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Reactionary – electrodiffusion equations of transport processes of electrolyte solutions of radioelements through porous clayey structures

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The statistical model of the water solution of radioactive elements and the porous clayey matrix is proposed. The generalized transport equations for the description of diffusion, sorption, radiative processes and chemical reactions are obtained taking into account the electromagnetic processes.

Key words: *diffusion, sorption, electromagnetic processes, porous clayey matrix, Chornobyl catastrophe*

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1. Introduction

The experimental and theoretical studies of migration processes of radionuclides in soils [1,2] which were intensively carried out prior to Chornobyl catastrophe, have shown that the diffusion processes are the basis mechanisms of the radionuclide transport. These processes become more complicated because the soil has such features as heterogeneity, porosity, capability of adsorbing ions, etc. Therefore, the study of the mechanisms of adsorption, desorption, radionuclide diffusion in soil are of considerable interest from the viewpoint of their use in designing the radiation-absorbing barriers. These barriers can be constructed as obstacles on the way of subsoil waters which contain isotopes of caesium, strontium, europium, plutonium, americium, etc. Such a composition of isotopes in subsoil waters is characteristic of Chornobyl zone. Bentonite clay is of special interest while constructing such barriers. The phenomenological approach [2] with the application of the modified diffusion equation (the so-called Fick equation) is used for a general theoretical description of radionuclide diffusion in a soil. Additional parameters, which characterize the properties of a soil, are present in the equation of radionuclide diffusion. The soil is considered to be a continuous medium with stationary values of diffusion constants of radionuclides which are determined experimentally. Probably, such an approach cannot describe complicated migration processes of radionuclides including specific interactions with ions, molecules, and colloid particles in the soils. The mathematical modelling of radionuclide transport in the upper soil layers [3–10] is performed on the basis of macroscopic diffusion and hydrodynamic equations in which the transport coefficients, namely, diffusion coefficient and adsorption-desorption constants are the unknown parameters which should be primarily determined experimentally. Apparently, such an approach is incapable of describing the complex processes of radionuclide migration taking into account the specific interactions between ions, molecules, colloidal particles. Radioactive elements are capable of creating different forms of aquated ions, molecules, double and mixed complexes, mononuclear and polynuclear hydrolysates, colloidal particles and products of the radiolysis processes [11]. This is a specific feature of water solutions that contain radioactive elements ^{235,238}U,^{238,239}Pu, ^{241}Am, ^{90}Sr, ^{134,137}Cs, ^{242,244}Cm and others. From the analysis of radionuclide forms in water and other solutions it follows that the radionuclides basically create the composite complexes in three forms:

cationic, anionic and neutral (colloidal particles, polymers), which follows from the analysis of radionuclide forms in water and other solutions.

In particular, the sorption of plutonium in a "subsoil water – natural soil" system is investigated in [12] using a radiometric method (through α – radiation of ^{239}Pu) depending on the concentration of plutonium, its oxidative state and the composition of the soil. Subsoil water of carbonate-bicarbonate type with pH=7 contains ions Pu^{4+}, PuO_2^{2+}, PuO_2^{2+} in this system. It is shown that the soil, which contains the clay minerals of kaolinite and montmorillonite groups 30–35%, carbonates 20%, quartz 3–5%, minerals of micas and hydromicas group up to 30%, is a good adsorbent. However, it has not been found out reliablly which exactly mechanism decreases the quantity of Pu in a solution since the slightly soluble compounds $Pu(OH)_4$ and hydroxocarbonates $Pu(OH)_2CO_3$ at the given values of pH have been discovered. It is revealed that the composition of the soil has the greatest effect upon the interphase distribution of plutonium. Both the surface soil which contains aluminosilicates, plant remains, and the soil out of clayey minerals, micas and carbonates show the high enough and better properties with respect to Pu(V), Pu(VI). The presence of cations is typical of these soils. However, the results of desorption have shown that only a small part of Pu(V) and Pu(VI) caused by the ionic mechanism is sorbed. The relation of different forms of plutonium in subsoil waters depends on concentration of Pu, HCO_3^-, CO_3^{2-}, H^+. Interphase distribution of plutonium will be defined both by taking into account the composition and properties of subsoil waters and the physical and chemical features of soils. The existence of such forms should be taken into account at the description of the processes of radionuclide migration in soils and underground waters. Statistical models in which consideration is conducted at a microscopic level, satisfy the same requirements. Here in order to study the migration of radionuclides it is necessary to use the statistical approaches which are based on the equitable account of the radiative particles and ions, water molecules and colloidal particles. Their presence due to an interaction can strongly effect the transport of radionuclides. It is important to note the results of works [13,14], in which the processes of an adsorption of uranyl, caesium and strontium on a surface of silicates and aluminosilicates are explored using the quantum-chemical calculations (an ab-initio method). It is shown that the surfaces adsorb the compounds UO_2^{2+}, Cs^+, Sr^{2+}.

The detailed information on distribution of charges and distances between atoms of an adsorbate and sorbent is obtained, and the forces of bonds are calculated. These results are extremely important in constructing the statistical models of such systems. The detailed analysis of possible physicochemical processes which can occur at penetration of aqueous solutions through the layer of bentonite clay has been fulfilled. The obtained results give grounds to claim that the clayey porous matrix in an isoelectric state is characterized by coagulative compact structure. The ionization of functional groups causes the deformation of the porous associate skeleton. Thus, the density of porous clayey matrix due to the action of two factors is not a stationary value during the process of electrolyte infiltration. The first factor is the Coulomb repulsion of structural particles, the second one is the magnification of water sorption due to the swelling of clayey matrix. The effect of these two factors increases at the absence of strong chemical interaction when the ion sorption by a porous surface is defined by their charge condition. The superfine clay particles get a negative charge in the water medium. Therefore, ions H^+, Fe^{3+} , Cu^{2+}, $[Fe(CN)_6]^{4-}$ appear to be counterions for clayey structure. The dissociation degree of available acidic groups is defined by the level p of the disperse encirclement. Ions abstain with different force by the surface of porous associates at electrolytes entering the disperse clayey medium. The adsorption of ions that form nonsoluble compounds will be stronger than the adsorption of ions which are capable of forming the water-soluble salts. The expression which describes the ion exchange at the formation of nonsoluble compounds can be presented in the form:

$$\mathrm{RH}^+ + \mathrm{X}^{n+}\mathrm{Y}^{p-} \Rightarrow \mathrm{RX} + \mathrm{RH}^+\mathrm{Y}^{p-}.$$

