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

G. P. Brovka

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An asymptotic solution is obtained for the equation of convective diffusion of water-soluble compounds with account for sorption kinetics with the linear isotherm of the sorption of them by a solid disperse phase. It is shown that the hydrodispersion is proportional to the squared linear velocity of a liquid flow and is inversely proportional to the mass-transfer coefficient which determines the rate of establiment of the sorption equilibrium.

The processes of transfer of water-soluble compounds in soils and grounds play an important role in the life of plants and in propagation of water-soluble technogenic pollutants in the environment. Similar processes occur in filter-sorbents in purification of aqueous solutions of water-soluble technogenic pollutants.

The difficulty of a mathematical description of such processes lies in the fact that the transfer of water-soluble compounds in soil-grounds is carried out by diffusion and convection. Moreover, the nonequilibrium processes of mass exchange of water-soluble compounds between the solid phase of soil-grounds and the pore solution occur concurrently with this. Formulation of the problems of convective diffusion with account for sorption kinetics is widely presented in the literature. We would like to note that such problems are mainly solved by numerical methods. The known analytical solutions are concerned with the problems with a simplified formulation. Of interest is the problem of solving the equation of convective diffusion with account for sorption kinetics and without account for longitudinal diffusion for the linear sorption isotherm [1, 2]. Its solution in the form of integral equations, in which Bessel functions appear, is of a rather complicated form, and particular data can be obtained only through computer-assisted integration of the reduced solutions. For a routine analysis of the processes of transfer of water-soluble compounds in addition to numerical and analytical solutions, it is also necessary to use simplified approximate solutions that show the mode and the regularities of the transfer and distribution of water-soluble compounds in soils and grounds and allow one to obtain preliminary estimates. For this purpose, an asymptotic solution of the equation of convective diffusion with allowance for sorption kinetics for a semiinfinite medium has been obtained that is similar to the solution indicated above. It has the form

$$C_1(x) = 0.5\,(C_{\text{in}} - C_0)\left[1 - \operatorname{erf}\left(\frac{x - 0.5\Delta\zeta - U\tau}{2\sqrt{D_{\text{d}}\tau}}\right)\right], \tag{1}$$

$$C_2(x) = 0.5K_{\text{d}}\,(C_{\text{in}} - C_0)\left[1 - \operatorname{erf}\left(\frac{x + 0.5\Delta\zeta - U\tau}{2\sqrt{D_{\text{d}}\tau}}\right)\right], \tag{2}$$

$$U = \frac{V}{\dfrac{K_{\text{d}}}{W} + 1}, \tag{3}$$

Institute of Problems of Utilization of Natural Resources and the Environment, National Academy of Sciences of Belarus, Minsk, Belarus; email: fcmnd@ns.ecology.ac.by. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 74, No. 3, pp. 25–29, May–June, 2001. Original article submitted November 3, 2000.

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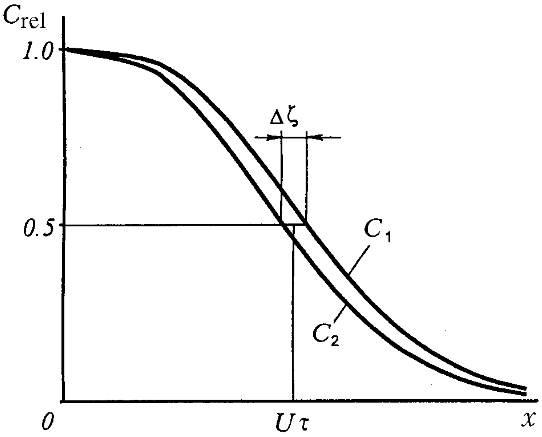

Fig. 1. Concentration distribution in the pore solution (C_1) and in the solid phase of the material (C_2) in relative units with convective transfer of water-soluble compounds.

$$\Delta\zeta = W\frac{V}{\alpha}\frac{1}{1+\dfrac{W}{K_{\text{d}}}}, \tag{4}$$

$$D_{\text{d}} = \frac{V^2}{\alpha}\frac{K_{\text{d}}^2W^2}{(K_{\text{d}}+W)^3}. \tag{5}$$

