

CALCULATION OF DIFFUSIONAL TRANSFER OF WATER-SOLUBLE COMPOUNDS WITH ACCOUNT FOR SORPTION KINETICS

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Based on computational experiments, approximate formulas and nomograms are suggested for calculation and evaluation of the processes of diffusional transfer of water-soluble compounds under conditions of contact of two semiinfinite media.

Solution of purely diffusional problems with account for the kinetics of sorption encounters certain difficulties in both calculating the processes of transfer of water-soluble compounds and experimental determination of the transfer characteristics. The available analytical solutions of such problems [1] are given in the form of either a sum of infinite series or transcendental equations. Direct use of these solutions is not easy, and they are of interest mainly for evaluation of different numerical methods of solution of problems of the diffusional type. Therefore, just as in the case of problems of convective diffusion, one can use simple approximate solutions, which allow evaluation of the processes and determination of the characteristics of diffusional transfer.

Based on a series of numerical calculations of the diffusion processes for two contacting semiinfinite media with variation of the characteristics of mass exchange, the functional relations have been established between certain complex parameters and integral characteristics of mass transfer.

Mathematically, the problem has been formulated as follows:

$$\frac{\partial C_1}{\partial \tau} = D_1 \frac{\partial^2 C_1}{\partial x^2} + \frac{\alpha}{W} (C_2/K_d - C_1), \quad (1)$$

$$\frac{\partial^2 C_2}{\partial \tau} = -\alpha (C_2/K_d - C_1), \quad (2)$$

$$C_1(x, 0) = C_{1\text{don}}, \quad C_2(x, 0) = K_d C_{1\text{don}} \quad \text{for } x < 0; \quad C_1(x, 0) = C_{1a}, \quad C_2(x, 0) = K_d C_{1a} \quad \text{for } x > 0.$$

In the calculation, the parameters D_1 , K_d , α , and W were varied. The medium with a higher concentration of the water-soluble compound will be called the donor medium, while the medium with a lower concentration will be referred to as the acceptor medium. An analysis of the results has shown that between the total amount of the water-soluble compound M_m diffused through the plane of contact of the two media and the set of the above parameters the following functional dependence exists:

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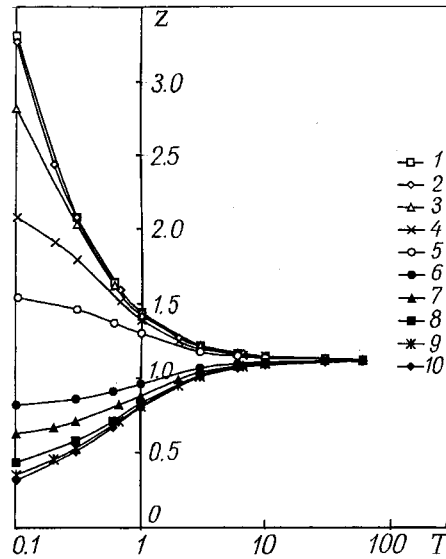


Fig. 1. Functions Z_1 (1-5) and Z_m (6-10) versus dimensionless time T for different K_d/W : 1 and 10) 100; 2 and 9) 30; 3 and 8) 10; 4 and 7) 3; 5 and 6) 1.

$$M_m = 0.5Z_m \left(\frac{\alpha\tau}{K_d}, \frac{K_d}{W} \right) \left[\frac{D_1\tau}{\left(\frac{K_d}{W} + 1 \right)} \right]^{1/2} \rho_{sk} (W + K_d) (C_{1don} - C_{1a}). \quad (3)$$

Similar functional relations exist for the integral changes in the concentrations of the water-soluble solution in the pore solution M_1 and in the solid phase M_2 of the two media:

$$M_1 = 0.5Z_1 \left(\frac{\alpha\tau}{K_d}, \frac{K_d}{W} \right) \left[\frac{D_1\tau}{\left(\frac{K_d}{W} + 1 \right)} \right]^{1/2} \rho_{sk} W (C_{1don} - C_{1a}), \quad (4)$$

$$M_2 = 0.5Z_2 \left(\frac{\alpha\tau}{K_d}, \frac{K_d}{W} \right) \left[\frac{D_1\tau}{\left(\frac{K_d}{W} + 1 \right)} \right]^{1/2} \rho_{sk} K_d (C_{1don} - C_{1a}). \quad (5)$$

