Journal of Engineering Physics and Thermophysics, Vol. 74, No. 1, 2001

THEORY OF THE EFFECT OF INHIBITION OF THE TRANSFER OF RADIONUCLIDES AND HEAVY METALS FROM SOIL TO PLANTS BY AN AMELIORANT. V. CALCULATION OF THE BINDING ENERGY OF EXCHANGE IONS IN DISPERSE SYSTEMS WITH A LOW pH

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UDC 541.18:631.4

Based on a number of methods (adsorption, diffusion, IR spectroscopy) the author calculated the binding energy of cesium-137 and strontium-90 in disperse systems in the presence of hydroxonium ions and with their being removed and evaluated the transfer of radionuclides from soil to plants.

The proposed work is an extension of investigations published in [1–4] and is devoted to the problem of obtaining uncontaminated agricultural products on soils that are contaminated by radionuclides or heavy metals. The technology for production of such products is based on application of quicklime and phosphogypsum to the soil.

The development of the technology was started in 1981 when we were able to detect for the first time the effect of a sharp increase in the filtration coefficient of heavy soils modified by calcium oxide. From 1986 to 1992 we used this ameliorant to solve three problems: to improve the water permeability of heavy soils (Vitebsk Region, Stavropol' Territory), to intensify the processes of washing of saline solonetz soils (Stavropol' Territory), and to protect chernozem soils against the processes of sodium and magnesium solonetzization in irrigating them with slightly mineralized water (Lugansk Region).

The introduction of technology for obtaining environmentally clean agricultural products on radionuclide-contaminated soils was started in 1993 in the Loev District of the Gomel' Region. A pilot plot was set up there on soils with a total activity of 20 Ci/km^2. The soils were loamy sand with contents of physical clay of 17–19%, clay (argillaceous) particles of 6.7%, and humus of 3.5%; the pH of the water and salt extracts was 7.01 and 6.5, respectively.

In 1993, in the variant of application of quicklime and phosphogypsum the increase in the fresh yield of a pea-oat mixture amounted to 49% relative to the control, while the content of cesium-137 in the green mass of peas decreased by a factor of 4.5, and the resultant fodder was uncontaminated.

In 1994–1995, when the same variants were compared on the same plot, the increase in the grain yield of winter rye turned out to be equal to 18% while the content of cesium-137 in the rye heads was half as much.

In 1996 (the fourth year after ameliorant application), oats were sown on the pilot plot for grain. Their yield increased by 20% as compared to the control, while the content of cesium-137 decreased by a factor of 3.6. The same year a second pilot plot (a pasture), 15 ha in area, was set up here. The soils were loamy sand with average contents of physical clay of 13.1%, clay particles of 5.0%, and humus of 3.7%; the pH of the water and salt extracts was 7.03 and 6.2, respectively. The average radiocontamination level was 15 Ci/km^2. A vetch-oat mixture with interplanted timothy grass for green material was sown several days

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Central Research Institute of Integrated Water Management, Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 74, No. 1, pp. 170–174, January–February, 2001. Original article submitted March 30, 2000.

after application of the ameliorant. In the case of the ameliorant, the fresh yield increased by 50% and the content of cesium-137 decreased by a factor of 3.1 as compared to the control.

In 1997, a third pilot plot was set up in the Bragin District of the Gomel’ Region. The area of the plot was 40 ha; the soils were loamy sand with contents of physical clay of 12.9%, clay fraction of 3.55%, and humus of 2.47%; the pH of the salt extract was 6.56; the level of contamination by strontium-90 was 3.1 Ci/km^2. Several days after application of the ameliorant oats were sown for grain. The yield of the oats in the variant with the ameliorant applied increased by 17% in relation to the control, while the content of strontium-90 decreased by a factor of 1.5 and of cesium-137, by a factor of 1.9.

However in all three pilot plots the soils were neutral. Therefore it was of interest to obtain the result on acid soils, too. For this purpose, an object with a 5 Ci/km^2 level of contamination of soils by strontium-90 was selected in the Khoiniki District of the Gomel’ Region. Here the soils were also loamy sand with average contents of clay particles of 4.24% and physical clay of 14.06% but the pH was 4.43 for the water extract and 4.09 for the salt extract.