The physical meaning of the parameters used in formulas (1)–(5) can be illustrated using Fig. 1. It is seen from the figure that U corresponds to the velocity of propagation of the mean-concentration front. This dependence is known in the literature. The parameter $\Delta\zeta$ characterizes the displacement of equilibrium concentrations in the pore solution and in the solid phase of the soil. As is seen from formula (4), this parameter mainly depends on the linear velocity of a moisture flow V, the mass-transfer coefficient α, and the moisture content of the soil W. For $K_{\text{d}} >> W$, it practically exerts no influence on the displacement of the equilibrium values of the concentrations. The use of the parameter $\Delta\zeta$ allows more exact determination of the location of the mean values of the concentrations. Here it is pertinent to note that the mean concentration of the pore solution is shifted toward the moisture flow by $0.5\Delta\zeta$ as compared to the location calculated by formula (3). The analogous concentration of the solid phase is shifted in the opposite direction by the same value.

The distribution of the relative concentrations in both the pore solution and the solid phase is described by identical functions of the erf type shifted by $\Delta\zeta$. The main parameter of these functions is the hydrodispersion coefficient D_{d}. It is of interest to analyze the influence of the distribution coefficient and of the moisture content on the value of the hydrodispersion. As is seen from expression (5), the dependence of D_{d} on K_{d} and W is of a rather complicated form. In relation to the parameters K_{d} and W it is symmetric. In the case $K_{\text{d}} >> W$, expression (5) can be reduced to the form

$$D_{\text{d}} = \frac{V^2W^2}{\alpha K_{\text{d}}}. \tag{6}$$

For $K_{\text{d}} << W$, the following formula will hold:

$$D_{\text{d}} = \frac{V^2K_{\text{d}}^2}{\alpha W}. \tag{7}$$

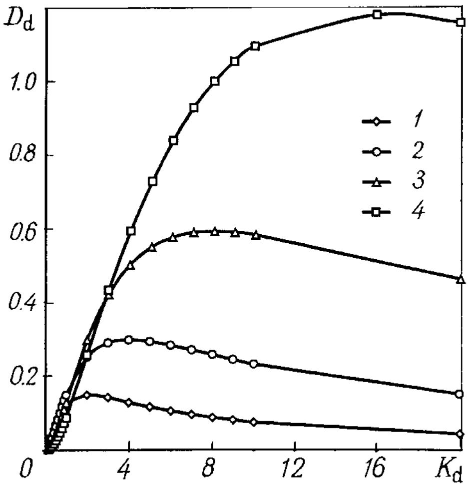

Fig. 2. Hydrodispersion coefficient vs. distribution coefficient K_d for different moisture contents W: 1) 1; 2) 2; 3) 4; 4) 8.

When K_d and W are of the same order of magnitude it is necessary to use expression (5) since in this case the dependence is nonmonotonic. Figure 2 shows a series of the curves of D_d versus K_d for single values of V and α and different W. As is seen from the figure, this dependence has a maximum for the ratios of K_d to W equal to 2, which increases with W. A similar dependence will also be observed for D_d as a function of W for different K_d.

Next we will analyze the influence of the hydrodispersion coefficients of the parameters α and V. The hydrodispersion coefficient, just as the parameter $\Delta\zeta$, is inversely proportional to the mass-transfer coefficient. It should be noted that D_d has a square dependence on the linear velocity of the moisture flow. To express a similar dependence, a number of empirical formulas with the exponent of V ranging from 1 to 2 are suggested in the literature [3–5]. Herein the presence of hydrodispersion is interpreted as the influence of turbulence or velocity pulsations in a dispersed material. Use is often made of the empirical linear dependence [3]

$$D_d = D_{mol} + \lambda V . \tag{8}$$

It can be justified as the empirical one for a narrow range of variation of the linear velocity of the moisture flow, while for a wide range of V, in our opinion, the square dependence is the most acceptable one. It is noteworthy that, analyzing the hydrodispersion in a cylindrical capillary with a laminar flow, Taylor [6] has derived a formula in which the relationship between D_d and V is square:

