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The influence of freeze – thaw process on the stability of natural geochemical barriers during sorpting radionuclides on them

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Modern periodic variations in climate affect the steady-state equilibrium processes in both natural and anthropogenic systems. Reveal regularities of influence of climatic parameters changing on the natural environment in order to forecast ecological consequences is a challenge. In recent decades for the environmental protection there is a tendency to safe disposal of radioactive wastes using natural materials. The use of peats as a matrix for binding and long-term retaining of radionuclides allows one the hand to ensure reliability and durability of conservation, on the other hand to reduce the production costs, because peat is cheap to obtain.

Humic substances (HS) contained in peat form stable compounds with radionuclides and can be used as a powerful geochemical barrier. In addition, the HS show a high resistance to chemical and thermal destruction. However, in conditions of global climate fluctuation, structural parameters of the mineral matrix and their ability to absorb toxicant elements as sorption barriers have been changed.

Below there are some experimental results about the uranium absorption from solutions by the peat samples of different genesis (high-moor, transitional and valley), and also establishment of relationship between the structural changes under the influence of climate variations and their sorption capacity. We used samples of peat of different origin - high-moor, transitional and valley, obtained from different Siberian deposits.

Sample preparation included screening peat patterns and then splitting into fractions by sedimentation. For experiments on the uranium sorption the peat fractions less than 2 microns were used. Sorption capacity was determined by changes in the concentration of initial solutions of uranyl in the liquid phase after contact with the sample of peat during the recorded time intervals. Proportion of liquid and solid phases varied in the range of 100:1 - 100:3. Phase separation (after sorption) was carried out in a centrifuge at 15 thousand rpm. Uranium concentrations in the range of 10^{-1} – 10^{-7} g/l were measured on an atomic emission spectrometer with inductively coupled plasma IRIS Advantage. The mass spectrometry method with inductively coupled plasma (ICP MS) of high-resolution ELEMENT by FINNIGAN MAT (Germany) with a magnetic sector and double focusing was used for the analysis of low concentrations of radionuclides. EPR researches were performed on radiospectrometer «Kadiopan», fmod= 100 kHz, T = 293°C. Shooting of infrared spectra were recorded on double-beam spectrometer Specord 75 IR in the range of 400-4000 cm^{-1} with a tablet of pure KBr in the parallel channel.

Table 1. Changing the uranium concentration in solution during the sorption by different types of peat (g/l). Initial concentration of uranium of $1.0*10^{-3}$ g/l

Sample	Sorption duration, min				
	5	10	20	30	50
High-moor peat	$1.2*10^{-4}$	$7.4*10^{-5}$	$2.1*10^{-5}$	$1.1*10^{-5}$	$8.2*10^{-6}$
Transitional peat	$0.9*10^{-4}$	$0.8*10^{-5}$	$6.8*10^{-6}$	$3.6*10^{-6}$	$2.3*10^{-6}$
Valley peat	$1.2*10^{-4}$	$9.8*10^{-5}$	$3.9*10^{-5}$	$1.6*10^{-5}$	$1.0*10^{-5}$

Table 1 shows the results of uranium absorption with initial concentration of $1·10^{-3}$ g/l by peat samples of different origin: high-moor, transitional and valley. It should be noted that the rate of interaction between the two phases was the largest on the initial pieces of kinetic curves (in the first 20-30 min. of the experiment), and then the binding rate of uranium by peats remained constant. Transitional peat (decrease the uranium concentration in a solution from $1*10^{-3}$ to $3.6*10^{-6}$ g/l for the first 30 min. of the experiment) has the highest sorption index. The absorptive capacity of high-and low-moor peat (up to $1.3*10^{-5}$ and $1.6*10^{-5}$ g/l) is rather lower with the ratio of liquid and solid phases 1:100. While changing the peat-solution ratio to 2:100 and 3:100, the absorption efficiency during 30 min. slightly reduced - for the transitional, high-and low-moor peats to values of $7.4*10^{-5}$–$3.8*10^{-5}$ g/l; $5.4*10^{-5}$–$8.9*10^{-5}$ g/l; $7.8*10^{-5}$–$1.1*10^{-4}$ g/l, respectively. But further while the period of contact of solution with peat was prolonged, absorption coefficients increased that indicates the diffusive nature of the process. High exchange capacity of humic acids (1200–1950 mg-eq/100g) provides the formation of strong complexes with radionuclides, that plays a crucial role in their distribution and deposition in natural conditions.