To obtain the concrete values of M_1 , M_2 , and M_m as functions of the time and characteristics of mass exchange, it is necessary to have the values of the functions Z_1 , Z_2 , and Z_m as functions of the complex parameters $\alpha\tau/K_d$ and K_d/W . Figure 1 shows the dependences of Z_1 and Z_m on the mentioned arguments obtained through computer modeling. From the presented data, it follows that the numerical value of these functions depends first of all on the parameter $\alpha\tau/K_d$, which can be called the dimensionless time of mass exchange T . The parameter K_d/W exerts a marked influence on Z_1 , Z_2 , and Z_m for small T and K_d/W . When $K_d/W > 100$, the indicated functions practically do not depend on this quantity. When $T > 10$, all the indicated functions Z asymptotically approach 1.128, which corresponds to the relative integral concentration for the equation of diffusion with equilibrium sorption. Consequently, for a sufficiently large time corresponding to $T > 10$ the diffusion processes in the case of contact of two semiinfinite media can be described by the diffusion equation without allowance for the kinetics of sorption.

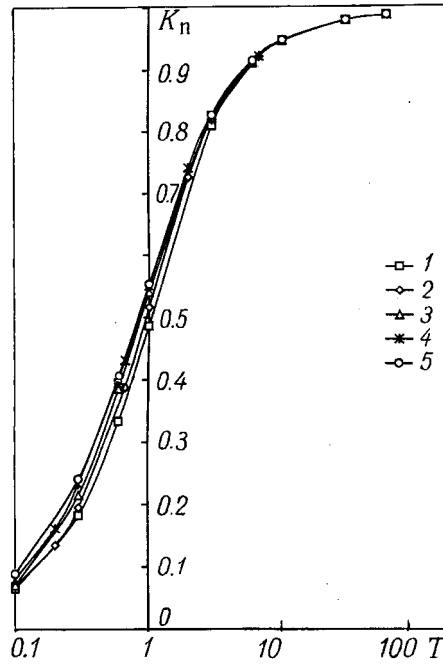


Fig. 2. Relative nonequilibrium distribution coefficient K_n versus dimensionless time T for different K_d/W : 1) 1; 2) 3; 3) 10; 4) 30; 5) 100.

It is of interest to analyze the change in the ratio of integral concentrations of a water-soluble compound that is in a pore solution and sorbed by a solid phase. For this purpose, we will use expressions (4) and (5) to obtain

$$\frac{M_2 W}{M_1} = \frac{Z_2(T, K_d/W) K_d}{Z_1(T, K_d/W)} = K_{dn} \quad (6)$$

Expression (6) corresponds to the distribution coefficient K_{dn} obtained under dynamic conditions. Unlike the equilibrium distribution coefficient K_d , the value of this coefficient depends on time and changes from 0 to K_d . The ratio of the indicated coefficients is determined by that of the functions Z_2 and Z_1 , and, consequently, similarly to these functions depends on T and K_d :

$$K_n = \frac{Z_2(T, K_d/W)}{Z_1(T, K_d/W)} \quad (7)$$

Figure 2 provides a series of curves of K_n vs. T for different K_d/W . From this figure it follows that for $T > 10$ the value of K_n approaches 1 independently of K_d/W , i.e., the value of the dynamic distribution coefficient approaches the value of the equilibrium coefficient. As T and K_d/W increase, the influence of K_d/W on K_n , as well as on the functions Z_1 and Z_2 , decreases.

Thus, the calculational procedures have shown that the main factor determining the difference of the diffusion processes in equilibrium and nonequilibrium sorption is the dimensionless time of mass exchange T . Here, the coefficients of mass exchange α and diffusion D_1 and the moisture content exert no direct influence on the indicated difference. This allows the limited number of graphical dependences to be used for evaluation of the diffusion processes in a wide range of the mass-exchange parameters D_1 , K_d , α , and W .

The graphical dependences obtained can be used as nomograms for calculation and evaluation of the processes of diffusional transfer of water-soluble compounds in contact of two semiinfinite media.

