = \alpha_{1,3} = 1$. This quantity should ultimately characterize the sorbability of tritium by soils as a result of isotope exchange. In all calculations it was assumed that

$$m_2 = 0.05 \cdot {}^1/_9\, m, \tag{14}$$

where m is the mass of absolutely dry soil in the column, determined by the hot-drying method, since for all the samples studied the content of molecularly sorbed water, in which the isotope effect is manifested in the distribution of tritium, was about 5% of the absolutely dry mass.

soil. According to the data obtained earlier ([3]), $\alpha_{1,2} = \alpha_{2,3} = 1.15$; $\alpha_{1,3} = 1.32$. The total mass of free and bound water in the soil column, $m_1 + m_2$, was determined by weighing the column with soil before and after the experiment.

The conditions under which the experiments were carried out and the results of the calculations are given in Table 1, where the masses $m_1, m_1^0, m_2, m_2^0, m_3, m_3^0$, and m_T are expressed in terms of H_2O. Also given there are the results of calculations of the effective distribution coefficient of tritium by formula (9), the distribution ratios h_H and h_T by formulas (2) and (3), the relative front velocities v_H/u and v_T/u by formulas (1) and (4), and v_T/v_H.

Table 1

Conditions of the experiments and results of analysis of experiments on the isotope-exchange sorption of tritium from aqueous solutions by heavy-loamy sod-podzolic soils under dynamic conditions

Soil	m	m_1^0	m_1	m_2^0	m_2	m_T	$m_3 = m_3^0$
Horizon A_1	11.28 *	11.14	11.14	0.56	0.56	12.19	0.74
Horizon A_1	9.48 **	0.05	8.21	0.47	0.47	0.580	0.16
Horizon A_1	10.82 ***	0.00	8.35	0.00	0.54	0.175	0.32
Horizon A_2	6.82 *	3.34	3.34	0.34	0.34	3.81	0.23
Horizon A_2	9.77 **	0.00	4.35	0.23	0.49	0.265	0.13
Horizon A_2	15.76 ***	0.00	7.19	0.00	0.79	0.135	0.31

Soil	m	m_1^0	m_1	m_2^0	m_2	m_T	$m_3 = m_3^0$
Horizon B	9.47 **	0.06	5.09	0.47	0.47	0.550	0.10
Horizon B	15.33 ***	0.00	7.44	0.00	0.77	0.125	0.29

Soil	C	C'	$\bar{\alpha}$	h_H	h_T	v_H/u	v_T/u	v_T/v_H
Horizon A_1	0.0073	0.0048	1.24	8.57	10.63	0.90	0.91	1.01
Horizon A_1	0.0019	0.0007	1.19	13.03	15.51	0.93	0.94	1.01
Horizon A_1	0.0033	0.0018	1.21	9.71	11.75	0.91	0.92	1.01
Horizon A_2	0.0037	0.0021	1.20	5.86	7.03	0.85	0.87	1.02
Horizon A_2	0.0015	0.0004	1.18	7.01	8.27	0.88	0.89	1.01
Horizon A_2	0.0022	0.0009	1.19	6.54	7.78	0.87	0.89	1.02
Horizon B	0.0012	0.0002	1.18	8.93	10.54	0.90	0.91	1.01
Horizon B	0.0021	0.0009	1.19	7.02	8.35	0.88	0.89	1.01

* Experiments with columns of soils completely saturated with moisture.
** Experiments with columns of air-dry soils.
*** Experiments with columns of soils dried at 105°.

The experiments give a quite definite picture of the behavior of tritium during the filtration of tritiated water through soil: the effective distribution coefficient of tritium $\bar{\alpha}$ in the soil-soil solution system is on average 1.20; as a result of isotope-exchange sorption of hydrogen by the soil, the mean transport velocity of new hydrogen and tritium is less than the mean velocity of the water flow in the soil pores by approximately 10%, which is consistent with the results of Kaufman et al. ([4]), obtained by another method; the difference in the transport velocities of tritium and of new nonradioactive hydrogen, characterized by the ratio v_T/v_H, is small—of the order of 1-2%. In practice, this difference may be neglected and it may be considered that the tritium tracer reproduces, with accuracy sufficient for practical purposes, the sorption dynamics of labeled water.

Timiryazev Agricultural Academy

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Note: Figure translations are in progress. See original paper for figures.