In the case when the water-soluble salts are formed, the expression for the description of ion exchange process is as follows:

$$\mathrm{R}^-\mathrm{H}^+ + \mathrm{A}^+\mathrm{B}^- \Leftrightarrow \mathrm{R}^-\mathrm{A}^+ + \mathrm{H}^+\mathrm{B}^-,$$

where R are the particles of the porous associate matrix which plays the role of an ion exchanger, X, Y, A, B, H are the ions which take part in the exchange. Therefore, with sufficient confidence it can be asserted that the entering of the water-soluble compounds causes structural changes of a porous matrix due to a sorption of polyvalent ions. The basic effect of this process is the formation of compact associates which decrease the charge of the surface. This decrease of the charge should be taken into account while constructing the transport equations on the border of electrolyte and the surface of the porous medium. These examinations are also actual at calculations within the framework of the molecular hydrodynamics of electro-osmotic processes in montmorillonite clay [15].

This paper proposes a statistical model of "the water solution of radioelements – the porous clayey matrix" system. The generalized reactionary-diffuse transport equations for the description of the diffuse, radiative, sorbtion processes and chemical reactions has been obtained.

2. Statistical model of "the water solution of radioelements – the porous clayey matrix" system. The generalized reactionary-diffusion transport equations

For theoretical estimations of superficial processes it is important to establish a set of parameters which can be defined experimentally. Superficial processes occur at interaction of water solutions of radioactive elements with the surface and porous space of clayey structures which are modified by ferrocyanide of iron and copper. The electrochemical impedance is one of the interesting standard approaches of theoretical estimations and experimental measurements in case of interaction of electrolytes with electroconductive systems [16]. It is important to consider the possibility of using the electrochemical impedance methods for the research of electrochemical reactions, diffusion and adsorption processes in superficial area "the electrolyte – the porous matrix". The experimental characteristics of electrochemical impedance can be connected with the reactionary-diffusion equations, which take into account the processes of diffusion of ions, molecules, and their adsorptions. Thus, one of the important problems is the calculation of the transport processes of water solution particles in a porous space of the clayey matrix where the adsorption processes can really take place. The electrolyte conductivity and the ion diffusion in pores can be given by the expression:

$$\sigma^{\mathrm{E}} = \phi^{3/2}\sigma, \quad D^{\mathrm{E}} = \phi^{3/2} D,$$

where ϕ is the porosity of clayey matrix. The change of ion concentration in porous space of the clayey matrix in the semi-phenomenological theory of electrochemical processes can be described within the framework of the generalized diffusion model, in which the driving force is the difference of potentials Φ_{E} of electrolyte and Φ_{s} of clayey matrix $U = \Phi_{\mathrm{s}} - \Phi_{\mathrm{E}}$:

$$\phi\frac{\partial}{\partial t}C = D\nabla^2 C + \frac{(1-t^{+})}{F}\vec{\nabla}\cdot\vec{j}_{\mathrm{E}} - K_{\mathrm{ad}}C - \lambda C, \tag{2.1}$$

where

$$\vec{j}_{\mathrm{E}} = -\sigma\vec{\nabla}\Phi_{\mathrm{E}} + \frac{\sigma R_{\mathrm{B}} T}{F}(1-t^{+})\frac{1}{\tilde{C}}\vec{\nabla}C \tag{2.2}$$

is the electric current of solution anions (Cs^{+}, Sr^{2+}, UO_2^{2+}, PuO_2^{2+}), C is the ion concentration, t^{+} is the transfer number of ions, D is their diffusion constant, R_{B} is the gas constant, F is the Faraday constant, K_{ad} is the constant of ion adsorption on the pore surface of the clayey matrix, λ is the decay constant of the corresponding radionuclide. In the solid phase of a porous matrix the change of the filled density Θ by radionuclide ions of solution can be described by the equation:

$$\frac{\partial}{\partial t}\Theta = D_{\mathrm{s}}\vec{\nabla}\cdot\left[(1+\frac{\mathrm{d}\ln\gamma}{\mathrm{d}\ln\Theta})\vec{\nabla}\Theta\right] - \lambda\Theta, \tag{2.3}$$

where D_{s} is the diffusion constant of ions in the solid phase of matrix, γ is the ion activity coefficient. Thus, the potential Φ_{s} of the porous matrix is determined by the electric current:

$$\vec{j}_{\mathrm{s}} = -\sigma_{\mathrm{s}}\vec{\nabla}\cdot\Phi_{\mathrm{s}}, \tag{2.4}$$

where $\sigma_{\rm s}$ is the electrical conductivity of the porous matrix. The essential shortcoming of this approach is the absence of the dynamics of the solvent molecules, of the polarization effects on "the electrolyte – the porous matrix" interface, of the physical processes connected with $\alpha-\beta-\gamma-$ radiation of radionuclides, namely of the microradiolysis processes, of the oxidation-reduction reaction.

