## ON THE THEORY OF SUPPRESSION OF RADIONUCLIDE AND HEAVY METAL TRANSFER FROM SOIL TO PLANTS BY THE AMELIORANT. IV. CALCULATION OF BINDING ENERGY OF EXCHANGE IONS IN DISPERSE SYSTEMS. OPTIMAL AMELIORANT APPLICATION RATE

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On the basis of the theory of chemical capture in solids, a method is suggested for calculation of the binding energy of exchange cations in disperse systems. The method can be used to estimate the relative diffusion coefficient of the cations in soil modified by an ameliorant and the optimal ameliorant application rate.

The present work is an extension of the studies published in [1-3] and its goal is to obtain uncontaminated agricultural products from crops grown on radionuclide- or heavy-metal-containinated soils. The technology consists in application of quicklime and phosphogypsym to the soil.

Development of this technology was started in 1981, when we observed for the first time a sharp increase in the filtration coefficient of heavy soils modified by calcium oxide. From 1986 to 1992 this ameliorant was used to achieve three objectives: to increase water permeability of heavy soils (Sharkovshchinskii Collective Farm, Vitebsk Region, Belarus; Nagutskii State Farm, Stavropol Region, Russia), to intensify saline and solonetz soil washing (Nagutskii State Farm), and to protect chernozem soils irrigated by slightly mineralized water from sodium and magnesium solonetzization (Pravda State Farm, Lugansk Region, Ukraine).

Introduction of the technology of production of uncontaminated agricultural products was started at the Karl Marx Collective Farm, Loev District, Gomel Region, Belarus, in 1993. A pilot plot was set up there on soil with a total activity of 20 Ci/km<sup>2</sup>. The soil was sandy loam with contents of physical clay of 17-19%, argillaceous particles of 6.7%, humus of 3.5%; the pH of the water and salt extracts was 7.01 and 6.5, respectively.

In 1993 the application of quicklime and phosphogypsum resulted in a 49% increase in the fresh yield of a pea-oat mixture, relative to the control, while the <sup>137</sup>Cs content in the green mass of the pea was 4.5 times lower and the resultant fodder was uncontaminated.

In 1994 and 1995 winter rye was sown in the same plot. The grain yield was 18% higher and the <sup>137</sup>Cs content in the rye heads was twice as low as that in the control.

In 1996 (the fourth year after ameliorant application) oats were sown in the pilot plot. In the case of ameliorant application, its productivity was 20% higher and the  $^{137}$ Cs content, 3.6 times lower.

The same year at the same farm a second pilot plot, 15 ha in area (a pasture), was set up. The soil was sandy loam with average contents of physical clay of 13.1%, argillaceous particles of 5.0%, and humus of 3.7%; the pH of the water and salt extracts was 7.02 and 6.2, respectively; the average radiocontamination level was 15 Ci/km<sup>2</sup>. A vetch-oat mixture with interplanted timothy grass for green material was shown several days after application of the ameliorant. In the case of the ameliorant, the fresh yield was 50% higher and the <sup>137</sup>Cs content was 3.1 times lower than the control.

The theory of suppression of radionuclide transfer from soil to plants was presented in my works [1-3]. The main point of the theory is calculation of the relative ionic diffusion coefficient in soil with the use of IR spectral properties of adsorbed water molecules.

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Fig. 1. Schematic diagram of argillaceous particle.

However, for light soils with a physical clay content lower than 15% (these soils are mainly present in the radionuclide-contaminated zone of the Republic of Belarus), it is very difficult to obtain IR spectra of adsorbed water; therefore, another approach to the problem was used which gave new fundamental results. It is known [4] that ionic surface diffusion can be described in terms of the diffusion coefficient in the ordine. y Arrhenius form as

$$D = D_0 \exp\left(-\frac{E_m}{kT}\right),\tag{1}$$

where  $D_0$  is the pre-exponential factor  $(D_0 = \nu l)$ . Then,

$$\frac{D_1}{D_2} = \exp\left(-\frac{(E_1 - E_2)}{kT}\right).$$
 (2)

Calculation of  $E_1$  and  $E_2$  requires knowledge of the surface structure of the argillaceous particle.