To evaluate the influence of the ameliorant on the effect of change in the transfer of radionuclides from the soil to plants, it was necessary to calculate the energy of binding of a hydroxonium (hydrogen) ion with the lattice of clay minerals. The theory of chemical trapping was used as the basis for the calculation.

The energy of chemical trapping is determined by the contributions of noncentral forces, and, according to [5], the formula for calculating it can be represented as follows:

$$E_{\mathrm{tr}} = \frac{4W_2^4}{[2W_3]^3} \sum_{\alpha<\beta} \cos^2 \theta_{\alpha\beta} . \tag{1}$$

The interaction W_2 corresponds to the matrix element $V_{\mathrm{sp}\delta}$:

$$W_2 = V_{\mathrm{sp}\delta} = 14.0208/d^2 \ \mathrm{eV} . \tag{2}$$

The interaction W_3 is identified with the width of the forbidden band in the crystal E_{g}, which is determined as the difference of terms [5]

$$E_{\mathrm{g}} = \varepsilon_{\mathrm{s}}^{\mathrm{c}} - \varepsilon_{\mathrm{p}}^{\mathrm{a}} . \tag{3}$$

A method for determining the atomic term of the anion of the p-state in the lattice is presented in [4]. In what follows we dwell on the determination of $\varepsilon_{\mathrm{s}}^{\mathrm{c}}$ of a hydrogen ion in the lattice. We will determine the term of the s-state of the electron of a hydrogen atom that is bound with the lattice as follows.

It is known that the value of the ground term (the optical limit) of the hydrogen atom ($1S - {}^2S_{1/2}$) is 13.6 eV. Assuming that a hydrogen atom in the lattice forms strong donor-acceptor bonds with an oxygen anion, we will determine the term of this state of the hydrogen ion as the term $[2\mathrm{p}({}^2\mathrm{P}^0_{1/2})]$ of the excited state of the hydrogen atom. According to [6], its value is equal to 10.2 eV.

The next necessary point for determining the energy of binding of a hydroxonium cation with clay minerals is evaluation of the parameter d:

$$d = r_{\mathrm{c}} + r_{\mathrm{O}} . \tag{4}$$

In order to evaluate r_{c} we will use literature data. According to [7], where works on quantum chemical study of ion-molecular complexes with hydrogen bonds are reviewed, the distance H–O in the H_3O^+–H_2O complex is equal to 2.445 Å, and

TABLE 1. Energy of Binding of Cesium, Strontium, and Hydroxonium Ions with Clay Minerals

Ion	Clay mineral	Energy of binding of ions with clay minerals, kcal/mole	
		in the presence of the hydroxonium ion (acid soils)	in the absence of the hydroxonium ion (neutral soils)
Cs^+	Kaolinite	2.187	3.610
	Muscovite	5.458	10.123
Sr^{2+}	Kaolinite	0.635	1.177
	Muscovite	1.806	4.473
H_3O^+	Kaolinite	37.990	
	Muscovite	85.955	

TABLE 2. Energy of Binding of Cesium and Strontium Ions with the Clay Fraction (kcal/mole)

Ion	Acid soils	Neutral soils	Neutral soils modified with calcium oxide
Cs^+	4.825	8.863	10.263
Sr^{2+}	1.580	3.836	4.331

$$r_c = r_{H\text{–}O} + r_{O\text{–}D}\,, \tag{5}$$

where $r_{O\text{–}D}$ is the distance from the oxygen atom of the water molecule to the center of its dipole. According to [8], $r_{O\text{–}D}$ = 0.355 Å. Hence

$$d = 2.445 \text{ Å} + 0.335 \text{ Å} + 1.4 \text{ Å} = 4.18 \text{ Å}\,.$$

Table 1 presents data on the energy of binding of Cs^+, Sr^{2+}, and H_3O^+ ions with the crystal lattice of kaolinite and muscovite.

As follows from Table 1, the binding energy of the hydroxonium ion on kaolinite is 17 times higher than the binding energy of the cesium ion and 60 times higher than the binding energy of the strontium ion, while on muscovite it is, respectively, 16 and 48 times higher. At the same time, the binding energy of the cesium ion in the presence of a hydroxonium ion is 1.65 times lower on kaolinite and 1.86 lower on muscovite while the binding energy of the strontium ion is 1.85 times lower on kaolinite and 2.5 times lower on muscovite than the binding energy of the same ions in the absence of a hydroxonium ion (neutral soils).