$$D_d = \frac{V^2 R^2}{48 D_{mol}} . \tag{9}$$

Thus, as is shown in our example and in [6], hydrodispersion occurs in the absence of turbulence. On the contrary, in our opinion, the presence of turbulence can lead to an increase in the mass-transfer coefficient α used in formula (5) or to an increase in the coefficient of effective molecular diffusion used in formula (9), and this will cause a substantial decrease in the hydrodispersion coefficient. It should also be noted that one must consider the latter not as a physical characteristic of transfer but as a complex parameter characterizing the process of blurring of the front of propagation of a water-soluble compound in convective transfer. This blurring can occur for two main reasons: the nonequilibrium character of sorption of the water-soluble compound by a disperse phase or the nonuniform linear velocity of a liquid flow in the direction perpendicular to the direction of propagation.

Despite the apparent fundamental difference, these reasons are of a similar nature determined by the inertia of mass exchange between different phases or by different fractions of the same phase. With nonuniformity of the linear velocity of a liquid flow in the direction perpendicular to this flow, which occurs when the liquid flows in a capillary, we can conventionally single out two fractions. We assume that the first of them represents the central part of the capillary equal to half its cross section, while the second fraction corresponds to the near-wall region. In this case the mean integral velocity of the first fraction is 1.5-fold higher than that of the liquid flow in a capillary. The mean integral velocity of the second fraction will, on the contrary, be $0.5V_m$. Consequently, the fractions will move with a relative velocity equal to the mean integral velocity V_m. When a water-soluble compound arrives at the capillary inlet, the front of its concentration in the first fraction will propagate more quickly than in the second fraction. This will cause the exchange between the fractions due to the radial molecular diffusion. Proceeding from the geometric parameters, the intensity of this mass exchange can be calculated in the first approximation from the formula

$$\alpha = 5.76 \frac{D_{mol}}{R^2} . \tag{10}$$

Next, using formula (5) and assuming that $K_d = 1$ and $W = 1$, we can calculate the hydrodispersion coefficient from the formula

$$D_d \approx \frac{V_m^2 R^2}{45 D_{mol}} . \tag{11}$$

As is seen, in a first approximation we have obtained a result close to the Taylor formula (9). This confirms the proposition that the main reason for the hydrodispersion in convective transfer is the inertia of the mass exchange of a water-soluble compound between different phases or different fractions of the same phase.

The use of the hydrodispersion coefficient is quite justified for approximation of the analytical solutions of the equations of convective diffusion. In this case, account must be taken of the shift of the concentration fronts of the water-soluble compound in the pore solution and in the disperse phase by a value determined by the relationship between the liquid-flow velocity V and the mass-transfer coefficient α according to formula (4). This formula allows evaluation of the degree of the nonequilibrium state of the sorption processes and the calculation errors in the case of neglect of the sorption kinetics.

For a rather large coefficient α and a small velocity of the moisture flow, the hydrodispersion will be slight and the distribution of a water-soluble compound will correspond to equilibrium sorption. Thus, for instance, for a linear velocity of 10^{-6} m/sec of the moisture flow and a mass-transfer coefficient of 10^{-3} sec^{-1}, the hydrodispersion coefficient will be commensurable to the coefficient of molecular effective diffusion. Therefore, in the general case, for low velocities of the moisture flow and rather large α, in formulas (1) and (2) it is necessary to use the coefficient D_t, which is equal to the sum of the coefficients of hydrodispersion D_d and effective diffusion D_{eff}:

$$D_t = D_d + D_{eff} . \tag{12}$$

With regard for the fact that D_{eff} is determined by a number of parameters, as is shown in [7], we can write

$$D_t = \frac{V^2}{\alpha} \frac{K_d^2 W^2}{K_d + W} + \frac{D_{mol} K_{tor}}{K_d / W + 1} . \tag{13}$$