In what follows we study koalinite and muscovite. An argillaceous particle is considered as a set of elementary crystal lattices (layers) inherent in any argillaceous mineral. For example, following [5], three varieties of koalinite can be distinguished according to their morphological properties: regular or almost regular pseudohexagonal plates with a thickness of 0.0002-0.0008 mm; fractures of pseudohexagonal plates that have partly or fully lost their initial shape; idiomorphic pseudohexagonal plates without contours; kaolinite in the form of plates of nonuniform thickness (micalike kaolinite) is also known.

In [5], electron microscopic studies of two varieties of hydromica are also presented. The first variety has the form of isometric or nearly isometric particles. Unlike kaolinite, in such particles, especially in the largest ones, nonuniform density is observed. As a rule, the central part of the plates scatters electrons more intensely and appears darker in the photographs as compared with the periphery. In hydromica several darkening steps are observed. The first step (periphery) is the least dark with the density increasing towards the center. Thus, regions of different density appear, and the boundaries between them are not always clear-cut, are often irregular, and have acute angles, as if broken. For the first variety of hydromica, the particle size varies over rather wide ranges from 0.0001 and smaller to 0.002-0.003 mm. The second variety of hydromica is represented by thin elongated plates with a width-to-length ratio of 1:1.5 to 1:3-1:4. The particles are usually semipermeable for electrons; therefore, they appear light gray on the display of the electron microscope. The thickness of the elongated plates rarely exceeds 0.0003 mm and their length is usually at most 0.0009-0.0012, occasionally, 0.0025 mm. On the basis of these data, the structure of the argillaceous particle is presented in the form shown in Fig. 1, where a, b, and c are lattice parameters of argillaceous minerals. The size of each step is also equal to the lattice parameters.

In outline, the scheme shown in Fig. 1 resembles a truncated octahedron in which section planes (111) are replaced by a step-like surface.

According to [6], the density of broken bonds is the lowest on plane (111). Therefore, the present structure of the argillaceous particle has a surface with minimal energy.

The surface area of the particle is calculated as follows

$$S_1 = 2 \int_m^n (2ban + 2abn + 2bcn + 2acn) dn + 2abm^2 = 2abm^2 + (n^2 - m^2) (2ab + S_0).$$
(3)

The volume of the particle is defined by

$$V_1 = 2 \int_m^n abcn^2 \left(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma\right)^{-1/2} dn = \frac{2}{3} \left(n^2 - m^2\right) V_0.$$
(4)

Then,

$$\frac{V}{S} = \frac{\frac{2}{3}(n^3 - m^3) V_0}{2abm^2 + (n^2 - m^2) (2ab + S_0)},$$
(5)

where V is the specific volume of the argillaceous mineral; S is its specific surface area.

The number of argillaceous particles f per unit mass of the mineral is defined as

$$f = \frac{S}{2abm^2 + (n^2 - m^2)(2ab + S_0)}.$$
 (6)

The total number of unit cells per unit mass of the mineral

$$N=f\left(n^2+m^2\right),$$

and the particle dimensions are A = an, B = bn, C = 2cm.

On the basis of electron microscopic studies carried out in the present work with suspension samples and replicas, it can be suggested that for many argillaceous particles the following condition exists:  $(an + bn)/2 = 2cm\alpha$ , where  $\alpha \approx 1$ . Then, for kaolinite: a = 5.13 Å; b = 8.89 Å; c = 7.25 Å;  $\alpha = 91^{\circ}40'$ ;  $\beta = 104^{\circ}40'$ ;  $\gamma = 90^{\circ}$ ;  $S_0 = 292.04$  Å<sup>2</sup>;  $V_0 = 319.74$  Å<sup>3</sup>;  $V = 0.3788 \cdot 10^{24}$ Å<sup>3</sup>;  $S = 49.36 \cdot 10^{20}$  Å<sup>2</sup>; n = 2.07m = 127;  $f = 9.703 \cdot 10^{14}$ ;  $N = 1.93 \cdot 10^{19}$ ;  $A = 0.07 \,\mu$ m;  $B = 0.11 \,\mu$ m;  $C = 0.009 \,\mu$ m. For muscovite: a = 5.19 Å; b = 8.996 Å; c = 20.096 Å;  $\beta = 95^{\circ}11'$ ;  $S_0 = 662.68$  Å<sup>2</sup>;  $V_0 = 930.61$  Å<sup>3</sup>;  $V = 0.3413 \cdot 10^{24}$ Å<sup>3</sup>;  $S = 120 \cdot 10^{20}$  Å<sup>2</sup>; n = 5.66m = 339;  $f = 1.42 \cdot 10^{14}$ ;  $N = 1.58 \cdot 10^{19}$ ;  $A = 0.18 \,\mu$ m;  $B = 0.3 \,\mu$ m;  $C = 0.24 \,\mu$ m.