According to our performed analysis of a number of published works on many varieties of soils, the average ratio of kaolinite and mica (muscovite is a variety of mica) in the clay fraction is equal to 1:4. Using this ratio, we obtain the values of the energy of binding of the cesium and strontium ions with the clay fraction of acid soils, neutral soils, and soils modified by calcium oxide (Table 2).

Using the values of the binding energies (Table 2) and also results of filtration experiments, a granulometric analysis, and determinations of the density, bulk weight, and humus of soil taken in the Khoiniki District of the Gomel’ Region, we calculated the degree of decrease in the contents of cesium-137 and strontium-90 in agricultural products due to application of quicklime. For this purpose we used formulas obtained in [3]:

$$\frac{Q_1}{Q_2} = \left(\frac{D_1}{D_2}\right)^4 \left(\frac{\varepsilon - \varepsilon_{0(2)}}{\varepsilon - \varepsilon_{0(1)}}\right)^3, \tag{6}$$

$$\frac{D_1}{D_2} = \exp\left(\frac{-n\Delta E_{\mathrm{M}}}{kT}\right). \qquad (7)$$

In our calculations, $D_1/D_2 = 0.541$ and $Q_1/Q_2 = 42$ for cesium, $D_1/D_2 = 0.733$ and $Q_1/Q_2 = 6$ for strontium; according to the data of our diffusion experiments, $Q_2/Q_1 = 11.0$. Thus, it becomes possible to solve the problem of obtaining environmentally clean agricultural products on acid soils that are contaminated with radionuclides, in particular, strontium-90, owing to application of quicklime (calcium oxide) to the soil. However, is it possible to achieve analogous effects of reduction in the content of radionuclides in plants when a traditional ameliorant – dolomite flour ($MgCO_3 \cdot CaCO_3$) – is applied to the soil? And if this cannot be achieved, what is the use of applying quicklime when dolomite flour was applied to the soil earlier (5 or 6 years ago)? We arrived at the answers to these questions using methods of IR spectroscopy and x-ray structural analysis of the soil.

In [4], it was shown that the optimum dose of application of the ameliorant corresponds to a content of it for which maximum deformations of the lattices of clay or nonclay minerals in the soil occur. According to [5], the change in the distance between two atoms in the lattice (for example, aluminum or silicon atoms) is determined as follows:

$$\delta R = \frac{R}{P_x} \frac{\delta P_x}{\left(1 - \frac{e_z}{Z^*}\right)} \qquad (8)$$

or

$$\frac{\partial P_x}{\partial R} = \left(1 - \frac{e_z}{Z^*}\right) \frac{P_x}{R}. \qquad (9)$$

Following [5],

$$e_z = Z^* + 3\cos^2\theta_0\, \beta_{\mathrm{p}x}(1 - \beta_{\mathrm{p}x}^2) + (3\cos^2\theta_0 - 1)\,\beta_{\mathrm{p}x}(1 - \beta_{\mathrm{p}z}^2), \qquad (10)$$

$$\beta_{\mathrm{p}z} = W_3 (2W_2^2 \cos^2\theta_0 + W_3^2)^{-0.5}, \qquad (11)$$

$$\beta_{\mathrm{p}x} = W_3 (2W_2^2 \sin^2\theta_0 + W_3^2)^{-0.5}, \qquad (12)$$

$$Z^* = (\beta_{\mathrm{p}z} + \beta_{\mathrm{p}x}). \qquad (13)$$

In formula (9), $\partial P_x/\partial R$ is the first derivative of the dipole moment with respect to the coordinate of molecular bonds in the crystal lattice of the minerals; it governs the intensity of the absorption bands in IR spectra of natural formations of this kind. In [9], it is shown that $\partial P_x/\partial R$ has a maximum on the curve of deformation of the lattice as a function of the content of the adsorbent. But it is the maximum deformation of the crystal lattice of clay and nonclay minerals of soils occurring in application of the ameliorant that corresponds to its optimum dose. Therefore it should be assumed that, in the IR spectrum of each soil, we can find an absorption band whose intensity will depend on the dose of application of the ameliorant and will achieve a maximum value for a certain dose. To prove this proposition, we obtained IR spectra of soils taken in the Khoiniki District of the Gomel' Region.