The statistical theory of diffusion processes for water solutions of radioelements in soils and in subsoil waters was developed in work [17]. Here the generalized diffusion equations are obtained taking into account the spontaneous radioactive decays and the decays under the action of neutrons. They can be modified with the inclusion of processes of an adsorption and a desorption of solution ions on the soil particles as well as of electromagnetic processes:

$$\begin{aligned}
\vec{\nabla}\cdot\vec{B}(\vec{r};t) &= 0, \qquad\qquad \vec{\nabla}\cdot\vec{D}(\vec{r};t)=\phi\sum_{\alpha}Z_{\alpha}e\delta n^{\alpha}(\vec{r};t),\\
\vec{\nabla}\times\vec{E}(\vec{r};t) &= \frac{\partial}{\partial t}\vec{B}(\vec{r};t), \qquad \vec{\nabla}\times\vec{H}(\vec{r};t)=\frac{\partial}{\partial t}\vec{D}(\vec{r};t)+\vec{j}(\vec{r};t), \qquad (2.5)\\
\vec{j}(\vec{r};t) &= \phi\sum_{\alpha}Z_{\alpha}e(\delta\vec{J}^{\alpha}_{d}(\vec{r};t)+\delta\vec{J}^{\alpha}_{\rm E}(\vec{r};t)+\ \delta n^{\alpha}(\vec{r};t)\vec{v}(\vec{r};t)),
\end{aligned}$$

where $\vec{B}(\vec{r};t)$, $\vec{E}(\vec{r};t)$ are the intensity vectors of the average values of magnetic and electric fields and $\vec{H}(\vec{r};t)$, $\vec{D}(\vec{r};t)$ are the induction vectors that correspond to them. $\phi=V_f/V$ is the porosity of clay matrix, V_f is the volume which occupies the water solution of electrolyte in a porous space of the matrix, V is the complete volume, Z_{α} is the valency of ions, $\delta n^{\alpha}(\vec{r};t)$ is the average value fluctuations of ion densities of sort α (namely Cs^{+}, Sr^{2+}, UO_2^{2+}, PuO_2^{2+}, etc.) of the water solution of electrolytes. $\vec{j}(\vec{r};t)$ is the density of the complete average ionic current which is expressed through diffusive $\delta\vec{J}^{\alpha}_{d}(\vec{r};t)$, ionic $\delta\vec{J}^{\alpha}_{\rm E}(\vec{r};t)$ and convective $\delta n^{\alpha}(\vec{r};t)\vec{v}(\vec{r};t)$ currents. $\vec{v}(\vec{r};t)$ is the average velocity of the water solution in porous matrix. $\delta n^{\alpha}(\vec{r};t)$ and $\delta\vec{J}^{\alpha}_{d}(\vec{r};t)$, $\delta\vec{J}^{\alpha}_{\rm E}(\vec{r};t)$, $\delta n^{\alpha}(\vec{r};t)\vec{v}_f(\vec{r};t)$ are interlinked by transport equations for each phase. They are obtained using the method of nonequilibrium statistical operator similar to [17] and are as follows:

$$\begin{aligned}
\frac{\partial}{\partial t}\delta n^{\alpha}(\vec{r}_l;t) &= -\frac{\partial}{\partial\vec{r}_l}\Big(\delta\,\vec{J}^{\alpha}_{d}(\vec{r}_l;t)\ +\ \delta\,\vec{J}^{\alpha}_{\rm E}(\vec{r}_l;t)+\delta n^{\alpha}(\vec{r}_l;t)\vec{v}(\vec{r}_l;t)\Big)\\
&\quad -\sum_{\beta}A^{\alpha a}(\vec{r}_l;t)\,\delta n^{a}(\vec{r}_l;t)\ -\ A^{\alpha}(\vec{r}_l;t)\delta n^{\alpha}(\vec{r}_l;t), \qquad (2.6)
\end{aligned}$$

where

$$\begin{aligned}
A^{\alpha\beta}(\vec{r}_l;t) &= \int_0^{\infty}J(\vec{r}_l;E;t)\,\sigma_{\alpha\beta}(E)\,{\rm d}E\ +\ L_{\alpha\beta}\lambda_{\beta}, \qquad (2.7)\\
A^{\alpha}(\vec{r}_l;t) &= \int_0^{\infty}J(\vec{r}_l;E;t)\,\sigma_{\alpha}(E)\,{\rm d}E\ +\ L_{\alpha}\lambda_{\alpha},\\
\vec{J}^{\alpha}_{d}(\vec{r}_l;t) &= \sum_{as}\frac{1}{V_{\rm s}}\int\limits_{V_{\rm s}}{\rm d}\vec{r}^{\prime}_{\rm s}\int_{-\infty}^{t}{\rm e}^{\varepsilon(t'-t)}D^{\alpha a}(\vec{r}_l,\vec{r}^{\prime}_{\rm s};t,t')\\
&\quad\times\frac{\partial}{\partial\vec{r}^{\prime}_{\rm s}}\delta n^{a}(\vec{r}^{\prime}_{\rm s};t,t')\ +\sum_{a,b}\sum_{k,s}\frac{1}{V_{\rm s}}\int\limits_{V_{\rm s}}{\rm d}\vec{r}^{\prime}_{\rm s}\frac{1}{V_k}\int\limits_{V_k}{\rm d}\vec{r}^{\prime}_k\int\limits_{-\infty}^{t}{\rm e}^{\varepsilon(t'-t)}\\
&\quad\times K^{\alpha,ab}(\vec{r}_l,\vec{r}^{\prime}_{\rm s},\vec{r}^{\prime}_k;t,t')\delta n^{a}(\vec{r}^{\prime}_{\rm s};t')\delta n^{b}(\vec{r}^{\prime}_k;t'){\rm d}t',\\
\delta\vec{J}^{\alpha}_{\rm E}(\vec{r};t) &= \sum_{\gamma a}\sum_{sk}\frac{1}{V_{\rm s}}\int\limits_{V_{\rm s}}{\rm d}\vec{r}^{\prime}_{\rm s}\frac{1}{V_k}\int\limits_{V_k}{\rm d}\vec{r}^{\prime}_k\int\limits_{-\infty}^{t}{\rm e}^{\varepsilon(t'-t)}D^{\alpha a}(\vec{r}_l,\vec{r}^{\prime}_k;t,t')\Phi^{a\beta}_{nn}(\vec{r}^{\prime}_k,\vec{r}^{\prime}_{\rm s})Z_{\beta}e\vec{E}(\vec{r}^{\prime}_{\rm s};t). \qquad (2.8)
\end{aligned}$$

In these formulas $\Phi^{a\beta}_{nn}(\vec{r}^{\prime}_k,\vec{r}^{\prime}_{\rm s})=\langle\hat{n}^{a}(\vec{r}^{\prime}_k)\hat{n}^{\beta}(\vec{r}^{\prime}_{\rm s})\rangle_0$ is the equilibrium pair distribution function of particles, $\langle\ldots\rangle_0$ denotes the averaging with the grand canonical Gibbs distribution. $\hat{n}^{\alpha}(\vec{r}^{\prime}_k)=$