The calculated particle sizes agree with the values reported in [5, 7]. For subsequent calculations it is necessary to know the number of unit cells on the surface of these minerals.

In the adopted structural model of argillaceous particles, every unit cell is identical relative to adsorbed ions. Using this model, it is easier to prevent the coagulation (binding) mechanism of argillaceous particles in soil modified by calcium oxide.

Calculation of the binding energy of the exchange cation with the crystal lattice of argillaceous minerals is based on the theory of chemical capture [6] caused by interatomic matrix elements of interaction between the state of the ceiling of the valence band and the bottom of the conduction band. The energy of chemical capture is determined by the contributions of noncentral forces, and, according to [6], the calculation formula for this energy can be expressed as follows:

$$E_{\text{capture}} = 2 \left( \frac{14.0208}{d^2} \right)^4 \frac{1}{(E_g)^3} \sum_{\alpha_1 < \beta_1} \cos^2 \theta_{\alpha_1, \beta_1} , \qquad (7)$$

where  $E_g$  is the width of the forbidden band in the crystal;  $\theta_{\alpha_1\beta_1}$  are the angles between the vectors formed by the central ion (the exchange cation considered) and the neighboring atoms (anions) located at the mineral lattice points. The width  $E_g$  is defined as the difference [6]

$$E_{\rm g} = \epsilon_{\rm s}^{\rm c} - \epsilon_{\rm p}^{\rm a} \,, \tag{8}$$

where  $\varepsilon_s^c$  is the atomic term of the s-cation;  $\varepsilon_p^a$  is the atomic term of the p-anion. Values of the terms are given in "The Generalized Periodic System" [6].

Using formula (8), we assume that the atomic term  $\varepsilon_s^c$  belongs to the exchange cation (for example, Cs<sup>+</sup>, Sr<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup>), and the atomic term  $\varepsilon_p^a$ , to the oxygen atom located at the lattice point. But in the lattice the oxygen anion is surrounded by different ions, such as silicon, aluminium, and hydrogen ions, and in the case of CaO introduced into the system, also by the calcium ion that replaces hydrogen.

Consequently, the atomic term of the oxygen anion should be constructed with the use of atomic terms of cations that form chemical bonds with oxygen. For this operation, use will be made of the ideas of W. Harrison in [6]. In this procedure it is established with account of conditions of orthonormality of wave functions of atomic (nonhybridized) states that wave functions of hybridized states are orthonormal. These hybridized orbitals are not eigenfunctions corresponding to states with a specified energy. The expected energy, called a hybridized state, is an average:

$$\varepsilon = \frac{(\varepsilon_s + 3\varepsilon_p)}{4}.$$
 (9)

Measurements of electron energy in the state described by the hybridized wave function shows that for 25% of the time the electron has energy  $\varepsilon_s$  and for 75% of the time energy  $\varepsilon_p$ . For covalent crystals with appreciable ionicity  $\varepsilon_p^3$ , the hybridized orbitals are oriented towards the nearest neighbors and can be constructed for every atomic species that forms the crystal.

For determination of the terms  $\varepsilon_p^a$  of the oxygen atom in the lattice of argillaceous minerals, we use data from "The Generalized Periodic System" [6].