Based on the parameters of mass exchange, we can calculate from formulas (1)–(5) the distribution of a water-soluble compound in the pore solution and in the solid phase of a sorbing material. As the preliminary calculations have shown, in this case the larger the distance between the dispersion zone of the water-soluble compound and the inlet of the filtered solution, the smaller the error. To evaluate the size of the dispersion zone in explicit form and to simplify further analysis, we will replace the function erf (x) by the square dependence, which, with an error not exceeding 6%, approximates the indicated function. As a result, we arrive at the following dependences:

$$C_1(x) =$$

$$= (C_{\text{in}} - C_0)\left[1 - 0.5\left(\frac{x + \sqrt{12D_{\text{d}}\tau} - 0.5\Delta\zeta - U\tau}{\sqrt{12D_{\text{d}}\tau}}\right)^2\right] + C_0\,, \quad 0.5\Delta\zeta + U\tau > x > 0.5\Delta\zeta + U\tau - \sqrt{12D_{\text{d}}\tau}\,; \tag{14}$$

$$C_1(x) = 0.5\,(C_{\text{in}} - C_0)\left(\frac{x - \sqrt{12D_{\text{d}}\tau} - 0.5\Delta\zeta - U\tau}{\sqrt{12D_{\text{d}}\tau}}\right)^2 + C_0\,,$$

$$0.5\Delta\zeta + U\tau - \sqrt{12D_{\text{d}}\tau} > x > 0.5\Delta\zeta + U\tau\,; \tag{15}$$

$$C_2(x) = K_{\text{d}}\,(C_{\text{in}} - C_0)\left[1 - 0.5\left(\frac{x + \sqrt{12D_{\text{d}}\tau} + 0.5\Delta\zeta - U\tau}{\sqrt{12D_{\text{d}}\tau}}\right)^2\right] + K_{\text{d}}C_0\,,$$

$$U\tau - 0.5\Delta\zeta > x > U\tau - 0.5\Delta\zeta - \sqrt{12D_{\text{d}}\tau}\,; \tag{16}$$

$$C_2(x) = 0.5K_{\text{d}}\,(C_{\text{in}} - C_0)\left[1 - 0.5\left(\frac{x - \sqrt{12D_{\text{d}}\tau} + 0.5\Delta\zeta - U\tau}{\sqrt{12D_{\text{d}}\tau}}\right)^2\right] + K_{\text{d}}C_0\,,$$

$$U\tau - 0.5\Delta\zeta - \sqrt{12D_{\text{d}}\tau} > x > U\tau - 0.5\Delta\zeta\,. \tag{17}$$

From the presented dependences it follows that the diffusion zone antisymmetrically propagates from the mean-concentration front by $\zeta = \sqrt{12D_{\text{d}}\tau}$.

A comparison of the results of the approximate calculation from formulas (1)–(5) to an exact analytical calculation has shown that the indicated formulas give an error of no more than 2% with the mean-concentration front located at a distance from the inlet exceeding the size of the diffusion zone. Here, the following relation will be fulfilled:

$$U\tau \geq \sqrt{12D_{\text{d}}\tau}\,. \tag{18}$$

If we use relations (3) and (6), we obtain

$$\tau \geq \frac{12}{\alpha}K_{\text{d}} \tag{19}$$

Consequently, the processes of convective diffusion involving nonequilibrium sorption will be described by an asymptotic solution with a sufficiently good accuracy, provided condition (19) is fulfilled. Approximate evaluation of the concentration distribution of a water-soluble compound can also be carried out

TABLE 1. Calculation Errors (ε, %) in Different Ranges of Relative Concentration, Relative Time of the Process, and the Ratio K_d/W

K_d/W	$\tau\alpha/K_d$	C/C_{in}				
		0.1	0.3	0.5	0.7	0.9
10	3	3.2	0.8	0.03	2.5	7.5
10	5	2.7	0.8	0.015	2.0	5.2
10	10	2.3	0.8	0.05	1.4	3.2
100	3	4.0	1.6	0.3	3.0	8.8
100	5	3.2	1.5	0.1	2.8	6.0
100	10	2.5	1.3	0.04	1.5	3.5
1000	3	4.0	1.0	0.3	2.8	8.8
1000	5	3.5	1.0	0.13	1.9	6.0
1000	10	2.6	0.7	0.04	1.3	3.8

for a time two or three times shorter than that determined by relation (19). In this case, the error does not exceed 9%. In Table 1, the calculation error ε is given in different ranges of relative concentration, relative time of the process, and the ratio K_d/W. As is seen from the data presented the smallest calculation error corresponds to the range of relative concentrations from 0.3 to 0.7, and the maximum error is obtained for a relatively small time from the onset of filtration of the solution. For τ larger than 0.2 of the critical value determined by (19), we can use formulas (14)–(17) for preliminary approximate calculations, taking into account that the calculation error near the filtrate inlet does not exceed 9%.