$\sum_{i=1}^{N_\alpha} \delta(\vec{r}_i - \vec{r}'_k)$ is the microscopic density of particle number of α sort in the k phase. α indicates the sorts of ions of water molecules and of clayey matrix particles. $D^{\alpha\beta}(\vec{r}_l, \vec{r}'_s; t, t')$ are the generalized diffusion coefficients as functions of coordinates and time, which describe dissipative processes; $K^{\alpha,ab}(\vec{r}_l, \vec{r}'_s; \vec{r}_k"; t, t')$ are the generalized coefficients of reactions which describe the processes of adsorption, desorption and possible chemical reactions of the hydrolysis, radiolysis, complexations. The last two terms in (2.6) describe the change of radionuclide density with time, caused by neutron currents and spontaneous decays. The first summand describes the origination of radionuclides of α sort from all other nucleuses of β sort owing to (n, γ), as well as (n, f) reactions when the corresponding radionuclide of α sort belongs to decay products. The second summand describes the radionuclide decay of α sort under the action of neutrons and the spontaneous radioactive decay. The functions $A_{\alpha\beta}(\vec{r}_l; t)$, $A_\alpha(\vec{r}_l; t)$ are the velocities of corresponding reactions. $J(\vec{r}_l; E; t)$ is the spectrum of the neutron density current at the point $\vec{r}_l$ at the moment of time t. $\sigma_{\alpha\beta}(E)$ is the microscopic cross-section of radionuclide formation of α sort at the capture of neutrons with energy E by nucleus of β sort. $L_{\alpha\beta}$ is the probability of radionuclide formation of α sort at the radioactive nucleus decay of β sort. λ_α, λ_β are the nucleus decay constants of α, β sorts. The set of equations (2.6)–(2.8) is nonlinear. This set takes into account the diffusion, adsorption, desorption, ionic conduction, electromagnetic as well as radiative processes with the consideration of the porosity of a clayey matrix. Each of the currents (2.7), (2.8) gives the contribution to (2.5), while $\delta\vec{J}^{\alpha}_{\mathrm{E}}(\vec{r}_l; t)$ has the field contribution which is connected with the generalized ionic conductivity of electrolyte solution in the clayey matrix.

The generalized reactionary transport equations for ions, electrons and water molecules, products of radiolysis are obtained for the description of the reactionary phenomena in a system of the aqueous solution of radioelement-porous clayey structures taking into account the electromagnetic processes. These equations are convenient for more severe comprehension of complexity of the physicochemical processes and the statistical substantiation of the electrochemical impedance methods. They agree with the averaged Maxwell equations for electromagnetic processes:

$$\begin{aligned}
\vec{\nabla} \cdot \vec{B}_l(\vec{r}, t) &= 0, \\
\vec{\nabla} \cdot \vec{D}_l(\vec{r}, t) &= \sum_{a=1}^{N} Z_a e n^l_a(\vec{r}, t) + e n^l_e(\vec{r}, t) + \sum_f \vec{d}_f \cdot \vec{\nabla} n^l_f(\vec{r}, t) + e n^l_\beta(\vec{r}, t), \\
\vec{\nabla} \times \vec{E}_l(\vec{r}, t) &= -\frac{\partial}{\partial t} \vec{B}_l(\vec{r}, t), \\
\vec{\nabla} \times \vec{H}_l(\vec{r}, t) &= \frac{\partial}{\partial t} \vec{D}_l(\vec{r}, t) + \vec{j}^l_i(\vec{r}, t) + \vec{j}^l_d(\vec{r}, t) + \vec{j}^l_e(\vec{r}, t) + \vec{j}^l_\beta(\vec{r}, t),
\end{aligned} \tag{2.9}$$

where $\vec{B}_l(\vec{r}, t), \vec{E}_l(\vec{r}, t), \vec{D}_l(\vec{r}, t), \vec{H}_l(\vec{r}, t)$ are, respectively, the intensities and the inductions of electrical and magnetic fields of water solution. These intensities and the inductions are created by ions of a sort with density $n^l_a(\vec{r}, t)$; by electrons with density $n^l_e(\vec{r}, t)$ which arise from the radiolysis of water solution by $\beta-$ electrons; by electrons with the density $n^l_\beta(\vec{r}, t)$, which are radiated by radionuclides in solution volume and on the surface of clayey matrix; as well as by water molecules and by radiolysis products H_2O_2, HO_2 with particle density $n^l_f(\vec{r}, t)$ of f sort and with electrical dipole moment $\vec{d}_f$. Z_a is the ion valency of specie a. $\vec{j}^l_i(\vec{r}, t)\vec{j}^l_e(\vec{r}, t)\vec{j}^l_\beta(\vec{r}, t)$, $\vec{j}^l_d(\vec{r}, t)$ are respectively the average currents of ion charge, of low-energy electrons and β-electrons, as well as of the dipole moment of the polarized molecules. The expressions for currents can be obtained using the method of nonequilibrium statistical operator [17]. In approximation of the constant transport coefficients they have the following structure for ions:

$$\begin{aligned}
\vec{j}^l_i(\vec{r}, t) = \sum_a Z_a e \Big(&- \sum_\xi D^{l\xi}_{aa} \vec{\nabla} \cdot n^\xi_a(\vec{r}, t) - \sum_\xi \sum_b D^{l\xi}_{ab} \vec{\nabla} \cdot n^\xi_b(\vec{r}, t) - \sum_f D_{af} \vec{\nabla} \cdot n^l_f(\vec{r}, t) \\
&- \sum_\xi D^{l\xi}_{ae} \vec{\nabla} \cdot n^\xi_e(\vec{r}, t) + \sum_\xi D^{l\xi}_{a\beta} \vec{\nabla} \cdot n^\xi_\beta(\vec{r}, t) + n^l_a(\vec{r}, t) \vec{v}_l(\vec{r}, t) \Big) + \sum_{ab} \sigma_{ab} \vec{E}_l(\vec{r}, t)
\end{aligned}$$