For example, for the point at which the oxygen atom forms two chemical bonds with silicon atoms:

$$\varepsilon_{p(\text{of lattice oxygen})}^{a} = \left(\frac{(3\varepsilon_{p(0)}^{a} + \varepsilon_{s(\text{Si})}^{c})}{4} 3 + \varepsilon_{s(\text{Si})}^{c}\right) \cdot 0.25.$$
(10)

For the point where the oxygen atom forms three bonds (one with a hydrogen atom and two with aluminum atoms):

$$\varepsilon_{p(\text{of lattice oxygen})}^{a} = \left\{ \left( \frac{(3\varepsilon_{p(0)}^{a} + \varepsilon_{s(H)}^{c})}{4} 3 + \varepsilon_{s(AI)}^{c} \right) \cdot 0.75 + \varepsilon_{s(AI)}^{c} \right\} \cdot 0.25.$$
(11)

When calcium oxide is introduced:

$$\varepsilon_{p(\text{of lattice oxygen})}^{a} = \left\{ \left( \frac{(3\varepsilon_{p(0)}^{a} + \varepsilon_{s(\text{Al})}^{c})}{4} 3 + \varepsilon_{s(\text{Al})}^{c} \right) \cdot 0.75 + \varepsilon_{s(\text{Ca})}^{c} \right\} \cdot 0.25.$$
(12)

Substitution of calcium for hydrogen decreases the term of valence electrons of the oxygen atom in the lattice. Consequently, for all three diffusing ions in which the term of the s-atom is lower in comparison with the the term of the oxygen p-atom in the lattice, the ion-lattice binding energy increases when calcium oxide is introduced into the system. Among these ions we can mention cesium, strontium, cadmium, lead, and other ions. For all three diffusing ions in which the term of the s-atom is higher than the term of the oxygen p-atom in the lattice, the ion-lattice binding energy decreases. Among these ions we can mention phosphorus, copper, cobalt, chromium, and other ions. In view of this, experimental results on suppression of  $^{137}$ Cs,  $^{90}$ Sr, Cd, and Pb transfer from soil to plants and to ground water as well as higher yields of farm crops become clear.

The basic point in calculation of the exchange cation-lattice binding energy in argillaceous minerals is choice of the parameter d in Eq. (7). In the present calculations

$$d = r_{\rm c} + r_{\rm (0)} \,. \tag{13}$$



Fig. 2. Plot of parameter b in crystal lattice of kaolinite versus adsorbed water content P: 1) kaolinite in initial state (a) and modified by CaCO<sub>3</sub> (b); 2) CaO-modified kaolinite (c) for rate of one CaO molecule per unit cell; 3) the same, for rates of two, three and four CaO molecules per unit cell (d). b, Å; P, %.



Fig. 3. IR spectra of kaolinite in the region of stretching (a) and deformation (b) vibrations of H<sub>2</sub>O molecules: 1) kaolinite in initial state; 2) kaolinite modified by CaO, for rate of one molecule per unit cell; 3, 4, 5) the same, for rates of two, three, four CaO molecules per unit cell, respectively.  $\nu$ , cm<sup>-1</sup>.

Thus, all the parameters in formula (7) are determined in this way.

The exchange cation-lattice binding energy in argillaceous minerals is calculated for cesium, strontium, cadmium, and lead ions on kaolinite and muscovite.

Kaolinite. In experimental studies we found changes in the parameter b of the lattice of kaolinite in its initial state (control) and modified by CaO and CaCO<sub>3</sub> as well as IR spectra of OH groups and water adsorbed on these kaolinite forms. Results are presented in Figs. 2 and 3.

As follows from Fig. 2, adsorption of water molecules on kaolinite in its initial state and with added CaCO<sub>3</sub> increases the parameter *b*. In this case addition of CaCO<sub>3</sub> does not bring about any substantial changes. On the contrary, introduction of CaO gives rise to a sharp decrease in *b* (when the content of adsorbed water is close to zero). At an application rate of 0.166% of the dry weight of the mineral, which is equivalent to a content of one CaO molecule per unit cell of kaolinite, the parameter *b* is found to decrease smoothly as the amount of adsorbed water increases. With application rates of 0.323, 0.489, and 0.655%, which corresponds to two, three, and four CaO molecules per unit cell of kaolinite, the parameter *b* is found to increase smoothly, and at 5-6% of the moist mineral the effect of smooth deformation of the lattice is completely degenerated.