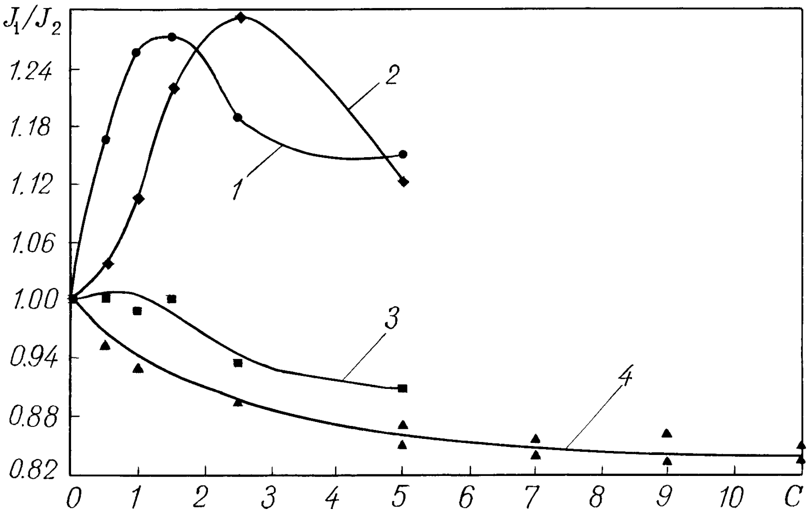

Fig. 1. Relative intensity of the stretching vibrations of bonds in the crystal lattices of soil (taken in the Khoiniki District) with an initial pH of 4–4.5 vs. dose of application of the following ameliorants: 1) quicklime; 2) quicklime and phosphogypsum; 3) quicklime, the soil is pretreated with $CaCO_3$; 4) dolomite flour and $CaCO_3$ separately. C, ton/ha.

Figure 1 presents relative values of the intensities of the bands of stretching vibrations in the crystal lattices of clay minerals of soils as functions of the content of the ameliorant. As follows from the figure, the optimum dose of application of calcium oxide (curve 1) is 1.5 ton/ha; according to the data of measurements of the diffusion coefficients of strontium in the soils, this dose also turned out to be equal to 1.5 ton/ha.

From the dependences of Fig. 1 we can also gain additional information. Using Eq. (9), we write

$$J_1/J_2 = (1 - e_{z(1)}/Z^*_{(1)})\,(1 - e_{z\,(2)}/Z^*_{(2)})^{-1}\,. \tag{14}$$

Substituting the values of e_z and Z^* taken from formulas (10)–(13) into (14) and knowing that for clay minerals (kaolinite and mica) the angle θ_0 is approximately equal to 45°, we obtain

$$J_1/J_2 = 1 + W^2_{3(2)}/W^2_{2(2)} - W^2_{3(1)}/W^2_{2(1)}\,. \tag{15}$$

In formulas (14) and (15) the parameters with the subscript (2) refer to the system of the control variant. According to [5], $W_2 = 28.423/d^2$ eV and $W_3 = (\varepsilon^c_s - \varepsilon^a_p)$ eV.

It should be noted that in acid soils the content of the hydroxonium ions is excessive. Therefore we can assume that in such systems there is an exchange of hydrogen atoms that belong to the crystal lattice of clay minerals with hydrogen ions of the soils; the term of the hydrogen atom in the OH groups of the crystal lattice of clay minerals (the excited-state term) will differ from the term of the hydrogen atom in the OH group of the ground state [6]. The value of this term is equal to 10.2 eV. In applying dolomite flour ($MgCO_3{\cdot}CaCO_3$) or calcium carbonate $CaCO_3$ to the soil, the excess of hydroxonium ions binds to $CaCO_3$ and $MgCO_3$ molecules with formation of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ molecules. This application results in strengthening of the bond in the OH group of clay minerals, and the term of the hydrogen atom in the OH group will be equal to 13.6 eV.