Present variations in climatic conditions (temperature jump, changing the amount of water in the structure, rising the ionic strength of solutions due to increased leaching of salts from minerals) lead to alteration of the equilibrium sorption parameters. This affects the absorption and the retention of peats. It is known that the peat ion-exchange properties are associated with the ability to chemical interaction of functional groups, mainly carboxyl and amino groups of organic acids. The method of infrared spectroscopy was used to evaluate structural changes in peats and to define the role of different functional groups in a stable binding of the radionuclides molecules. Water molecules that are parties in the formation of supramolecular structures acts an important role in operation of the peat geochemical barriers. According to differential thermal analysis it is revealed that water in peats has various forms (physically and chemically bound, structurally trapped water and water of mechanical retention). We have found that depending on the amount of water in the initial structure of peats (from 41,7 to 65,9%) carboxyl groups of humic acids of peats were ionized. While the number of freezing-thawing cycles increases, the transformation into carboxylate group: $\text{-COOH} \rightarrow \text{-COO}^-$ followed by interaction with a positively charged ion of uranyl. The appearance of absorption bands in the region of stretching vibrations 1580 – 1590 sm^{-1} in the infrared spectra is a direct evidence of interaction between the -COOH groups of humic acids with uranyl cations, affecting the ability of peat to absorb radionuclides. At the same time there is an increase in the number of hydroxo forms of uranium, which actively interact with other functional groups of humic acids and form donor-acceptor and hydrogen bonds. This fact is proved by significant reduction in the peaks intensity in the infrared spectra belonging to phenolic hydroxide of peat fulvic acids.

In comparison with the original samples significant changes in the region of stretching and deformation vibrations of ionized carboxyl groups, alcohol groups, were observed in the infrared spectra of uranium samples. While the cycles of thermal fluctuations with the freezing – thawing of uranium-bearing peats for the region below 950 - 980 sm^{-1} increased, the specific absorption of substituted aromatic structures of humic acids appeared. Later the bands at 600, 1100–1160 sm^{-1} arose that indicates the variations in peat of groups of $RCH{=}CH_2$, $CH_2{-}O{-}CH_2$, etc. The manifestation of these groups related to the components of humic acids showed the profound structural changes in peats. In general, the infrared-spectrometric researches of peats subjected to repeated freeze – thaw procedures revealed the presence of deformation disruptions, and also partial destruction of the initial supramolecular structures.

Along with the presence of the significant amount of functional groups in humic substances mineral matrix of peats contains all sorts of structural defects. The method of electron paramagnetic resonance (EPR) was used to fix such states and to estimate their number. The EPR recorded a free organic radical (FOR) and ion Fe^{3+} complexes in the studied peat patterns. Spectrum of FOR is represented as a single symmetric line in the samples of high-moor and transitional peats and as an asymmetrical line (due to the superposition of two points) in a sample of low-moor peat with a g-factor close to that for a free electron with an unresolved hyperfine structure. This paramagnetic center is typical of the high-molecular natural compounds to which humic acids belong. It has been established that the unpaired FOR electron is localized on broken links in the side branches of condensed carbon rings. FOR formation in peats can be represented as a result of the breaking of the carbon-hydrogen bonds under drastic temperature fluctuations. In addition, dehydroxylation (removal of OH groups), demethylation (removal of methyl groups, break of aliphatic chains) can cause the bond breaking. Simultaneously, the size of nets (the number of rings) increase. Detachment of side groups from the ring leads to the formation of new C–C bonds, that promotes the growth of the ring system. Parameters of FOR spectra are presented in Table 2.

ΔH (the width of the spectrum line) is determined by the unresolved splitting occurred due to interaction of the unpaired electron with the surrounding protons (shown by the DENR), but not due to direct interaction with other unpaired electrons or the spin-lattice interaction with the rest of the molecule.

Table 2. Parameters of free organic radicals spectra

Peat	№ 1 high-moor	№2 transitional	№3 valley
ΔH mTl	0.4	0.4	0.6
g-factor	2.0027	2.0026	2.0032
Line shape	Symmetric	symmetric	asymmetric
Int., rel. unit.	355	912	879(1270)*

*The total intensity of the two centers is shown in parentheses.

The g-factor value close to g_e (2,0023) testifies that the observed signal obeys the Curie law and is stipulated by localized centers of aromatic nature. If g > 2,0023, it can be the conduction electrons which obey Fermi-Dirac statistics.

Table 3. Parameters of the organic radicals' spectra in peat samples of different origins, subjected to freezing-thawing

Sample	Organic radical Nx spin/g X 10^{17}	ΔH mTl	g-factor
High-moor peat initial	0.61	0.42	2.0027
Transitional peat initial	1.52	0.41	2.0026
Valley peat initial	1.87	0.55	2.0028
High-moor peat (-18^0C)	1.43	0.38	2.0028
Transitional peat (-18^0C)	2.84	0.41	2.0027
Valley peat (-18^0C)	3.73	0.48	2.0033

Table 3 presents the results of changing in the structure parameters at fivefold freezing–thawing of peat samples of different genesis from Western Siberian deposits. It was experimentally shown that multiple freezing–thawing of peat considerably intensifies structural defects, and further leads to the destruction of the near-surface layer. In this case, the number of fine-grained debris that are carried away by surface water for significant distances increases.