Figure 3 shows that introduction of one CaO molecule per unit a cell increases the frequency v in the region of deformation vibrations of H<sub>2</sub>O by 6 cm<sup>-1</sup> and decreases the vibration frequency of OH groups by 5 cm<sup>-1</sup>. But when two or more CaO molecules are introduced per unit cell, in this kaolinite all vibrational frequencies are identical to those observed in the control.

Using the results of [8-10] and the data given in Figs. 2 and 3, the lattice deformation mechanism in hydration can be represented as follows. According to [8], water molecules are adsorbed on OH groups of the natural kaolinite form with electron charge transfer to the mineral, and this transfer results in expansion of the lattice. When one CaO molecule is introduced per unit cell of kaolinite, in the OH group of the mineral the bond is elongated, and water molecules are adsorbed with electron charge transfer to  $H_2O$ . This transfer brings about compression of the lattice. When two or more molecules are introduced per unit cell of kaolinite, the length of OH-bonds in the mineral is restored, and water molecules are adsorbed again with electron charge transfer to the mineral, i.e., conditions of expansion of the lattice appear.

According to [6, 10], the relative deformation of the lattice is determined by changes in the transverse charge in any atom of the crystal. For an ionic crystal, the transverse charge is determined as follows:

$$e_T = 1 + 4 \left(\frac{14.0208}{d^2 E_g}\right)^2 \text{ eV}.$$
 (14)

It follows from (14) that when deformation of the lattice degenerates in the hydration process that arises in the case of CaO application, the term of valence electrons in the oxygen atom of the mineral lattice also stops changing. This implies that the effect of changes in the ionic diffusion coefficients disappears in such systems. Consequently, rates of ameliorant application that are higher than the optimal ones for soils where kaolinite prevails in the clay fraction will result in disappearance of the effect of changes in the transfer of different ions from soil to plants.

For calculation of exchange ion-lattice binding energy for the argillaceous mineral, we determined all coordinates of active sites of the elementary lattice, the coordinates of the exchange ion, the distance between the exchange ion and the active sites, and the cosines of the angles between the vectors formed by the position of the exchange cation and calculated lattice points (active sites) of the mineral. The lattice parameters, some coordinates of the lattice points, and some distances between the lattice points are borrowed from [11].

The following minimum distances  $d_{\min}$  between ions and the nearest lattice points were taken in the calculations: 3.363 Å (Cs); 4.350 Å (Sr); 5.682 Å ((Cd); 6.855 Å (Pb).

Increases in the ion-kaolinite lattice binding energy due to application of CaO at a rate of one molecule per unit cell, or 0.166% of the dry weight of the mineral, is as follows (kcal/mole):  $(E_1 - E_2)_{Cd} = 0.759$ ;  $(E_1 - E_2)_{Cs} = 1.32$ ;  $(E_1 - E_2)_{Pb} = 0.119$ ;  $(E_1 - E_2)_{Sr} = 0.448$ .

Muscovite. In experimental studies we obtained changes in the parameter b in the crystal lattice of muscovite in its initial state control and IR spectra of OH groups of the mineral. Experimental results are presented in Fig. 4 (The IR spectra are not shown there).

As follows from Fig. 4, adsorption of water molecules on muscovite in its initial state and with added  $CaCO_3$  causes an increase in the parameter b. It should be noted that addition of  $CaCO_3$  does not make any substantial changes.