Thus, from these nomograms it is seen that for $T > 10$ the diffusion process involving nonequilibrium sorption practically does not differ from that with momentary establishment of the sorption equilibrium. The presented nomograms allow determination of the mass-exchange characteristics of water-soluble compounds based on the experimental data on their integral concentrations in two contacting samples representing plates of sufficient thickness with different initial concentrations of the investigated compounds. For this purpose, it is necessary to determine experimentally the changes in the integral concentrations in the samples as a certain time has passed after bringing the samples in contact. It is also necessary to determine the integral ratio of the amounts of the water-soluble compound that is in the pore solution and bound by the solid phase of the rock skeleton in the sample with the zeroth initial concentration of the water-soluble compound. Next, having calculated the distribution coefficient in the dynamic regime K_{dn} and the ratio of this coefficient to equilibrium K_d , one determines the parameter T using the nomogram. Knowing the time of contact of the samples and the equilibrium value of the coefficient K_d , we can calculate the mass-transfer coefficient α from the formula

$$\alpha = \frac{T}{\tau} K_d, \quad (8)$$

Using the nomogram, one determines the value of Z_m that corresponds to the parameter K_n . This makes it possible to calculate the diffusion coefficient of the water-soluble compound in the pore solution and the coefficient of effective diffusion from the formulas

$$D_{\text{eff}} = \frac{M_m^2}{0.25 Z_m^2 \rho_{\text{sk}}^2 (W + K_d)^2 (C_{1\text{don}} - C_{1a})^2 \tau}, \quad (9)$$

$$D_1 = D_{\text{eff}} \sqrt{\left(\frac{K_d}{W} + 1 \right)}. \quad (10)$$

A numerical analysis of the interrelation between the change in the integral amount of a water-soluble compound passed through the boundary of contact of the media and the parameter K_n fixed at a certain time has shown that for $T > 0.1$ the following approximation relation is fulfilled:

$$M_m \approx 0.564 (C_{1\text{don}} - C_{1a}) \rho_{\text{sk}} (W + K_d) \sqrt{K_n \tau D_{\text{eff}}}. \quad (11)$$

This indicates that if for calculating the diffusion coefficients D_1 and D_{eff} use is made of the formulas not taking into account the kinetics of establishment of the sorption equilibrium, then the value of the calculated characteristics will be underestimated by the number of times by which the values of the equilibrium and nonequilibrium distribution coefficients differ.

Consequently, for an approximate calculation of the diffusion coefficients D_1 and D_{eff} use can be made of a formula of the type

$$D_{\text{eff}} = \frac{M_m^2}{0.318 (C_{1\text{don}} - C_{1a})^2 \rho_{\text{sk}}^2 (W + K_d)^2 \tau K_n}. \quad (12)$$

Here, the calculation error for $1 > T > 0.1$ does not exceed 14%, while for $T > 1$ it is 8%.

It should be noted that, as expression (12) shows, neglect of the sorption kinetics can lead to greater calculation errors of the experimentally determined diffusion coefficients for sorbed water-soluble compounds.

The smaller the parameter T and, correspondingly, K_n , the larger the error. For T of about 0.4 the calculated diffusion coefficients will differ by a decimal order from the actual ones.

For large T , it is necessary to take into account the boundedness of the thickness of actual samples. An analysis of the diffusion equation shows that the propagation zone of a water-soluble compound does not exceed the sample thickness h provided

$$\tau \leq \frac{h^2}{12D_{\text{eff}}} . \quad (13)$$

For the time corresponding to the critical value, the concentration zone will propagate up to the external boundary of the sample and the amount of the water-soluble compound passed through the boundary of contact will amount to 30% of the maximum value attained on establishment of the total equilibrium of the concentrations. This is quite sufficient to reliably determine the diffusion coefficients. However, often it is difficult to evaluate in the first approximation the optimum duration of an experiment. Therefore, it is necessary to investigate how the duration of the experiment that is outside the limits determined by relation (13) affects the accuracy of the calculated characteristics. With this aim in view, a series of calculations was carried out for two contacting samples made in the form of plates of thickness 0.01 m, which is typical of experiments on determination of the diffusion coefficients of radionuclides. In the course of the calculation, the coefficients α , K_d , and D_1 were varied. An analysis of the calculated data has shown that even with a threefold excess of the time of contact over the critical value the error will not exceed 8% owing to the boundedness of the sample. Here, it is pertinent to note that as the duration of contact of the investigated samples increases, the parameter K_n increases as well and if it approaches 1, the kinetics of establishment of the sorption equilibrium can be neglected. In this case, for calculation of the diffusion coefficients the known Schofield integrated method [2] can be employed. For correct calculation of the diffusion coefficients with account for the sorption kinetics provided the unboundedness of the samples and without account for the kinetics for bounded samples, the following two conditions must be fulfilled simultaneously:

$$\frac{\tau\alpha}{K_d} > 10 , \quad \tau < \frac{h^2}{12D_{\text{eff}}} . \quad (14)$$