For the variant of application of quicklime to the soil, the calculated value of J_1/J_2 turned out to be equal to 1.273 and the experimental one to 1.270. For the variant of application of dolomite flour or calcium carbonate, the calculated value is J_1/J_2 = 0.794 and the experimental one is 0.830. The different values of the calculated quantites J_1/J_2 are attributable to the fact that we substituted different values of the term of the p-state of the oxygen atom in the lattice into the expression for W_3 in formula (15).

When quicklime is applied to the soil, the term is ε_p^a = 10.63 eV, and when dolomite flour is applied, ε_p^a = 12.672 eV. Then upon application of dolomite flour to the soil the energy of binding of cesium with the lattice will be 2 times lower and of strontium 2.5 times lower than in the case of quicklime, and correspondingly the decrease in the content of cesium-137 in plants in the case of dolomite flour will be 1.7-fold while the decrease in the content of strontium-90 will be 1.5-fold. This effect is achieved for doses of application of dolomite flour of 10 ton/ha (the optimum dose of quicklime is 1.5 ton/ha).

Now we consider investigation results obtained upon application of dolomite flour and then quicklime to an acid soil (curve 3 in Fig. 1). When 1.0–1.5 ton/ha quicklime is applied to this soil, J_1/J_2 = 1.00. For this content of quicklime we observe no change in the term of the oxygen atom in the lattice of clay minerals, and this means that inhibition of the transfer of radionuclides from the soil to plants cannot be expected.

With quicklime applied to the soil in an amount of 5 ton/ha the experimental value of J_1/J_2 is equal to 0.91, and the term of the oxygen atom in the lattice for this value of J_1/J_2 is equal to 12.1864 eV. This value of the term points to the fact that in applying quicklime to an acid soil that is premodified with dolomite flour the energy of binding of the hydrogen atom with the oxygen atoms in the hydroxyl group of the clay minerals of the soil increases. In this system, hydrogen will not be replaced by clcium.

Thus, use of quicklime with the aim of inhibiting the transfer of radionuclides from the soil to plants for acid soils that were pretreated with dolomite flour is not an efficient measure. But the effect from application of dolomite flour to acid soils is an order of magnitude lower than the effect from application of quicklime.

Hence, to solve the problem of obtaining environmentally clean agricultural product, it is necessary to use just quicklime.

NOTATION

W_2, energy of the covalent bond in the crystal; W_3, energy of the ionic bond in the crystal; θ_0, angles between the vectors formed by the central ions (the exchange cation in question) and the neighboring atoms (anions) at the nodes of the crystal lattice of the mineral (α and β are the numbers of the vectors); ε_s^c, atomic term of the cation of the s-state; ε_p^c, atomic term of the anion of the p-state; d, distance between the centers of the hydrated ion and the oxygen atom in the lattice; r_c, hydrated radius of the exchange cation; r_O, ionic radius of the oxygen atom; D, diffusion coefficient of the ion; D_1 and D_2, diffusion coefficients of the ion in soil modified and unmodified by the ameliorant, respectively; Q_1 and Q_2, arrival of radionuclides from soil that is modified and unmodified by the ameliorant, respectively, at plants; E_m, activation energy of the surface migration of the ions; E_1 and E_2, energy of binding of the cation with the hydrated surface of clay minerals modified and unmodified by the ameliorant, respectively; n, portion of the clay fraction and humus in the soil; ε, coefficient of porosity of the soil; $\varepsilon_{0(1)}$ and $\varepsilon_{0(2)}$, coefficients of porosity of the soil (for a vanishing filtration coefficient) modified and unmodified by the ameliorant, respectively; P_x, dipole moment of the bond between the atoms in the lattice; R, distance between two atoms of aluminum or silicon in the lattice; e_z, transverse charge in the atom; Z^*, effective charge of the oxygen atom in the lattice; β_{pz} and β_{px}, fractions of the ionicity of bonds in the crystal; J_1/J_2, ratio of the intensities of vibrational bonds in IR spectra of soils modified and unmodified by the meliorant, respectively. Subscripts: a, anion; c, cation; m, migration; O, oxygen; x, z, coordinates; g, gap.

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