Conversely, application of CaO brings about a sharp increase in b (with an adsorbed water content close to zero). When CaO is applied at a rate of 0.166% of the dry weight of the mineral, which corresponds to a content of one CaO molecule per unit cell of muscovite, a smooth decrease in the parameter b is observed as the amount of adsorbed water increases. At a rate of 0.323%, which corresponds to two CaO molecules per unit cell of muscovite, the parameter b remains the same as it was at a rate of 0.166%. This experimental fact can be explained as follows. In accordance with the crystal structure of muscovite [11], OH groups are blocked by potassium cations that belong to the unit cell. When CaO is added to this system, simultaneously with substitution of calcium for hydrogen, the potassium cation is also replaced and changes its nonexchange form to an exchange one. Just as in the case of kaolinite, in muscovite to which one CaO molecule per unit cell is added, one OH group per unit cell is broken. But while a second CaO molecule introduced into a kaolinite cell forms hydrogen bonds with the remaining



Fig. 4. Plot of parameter b of muscovite unit cell versus adsorbed water content P: 1) muscovite in initial state (a) and CaCO<sub>3</sub>-modified muscovite (b); CaO-modified muscovite at rate of one (c) and two (d) CaO molecules per unit cell.

OH groups, in muscovite this process is impossible because of blocking by potassium; therefore, a second and subsequent CaO molecules introduced into one muscovite cell do not have any effect on the character of lattice deformation. Consequently, for muscovite (or micalike minerals in general) disappearance of the effect of changes in the ionic diffusion coefficients is impossible as the ameliorant application rates increase beyond the optimal one.

The increases in the ion-muscovite lattice binding energy due to introduction of CaO are as follows (kcal/mole):  $(E_1 - E_2)_{Cs} = 1.426$ ;  $(E_1 - E_2)_{Sr} = 0.477$ ;  $(E_1 - E_2)_{Cd} = 0.595$ ;  $(E_1 - E_2)_{Pb} = 0.201$ .

Thus, for different systems such as kaolinite and muscovite, almost the same changes in the cesium, strontium, cadmium, and lead ion binding energies are obtained, even though the absolute values of these energies substantially differ. Argillaceous fractions of many soils contain chlorite. Studies of this mineral have already been started, but no final results have been obtained so far, but in view of the data on the crystal structure of chlorite, it can be assumed that for this argillaceous mineral modified by CaO, the same changes in the ion-lattice binding energy will be obtained. Apart from argillaceous particles of soils, humic acids of soils are also very important in ion binding. Meanwhile, for humic acids similar calculations are impossible so far. From an analysis of the known schemes of humic acids, it is possible to suggest that when calcium oxide is applied to the soil, some of the OH groups in these acids are destroyed, which results in substitution of calcium for hydrogen, and the change in the binding energy of the diffusing ion caused by addition of the ameliorant is the same as that determined for argillaceous minerals.

Now, we determine optimal ameliorant application rates. These studies are central to achievement of the objective, especially for light soils. Overestimated rates can lead not only to an increase in the project cost, but also to yield losses because of an increase in the pH of the soil solution, while underestimation can result in an insufficient decrease of radionuclide contents in plants.

The ameliorant application rate is certainly determined by the contents of argillaceous particles and humus in the soil. Determining this rate for argillaceous minerals (kaolinite, muscovite), we proceed from the principle of the effect of added CaO on deformation of the crystal lattice of these minerals.

As was already mentioned, deformation of the crystal lattice of kaolinite and muscovite is maximal when the ameliorant is applied at a rate of 0.166% of the weight of the mineral. This result also follows from the scheme of calculation of the diffusing ion-lattice points binding energy and the structural scheme of the argillaceous particle. In the calculations of the binding energy it is assumed that in each unit cell calcium is substituted for hydrogen in only one OH group. With the number of unit cells in the argillaceous particle and the particle number per unit mass of the mineral known, it is found that the CaO application rate that causes deformation of the lattice is 0.16-0.18%of the mass of the mineral, i.e., if the soil consisted only of argillaceous particles (100%), the application rate would be 5 t/ha.