$$+\sum_{af}\frac{1}{m_f}\vec{\sigma}_{af}\cdot\vec{\nabla}\vec{E}_l(\vec{r},t)+\sum_{a}\sigma_{ae}\vec{E}_l(\vec{r},t)+\sum_{a}\sigma_{a\beta}\vec{E}_l(\vec{r},t)-\sum_{a}K^a_{\mathrm{ad}}n_a(\vec{S}_\omega,t)\Theta_{\mathrm{s}}(\vec{S}_\omega,t)$$
$$+\sum_{a}K^a_{\mathrm{des}}n^l_a(\vec{r},t)\Theta_{\mathrm{s}}(\vec{S}_\omega,t), \tag{2.10}$$

where the index ξ indicates: l is the water solution, s is the porous matrix. K^a_{ad}, K^a_{des} are the constants of adsorption and desorption for ions of a sort. $n_a(\vec{S}_\omega,t)$ is the ion density of a sort adsorbed on the surface $\vec{S}_\omega$ of the interface of the systems the water solution of radioactive elements and the porous clay matrix. $\Theta_{\mathrm{s}}(\vec{S}_\omega,t)$ is the adsorption site density on the surface of a porous matrix. The ionic current of charges satisfies the conservation law:

$$\frac{\partial}{\partial t}\rho_i(\vec{r},t)=-\vec{\nabla}\cdot\vec{j}_i(\vec{r},t), \tag{2.11}$$

where $\rho_i(\vec{r},t)=\sum_a Z_a e n_a(\vec{r},t)$ is the complete density of ion charge. $\sigma_{ab}=Z_a e D_{ab} Z_b e$ is the partial electrical ion conductivity of the a and b sorts, D_{ab} is the interdiffusion coefficient. $\vec{\sigma}_{af}=Z_a e D_{af}\vec{d}_f$ is the partial electrical conductivity of ions of the a sort and molecules of the f sort, D_{af} is the interdiffusion coefficient of ions and molecules. $\vec{v}_l(\vec{r},t)$ is the average particle velocity in electrolyte. The current for molecules of the solvent has the following form:

$$\begin{aligned}
\vec{j}^l_d(\vec{r},t) \;=\;& \sum_f\frac{1}{m_f}\vec{d}_f\cdot\vec{\nabla}\Big(-D_{ff}\vec{\nabla}\cdot n^l_f(\vec{r},t)-\sum_\xi\sum_b D^{l\xi}_{fb}\vec{\nabla}\cdot n^\xi_b(\vec{r},t)\\
&-\sum_\xi D^{l\xi}_{fe}\vec{\nabla}\cdot n^\xi_e(\vec{r},t)-\sum_\xi D^{l\xi}_{f\beta}\vec{\nabla}\cdot n^\xi_\beta(\vec{r},t)+n^l_f(\vec{r},t)\vec{v}_l(\vec{r},t)\Big)\\
&+\sum_{bf}\frac{1}{m_f}\vec{\nabla}\cdot\vec{\sigma}_{fb}\vec{E}_l(\vec{r},t)+\sum_f\frac{1}{m_f}\vec{\nabla}\cdot\overleftrightarrow{\sigma}_{ff}\cdot\vec{\nabla}\frac{1}{m_f}\vec{E}_l(\vec{r},t)\\
&+\sum_f\frac{1}{m_f}\vec{\nabla}\cdot\vec{\sigma}_{fe}\vec{E}_l(\vec{r},t)+\sum_f\frac{1}{m_f}\vec{\nabla}\cdot\vec{\sigma}_{f\beta}\vec{E}_l(\vec{r},t),
\end{aligned} \tag{2.12}$$

where $\overleftrightarrow{\sigma}_{ff}=\vec{d}_f D_{ff}\vec{d}_f$ is the conductivity of dipole molecules of solution, D_{ff} is the diffusion constant of molecules. In the current (2.12) the processes of adsorption and desorption of solution molecules are not taken into account. The electrical current for electrons has the structure similar to the ions:

$$\begin{aligned}
\vec{j}^l_e(\vec{r},t) \;=\;& -e\sum_\xi\sum_b D^{l\xi}_{eb}\vec{\nabla}\cdot n^\xi_b(\vec{r},t)-e\sum_f D_{ef}\vec{\nabla}\cdot n^l_f(\vec{r},t)\\
&-e\sum_\xi D^{l\xi}_{ee}\vec{\nabla}\cdot n^\xi_e(\vec{r},t)-e\sum_\xi D^{l\xi}_{e\beta}\vec{\nabla}\cdot n^\xi_\beta(\vec{r},t)+en^l_e(\vec{r},t)\vec{v}_l(\vec{r},t)\\
&+\sum_b\sigma_{eb}\vec{E}_l(\vec{r},t)+\sum_f\frac{1}{m_f}\vec{\sigma}_{ef}\cdot\vec{\nabla}\vec{E}_l(\vec{r},t)+\sigma^l_{ee}\vec{E}_{\mathrm{s}}(\vec{r},t)+\sigma^l_{e\beta}\vec{E}_{\mathrm{s}}(\vec{r},t),
\end{aligned} \tag{2.13}$$

where σ^l_{ee}, $\sigma^l_{e\beta}$ are the electrical conductivities of electrons and β-electrons in electrolyte. The current of high-energy β-electrons has the same structure as $\vec{j}^l_e(\vec{r},t)$. Thus it is formally necessary to exchange the index e for β. However, by considering that the β-electrons have got a considerable energy, their correlations with molecules of the solution will be negligible in comparison with dynamic correlations with electrons and ions both in the solution and in the porous matrix. Therefore, for $\vec{j}^l_\beta(\vec{r},t)$ it is possible to write the expression:

$$\begin{aligned}
\vec{j}^l_\beta(\vec{r},t)=&-e\sum_\xi\sum_b D^{l\xi}_{\beta b}\vec{\nabla}\cdot n^\xi_b(\vec{r},t)-e\sum_\xi D^{l\xi}_{\beta e}\vec{\nabla}\cdot n^\xi_e(\vec{r},t)-e\sum_\xi D^{l\xi}_{\beta\beta}\vec{\nabla}\cdot n^\xi_\beta(\vec{r},t)+en^l_e(\vec{r},t)\vec{v}_l(\vec{r},t)\\
&+\sum_b\sigma_{\beta b}\vec{E}^(_l\vec{r},t)+\sigma^l_{\beta e}\vec{E}^(_{\mathrm{s}}\vec{r},t)+\sigma^l_{\beta\beta}\vec{E}^(_{\mathrm{s}}\vec{r},t),
\end{aligned} \tag{2.14}$$

$\vec{j}^{\,l}_e(\vec{r},t)$, $\vec{j}^{\,l}_\beta(\vec{r},t)$ as well as the ion current satisfy the conservation laws for the charge.