Relations (1)–(5) can also be employed in inverse problems for experimental determination of the characteristics of mass exchange in dynamic regimes. For this purpose it is necessary to obtain experimentally the concentration distribution of a water-soluble compound in the pore solution and in the solid phase in the column of investigated material for the prescribed filtration rate and the inlet concentration of the solution.

Using formulas (3)–(5) and the expressions approximating the asymptotic solution by a square dependence, we can calculate the optimal parameters of the sorbent filter. If the filtration rate and the time of protective action of the filter are prescribed, the filter thickness H, which provides practically total retention of the water-soluble compound, can be calculated from the formula

$$H = VW\left(\frac{\tau}{K_d} + \sqrt{\frac{12\tau}{\alpha K_d}} + \frac{1}{\alpha}\right). \tag{20}$$

If the filter is expected to be replaced periodically, we can calculate its optimum thickness and the time of replacement from the formulas considering that at the moment of replacement the filter is to be saturated with a water-soluble compound by no less than 50% of the maximum amount absorbed for the prescribed concentration of the filtrate:

$$H \geq 25\frac{VW}{\alpha}. \tag{21}$$

With formula (21) having the equality sign, the filter will be saturated by 50% of its sorption capacity and the time of replacement will be determined by the expression

$$\tau_{repl} = \frac{12K_d}{\alpha}. \tag{22}$$

For large thicknesses it is necessary to use formula (20). It should be noted that for the value of the time corresponding to expression (22) the extension of the diffusion zone on both sides of the mean-concentration front is determined by the expression

$$\zeta = 12\frac{VW}{\alpha}. \tag{23}$$

In this case, the size of the displacement zone will be 12-fold smaller, i.e., it will make up VW/α. The typical picture of such a distribution corresponds to Fig. 1.

Thus, the obtained asymptotic solution of the equation of convective diffusion with account for sorption kinetics and the approximate formulas approximating this solution by a square dependence allow us to relate in explicit form the hydrodispersion, the velocity of a liquid flow, and the characteristics of transfer and mass exchange of water-soluble compounds. This can be of help for evaluation of the convective transfer of water-soluble compounds in grounds and soils, for optimization of the processes of water purification by filter-sorbents, and for development of experimental methods of determination of the characteristics of transfer and mass exchange.

NOTATION

C_1 and C_2, concentration of the water-soluble compound in the pore solution and in the solid phase of the material, mole/kg; C_{10}, initial concentration of the water-soluble compound in the pore solution, mole/kg; $C_{1\text{in}}$, concentration of the filtrate at the inlet to the material layer, mole/kg; C_{rel}, relative concentration in the pore solution and in the solid phase; x, coordinate; K_d, distribution coefficient of the water-soluble compound; 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}; D_d, hydrodispersion coefficient, m^2/sec; D_{eff}, coefficient of effective diffusion of the water-soluble compound in the absence of the convective flow, m^2/sec; D_{mol}, coefficient of molecular diffusion of the water-soluble compound, m^2/sec; D_t, total diffusion coefficient, m^2/sec; λ, hydrodispersion parameter, m; K, coefficient of tortuosity or communication of the water-conducting channels of the porous material; W, moisture content of the material, kg/kg; V, linear velocity of the convective flow, m/sec; U, linear velocity of the mean-concentration front, m/sec; R, capillary radius, m; V_m, mean linear velocity of the water flow in the capillary, m/sec; H, filter thickness, m; τ_3, time of replacement of the filter, sec; ζ, extension of the diffusion zone, m; $\Delta\zeta$, displacement of the mean- concentration zones, m; ε, calculation error, %. Subscripts: 1, pore solution; 2, solid phase; rel, relative; 0, initial concentration; in, concentration at the inlet; d, distribution; eff, effective; m, mean; repl, replacement; mol, molecular; t, total; tor, tortuosity.

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