Having solved the system of these inequalities, we arrive at

$$h > 6 \sqrt{\frac{D_1 W}{\alpha}} . \quad (15)$$

The physical meaning of condition (15) is that on its fulfillment the process of diffusional transfer will attain the quasi-equilibrium regime of sorption exchange earlier than the diffusion zone exceeds the sample thickness by more than a factor of 1.7. In this case, for a rather large time of contact corresponding to $T > 10$ use can be made of the Schofield method, while for a small time it is reasonable to use the developed procedure. Since in determining the characteristics of mass exchange α and K_d it is difficult to calculate a priori the critical time of contact, experimental variants of calculation of the diffusion coefficients are chosen depending on how much the nonequilibrium value of K_{dn} differs from the equilibrium K_d and on whether the condition of unboundedness of the sample is fulfilled. In the case of fulfillment of condition (15), one of the variants will give a correct result.

It should be noted that for low concentrations of water-soluble compounds such as heavy metals and radionuclides, the distribution coefficients K_d have a value of about 1000, while the mass-transfer coefficients α are 10^{-4} – 10^{-5} sec^{-1} . In these cases, the time of onset of the quasi-equilibrium regime of sorption exchange will take from 10^7 to 10^8 sec, i.e., from 1 to 10 years, which will prevent realization of the variants of the

Schofield method. Therefore, for determination of the diffusion coefficients of water-soluble compounds with large distribution coefficients and small mass-transfer coefficients, the suggested procedure must be used.

With account for condition (15) and the ranges of D_1 , α , and W for the cations of alkaline-earth and heavy metals in soil grounds, the optimum thickness of the samples can change from 0.01 to 0.05 m. The minimum thickness of the samples is recommended for investigation of the diffusion characteristics of metal cations in the samples of soil grounds with relatively low moisture contents, while the maximum thickness is recommended for water-saturated samples.

For preliminary evaluation of the optimum experimental time, the experimental data on the characteristics of mass exchange and transfer of radionuclides Cs^{137} and Sr^{90} in typical rocks [3, 4] can be used.

To sum up, we would like to note that the suggested approximate formulas and nomograms can be of help for evaluation of the diffusional transfer of sorbed water-soluble compounds in soil grounds and sorbing filters. On their basis, methods of experimental determination of the mass-transfer and diffusion coefficients of the indicated compounds can be developed.

NOTATION

C_1 and C_2 , concentration of the water-soluble compound in the pore solution and in the solid phase of the material, respectively, mole/kg; $C_{1\text{don}}$ and $C_{1\text{a}}$, initial concentration of the water-soluble compound in the pore solution in the donor and acceptor media, mole/kg; K_d , distribution coefficient of the water-soluble compound; D_1 , diffusion coefficient of the water-soluble compound in the pore solution, m^2/sec ; D_{eff} , coefficient of effective diffusion of the water-soluble compound, m^2/sec ; α , mass-transfer coefficient of the water-soluble compound determining the rate of mass exchange between the pore solution and the solid phase of the material, sec^{-1} ; W , moisture content of the material, kg/kg; ρ_{sk} , skeleton density of the material, kg/m^3 ; x , coordinate, m; τ , time, sec; M_1 , M_2 , and M_m , integral amounts of the water-soluble compound, respectively, in the pore solution, the solid phase of the material, and the medium, mole; K_{dn} , nonequilibrium distribution coefficient; K_n , relative nonequilibrium distribution coefficient; Z_1 , Z_2 , and Z_m , functions determining the dependence of the integral amounts of the water-soluble compound on T and K_d , respectively, in the pore solution, the solid phase of the material, and the medium. Subscripts: 1, pore solution; 2, solid phase; m, medium; sk, skeleton (of the material); n, nonequilibrium; don, donor (medium); a, acceptor (medium); d, distribution.

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