The similar equation systems for average electromagnetic fields and currents are obtained for the "porous clayey matrix" subsystem:

$$
\begin{aligned}
\vec{\nabla}\cdot\vec{B}^{(}_{\mathrm{s}}\vec{r},t) &= 0,\\
\vec{\nabla}\cdot\vec{D}^{(}_{\mathrm{s}}\vec{r},t) &= \sum_{a=1}^{N} Z_a e n^s_a(\vec{r},t) + e n^s_e(\vec{r},t) + e n^s_\beta(\vec{r},t),\\
\vec{\nabla}\times\vec{E}^{(}_{\mathrm{s}}\vec{r},t) &= -\frac{\partial}{\partial t}\vec{B}^{(}_{\mathrm{s}}\vec{r},t),\\
\vec{\nabla}\times\vec{H}^{(}_{\mathrm{s}}\vec{r},t) &= \frac{\partial}{\partial t}\vec{D}^{(}_{\mathrm{s}}\vec{r},t) + \vec{j}^{\,s}_i(\vec{r},t) + \vec{j}^{\,s}_e(\vec{r},t) + \vec{j}^{\,s}_\beta(\vec{r},t),
\end{aligned}
\tag{2.15}
$$

where the currents of electrons and ions in a porous matrix are presented by expressions:

$$
\begin{aligned}
\vec{j}^{\,s}_i(\vec{r},t) &= \sum_a Z_a e\Big(-\sum_\xi D^{s\xi}_{aa}\vec{\nabla}\cdot n^\xi_a(\vec{r},t) - \sum_\xi\sum_b D^{s\xi}_{ab}\vec{\nabla}\cdot n^\xi_b(\vec{r},t)\\
&\quad - \sum_f D^{sl}_{af}\vec{\nabla}\cdot n^l_f(\vec{r},t) - \sum_\xi D^{s\xi}_{ae}\vec{\nabla}\cdot n^\xi_e(\vec{r},t) - \sum_\xi D^{s\xi}_{a\beta}\vec{\nabla}\cdot n^\xi_\beta(\vec{r},t)\\
&\quad + n^s_a(\vec{r},t)\vec{v}_{\mathrm{s}}(\vec{r},t)\Big) + \sum_{ab}\sigma_{ab}\vec{E}_{\mathrm{s}}(\vec{r},t) + \sum_a \sigma_{ae}\vec{E}_{\mathrm{s}}(\vec{r},t) + \sum_a\sigma_{a\beta}\vec{E}_{\mathrm{s}}(\vec{r},t),
\end{aligned}
\tag{2.16}
$$

$$
\begin{aligned}
\vec{j}^{\,s}_e(\vec{r},t) &= -e\sum_\xi\sum_b D^{s\xi}_{eb}\vec{\nabla}\cdot n^\xi_b(\vec{r},t) - e\sum_f D_{ef}\vec{\nabla}\cdot n^l_f(\vec{r},t)\\
&\quad - e\sum_\xi D^{s\xi}_{ee}\vec{\nabla}\cdot n^\xi_e(\vec{r},t) - e\sum_\xi D^{s\xi}_{e\beta}\vec{\nabla}\cdot n^\xi_\beta(\vec{r},t)\\
&\quad + e n^s_e(\vec{r},t)\vec{v}_{\mathrm{s}}(\vec{r},t) + \sum_b \sigma_{eb}\vec{E}_{\mathrm{s}}(\vec{r},t) + \sigma^s_{ee}\vec{E}_{\mathrm{s}}(\vec{r},t) + \sigma^s_{e\beta}\vec{E}_{\mathrm{s}}(\vec{r},t),
\end{aligned}
\tag{2.17}
$$

$$
\begin{aligned}
\vec{j}^{\,s}_\beta(\vec{r},t) &= -e\sum_\xi\sum_b D^{s\xi}_{\beta b}\vec{\nabla}\cdot n^\xi_b(\vec{r},t) - e\sum_\xi D^{s\xi}_{\beta e}\vec{\nabla}\cdot n^\xi_e(\vec{r},t)\\
&\quad - e\sum_\xi D^{s\xi}_{\beta\beta}\vec{\nabla}\cdot n^\xi_\beta(\vec{r},t) + e n^s_\beta(\vec{r},t)\vec{v}_{\mathrm{s}}(\vec{r},t)\\
&\quad + \sum_b \sigma_{\beta b}\vec{E}_l(\vec{r},t) + \sigma^s_{\beta e}\vec{E}_{\mathrm{s}}(\vec{r},t) + \sigma^s_{\beta\beta}\vec{E}_{\mathrm{s}}(\vec{r},t).
\end{aligned}
\tag{2.18}
$$