Now, we consider the role of humic acids of soil. According to [12], the following diminishing series is formed in adsorption of ions by humic acid:

$$Fe^{3+} > Al^{3+} >> Fe^{2+} >> Cu^{2+} >> Zn^{2+} > Co^{2+} > Pb^{2+} > Ca^{2+} > Mn^{2+} > Zn^{2+} > Cd^{2+}$$



Fig. 5. Plot of relative diffusion coefficient of cesium ions in sandy loam versus ameliorant application rate  $D_2 = 8.2 \cdot 10^{-7} \text{ cm}^2/\text{sec. } C$ , t/ha.

and when a sol of humic acid is coagulated from chernozem by metal chlorides, the following amounts of cations are bound (mg-eq. per 100 g of humic acid): 334 ( $AI^{3+}$ ), 1950 ( $Fe^{3+}$ ), 239 ( $Cu^{2+}$ ), 86 ( $Ni^{2+}$ ), 80 ( $Zn^{2+}$ ), and 177 ( $Co^{2+}$ ). This means that 100 g of humic acid binds less than 80 mg-eq. of  $Ca^{2+}$ , or less than 0.16% of the mass of humic acids.

Meanwhile, following [13], the maximum capacity of integrated binding of  $Ca^{2+}$  ions is 6.1 to 11.2% of the total capacity of organic matter in soil, and up to 90% of Ca is bound to the fulvic acid fractions following the type of simple salts. Using information presented in [12] about the contents of functional groups of fulvic acids in soddy podzolic soil of the order of magnitude of 1000 mg-eq. per 100 g of humic matter, we obtain an average content of calcium equal to 86.5 mg-eq. per 100 g of humic matter, or 0.173%. This means that if the soil consisted only of humic acids (100%)) (at a volume mass of 1.61 g/cm<sup>3</sup> [12]), the CaO application rate would be 5 t/ha.

Consequently, the calculated quicklime application rate is determined as follows:

$$C = (n_1 + n_2) \cdot 5 \text{ t/ha}$$
. (15)

The actual application rate that is calculated with account of application losses (blowing out of the field by wind) and losses due to poor mixing of the ameliorant with the soil should be somewhat higher than the optimum rate.

The optimum rates can be found in a different way on the basis of determination of the ionic diffusion coefficients in the soil.

Figure 5 is a plot of the relative diffusion coefficient of cesium ions in soil versus the ameliorant application rate. The soil is sandy loam taken from a pasture at the village of Vulkan (the same collective farm). The contents of physical clay, argillaceous particles, and humus in the soil are 13%, 5%, and 3.7%, respectively; the pH of the water and soil extracts is 7.0, and 6.25, respectively; the average radionuclide contamination level is  $15 \text{ Ci/km}^2$ . As follows from Fig. 5, the optimum rate was 500-600 kg/ha. Equation (15) predicts a similar result. On May 14-17, 1996, ameliorant was applied to the same pasture over 15 ha. On May 23, 1996, oats with interplanted timothy grass were sown. The crops were harvested on July 30. Application of the ameliorant resulted in a 50% increase in the yield, and the content of cesium-137 in the green material of the oat was 3.11 times lower.

## NOTATION

D, ionic diffusion coefficient;  $D_1$  and  $D_2$ , ionic diffusion coefficients in unmodified and ameliorant-modified soil, respectively;  $\nu$ , characteristic velocity of ion in soil; l, average length of ion jump;  $E_m$ , activation energy of surface migration of ions;  $E_1$  and  $E_2$ , binding energy of cation with hydrated surface of argillaceous minerals modified and unmodified by amelioratant, respectively;  $S_1$ , surface area of argillaceous particle; a, b, c,  $\alpha$ ,  $\beta$ ,  $\gamma$ , lattice parameters;  $S_0$ , surface area of elementary crystal lattice of mineral;  $V_0$ , volume of elementary crystal lattice;  $V_1$ , volume of argillaceous particle; d, distances between ions in lattice;  $E_g$ , width of forbidden band in crystal (g is gap);  $\varepsilon$ , energy of hybridized state of ion;  $r_c$ , hydrated radius of exchange cation;  $e_T$ , transverse charge in atom (T is tension); C, ameliorant application rate;  $n_1$ , argillaceous particle content in soil;  $n_2$ , humus content in soil; P, mineral water content; J, fraction of IR absorption by material;  $\nu$ , vibration frequency of molecules.

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