The porous space of matrix is filled with particles of the water solution, namely with water molecules, with the radiolysis products which evolved from $\alpha-\beta-\gamma$ – irradiations of the solution. In this case it is necessary to supplement the set of equations (2.16)–(2.18) by the current densities of solution molecules in porous space of clayey matrix:

$$
\begin{aligned}
\vec{j}^{\,s}_d(\vec{r},t) &= \sum_f \frac{1}{m_f}\vec{d}_f\cdot\vec{\nabla}\Big(-\tilde{D}_{ff}\vec{\nabla}\cdot n^s_f(\vec{r},t) - \sum_\xi\sum_b \tilde{D}^{l\xi}_{fb}\vec{\nabla}\cdot n^\xi_b(\vec{r},t)\\
&\quad - \sum_\xi \tilde{D}^{l\xi}_{fe}\vec{\nabla}\cdot n^\xi_e(\vec{r},t) - \sum_\xi \tilde{D}^{l\xi}_{f\beta}\vec{\nabla}\cdot n^\xi_\beta(\vec{r},t) + n^s_f(\vec{r},t)\vec{v}_l(\vec{r},t)\Big)\\
&\quad + \sum_{bf}\frac{1}{m_f}\vec{\nabla}\cdot\tilde{\sigma}_{fb}\vec{E}_{\mathrm{s}}(\vec{r},t) + \sum_f \frac{1}{m_f}\vec{\nabla}\cdot\tilde{\overleftrightarrow{\sigma}}_{ff}\cdot\vec{\nabla}\frac{1}{m_f}\vec{E}_{\mathrm{s}}(\vec{r},t)\\
&\quad + \sum_f \frac{1}{m_f}\vec{\nabla}\cdot\tilde{\sigma}_{fe}\vec{E}_{\mathrm{s}}(\vec{r},t) + \sum_f\frac{1}{m_f}\vec{\nabla}\cdot\tilde{\sigma}_{f\beta}\vec{E}_{\mathrm{s}}(\vec{r},t),
\end{aligned}
\tag{2.19}
$$

where $\tilde{D}_{ff}, \tilde{D}^{l\xi}_{fb}, \tilde{D}^{l\xi}_{f\beta}, \tilde{\overleftrightarrow{\sigma}}_{ff}, \tilde{\sigma}_{fe}$ are the interdiffusion coefficients and conductivities of ions and molecules in porous space of the clayey matrix. Thus, the combined equations (2.6)–(2.19) contain the coefficients of interdiffusion and self-diffusion as well as the conductivities of ions, electrons, molecules, the products of radiolysis in solution and porous space of the clayey matrix. The intensities and inductions of electrical and magnetic fields are connected by expressions $\vec{B}_\xi = \mu_0\vec{H}_\xi\vec{D}_\xi = \varepsilon_0\varepsilon_\xi\vec{E}_\xi$, where ε_ξ is the generalized dielectric function of the corresponding subsystem. The both systems of equations for the electrolyte solution and the porous matrix are interconnected by the interphase partial diffusion constants $D^{\xi'\xi}_{\alpha\beta}$, $(\xi,\xi' = l,s,\ \alpha,\beta = a,f,e)$ and by the limiting conditions on the boundary "the electrolyte solution – the porous matrix":

$$\begin{aligned}
\vec{n}\cdot(\vec{B}_\mathrm{s}-\vec{B}_l) &= 0, \qquad \vec{n}\cdot(\vec{D}_\mathrm{s}-\vec{D}_l) = Q(\vec{S}_\omega,t),\\
\vec{n}\times(\vec{E}_\mathrm{s}-\vec{E}_l) &= 0, \qquad \vec{n}\times(\vec{H}_\mathrm{s}-\vec{H}_l) = Q(\vec{S}_\omega)\vec{v}_\mathrm{s}(\vec{S}_\omega,t),
\end{aligned} \tag{2.20}$$

where $Q(\vec{S}_\omega,t)$ is the complete surface electrical charge on the boundary "the electrolyte – the porous matrix" which satisfies the conservation laws:

$$\begin{aligned}
\frac{\partial}{\partial t}Q(\vec{S}_\omega,t) &= \vec{n}\cdot\vec{j}_i(\vec{S}_\omega,t), \qquad \vec{v}_\mathrm{s}(\vec{S}_\omega,t) = \vec{v}_l(\vec{S}_\omega,t),\\
Q(\vec{S}_\omega,t) &= \sum_a Z_a e n_a(\vec{S}_\omega,t).
\end{aligned} \tag{2.21}$$

The unit vector $\vec{n}$ is directed perpendicularly to the interface "the electrolyte solution – the porous matrix". The density of adsorbed ions $n_a(\vec{S}_\omega,t)$ on the surface $\vec{S}_\omega$ satisfies the reactionary-diffuse equations taking into account the processes of radioactive decays of nuclides Cs^+, Sr^{2+}, UO_2^{2+}, PuO_2^{2+}:

$$\begin{aligned}
\frac{\partial}{\partial t}n_a(\vec{S}_\omega,t) &= \nabla_{\vec{S}_\omega}D^\mathrm{surf}_a\nabla_{\vec{S}_\omega}n_a(\vec{S}_\omega,t) + D_\mathrm{T}\nabla^2T(\vec{r};t) + K^a_\mathrm{ad}n_a(\vec{r},t)\Theta_\mathrm{s}(\vec{S}_\omega,t)\\
&- K^a_\mathrm{des}n^l_a(\vec{S}_\omega,t)\Theta_\mathrm{s}(\vec{S}_\omega,t) - \sum_\beta A^{a\beta}(\vec{S}_\omega,t)\,n_\beta(\vec{S}_\omega,t) \ - \ A^a(\vec{S}_\omega,t)n(\vec{S}_\omega,t),
\end{aligned} \tag{2.22}$$

where D_T is the constant of thermal diffusion of radionuclides adsorbed on the clayey matrix surface, $T(\vec{r};t)$ is the local temperature, D^surf_a is the diffusion of sort a particles on the clayey matrix surface. The temperature effects on the surface of clayey matrix are generated by radioactive decays of radionuclides. The presented system of the equations (2.6)–(2.22) describes the complicated physicochemical processes of diffusion, adsorption, desorption, radioactive decay, which include the surface phenomena on the boundary "the water radionuclides solution - the porous clayey matrix". The particles of clayey matrix will effect the mechanical characteristics (turgescency, dissolubility) since the clayey matrix can exude by water solution. Therefore, it is necessary to add to (2.6)–(2.22) the conservation laws for particle momenta of the solution and the clayey matrix, which have the following form in frequency representation:

$$-\mathrm{i}\omega\rho_l\vec{v}_l = \vec{\nabla}\cdot\overleftrightarrow{\tau}_l + \sum_j Z_j e(n^0_l\vec{e}_l + n_l E^0_\mathrm{s}), \qquad -\mathrm{i}\omega\rho_\mathrm{s}\vec{v}_\mathrm{s} = \vec{\nabla}\cdot\overleftrightarrow{\tau}_\mathrm{s}, \tag{2.23}$$

where $\overleftrightarrow{\tau}_l$, $\overleftrightarrow{\tau}_\mathrm{s}$ is the stress tensors of a solution and a matrix, and ρ_l, ρ_s are their complete densities, respectively. The sum of the right part describes the electrical force which operates on a redundant charge, without taking into account the Lorentz force. For stress tensors we have the corresponding expressions:

$$\begin{aligned}
\overleftrightarrow{\tau}_l &= K_l\vec{\nabla}\cdot\vec{v}_l - \mathrm{i}\omega\eta\left(\nabla\vec{v}_l + \nabla\vec{v}^T_l - \frac{2}{3}\vec{\nabla}\cdot\vec{v}_l\ \overleftrightarrow{I}\right),\\
\overleftrightarrow{\tau}_\mathrm{s} &= K_\mathrm{s}\vec{\nabla}\cdot\vec{v}_\mathrm{s} + G\left(\nabla\vec{v}_\mathrm{s} + \nabla\vec{v}^T_\mathrm{s} - \frac{2}{3}\vec{\nabla}\cdot\vec{v}_\mathrm{s}\ \overleftrightarrow{I}\right),
\end{aligned} \tag{2.24}$$

where $\overleftrightarrow{I}$ is the individual tensor, K_l, η are the coefficients of volumetric and shift viscosity of a solution and K_s, G are the modules of volumetric and shift elasticity of the porous clayey matrix.

The limiting conditions for stress tensors on the boundary of the phases are as follows:

$$\vec{n} \cdot (\overset{\leftrightarrow}{\tau}_l - \overset{\leftrightarrow}{\tau}_\mathrm{s}) = Q^0 \vec{e}_\mathrm{s}, \qquad \vec{v}_l - \vec{v}_\mathrm{s} = 0. \tag{2.25}$$

Thus, we have obtained the systems of transport particle equations (2.5)–(2.25) of the solution of radioactive element electrolytes through porous clayey matrix with the surface active centres of absorption $\Theta_\mathrm{s}(\vec{S}_\omega, t)$. They are centres of modifying the surface of carbonate-containing bentonite clayey by ferrocyanides of iron and copper [18,19]. Thus the composite physicochemical processes of diffusion, absorption, desorption, radioactive decay, mechanical tensions with inclusion of surface phenomena on the boundary “the water solution of radionuclides - the porous clayey matrix” were taken into account.

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References

1. Eisenbud M. Environmental Radioactivity. McGrawHill, New York, 1966.
2. Prokhorov V. Migration of Radioactive Contamination in Grounds. Energoizdat, Moscow,1981, (in Russian).
3. Burak Ya.I., Chapla Ye.Ya. Reports of Ukrainian Academy of Science, 1993, **10**, 59 (in Ukrainian).
4. Avramenko V.I., Kuzmenko M.V., Symenoh I.V., Sytnychenko A.I. Reports of Ukrainian Academy of Science, 1994, **1**, 57 (in Ukrainian).
5. Burak Ya.I., Chapla Ye.Ya. Reports of Ukrainian Academy of Science, 1995, **10**, 34 (in Ukrainian).
6. Ivanov Yu.A., Kashparov V.A., Levchuk S.E., Zvarych S.I. Radiokhimiya, 1996, **38**, No 3, 264 (in Russian).
7. Ivanov Yu.A., Kashparov V.A., Levchuk S.E., Zvarych S.I. Radiokhimiya, 1996, **38**, No 3, 272 (in Russian).
8. Ivanov Yu.A., Kashparov V.A., Khomutinin Yu.V., Levchuk S.E. Radiokhimiya, 1996, **38**, No 3, 278 (in Russian).
9. Kivva S.L. Cond. Matt. Phys., 1997, **12**, 121.
10. Zheleznjak M.I. Cond. Matt. Phys., 1997, **12**, 37.
11. Davydov Yu. State of Radionuclides in Solutions. Science and Technique, Minsk, (in Russian).
12. Kaimin E.P., Konstantinova L.I. Investigation of sorption Pu(IV),(V),(VI) by soils from natural waters. Radiokhimiya, 1993, No 3, p.133 (in Russian).
13. Krip I.M., Shymchuk T.V., Stasyuk I.V., Mysakovych T.S. Preprint of the Institute for Condensed Matter Physics, ICMP–04–14E, Lviv, Ukraine, 2004, 17 p.
14. Krip I.M., Shymchuk T.V., Stetsiv R.Ya., Krasnov V.O. Preprint of the Institute for Condensed Matter Physics, ICMP–04–15E, Lviv, Ukraine, 2004, 14 p.
15. Dufrêche J.-F., Marry V., Maliková N., Turq P. J. Mol. Liq., 2005, **118**, 145.
16. Stoinov Z. B., Grafov V.M., Savova-Stoinova B.S., Yelkin V.V. Electrochemical Impedance. Nauka, Moscow, 1991, (in Russian).
17. Yukhnovskii I.R., Tokarchuk M.V., Omelyan I.P., Zhelem R.I. Radiat. Phys. Chem., 2000, **59**, No 4, 361.
18. Krip I.M., Shymchuk T.V.,Tokarchuk M.V. Chornobyl Problems, 2004, **14**, 23 (in Ukrainian).
19. Krip I.M., Shymchuk T.V.,Tokarchuk M.V. Chornobyl Problems, 2004, **14**, 29 (in Ukrainian).

Реакційно-електродифузійні рівняння процесів переносу розчинів електролітів радіоактивних елементів крізь пористі глинисті структури

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Запропоновано стастичну модель "водний розчин радіоактивних елементів – пориста глиниста матриця". Отримано узагальнені рівняння переносу для опису дифузії, сорбції, радіоактивних процесів та хімічних реакцій з врахуванням електромагнітних процесів.

Ключові слова: *дифузія, сорбція, електромагнітні процеси, пориста глиниста матриця, Чорнобильська катастрофа*

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