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ONE-DIMENSIONAL MIGRATION OF AN ACTIVE SUBSTANCE INVOLVING SUBSURFACE ADVECTION, DIFFUSION, AND SORPTION PHENOMENA

JEDNOWYMIAROWA PODZIEMNA MIGRACJA SUBSTANCJI AKTYWNEJ W WARUNKACH SUPERPOZYCJI ADWEKCJI, DYFUZJI I SORPCJI

In this paper one-dimensional migration of the chemically active substance in the porous rock mass has been considered. It has been assumed that the active substance dissolved in water flowing through rocks is subjected simultaneously to the advection, diffusion, dispersion, sorption, ion exchange, and chemical disintegration processes. For the description of the problem the differential equations of balance and kinetics have been applied. The considerations are restricted to the initial phase of the migration process. Consequently, it has been assumed that at the initial time $t = 0$ the concentration of dissolved active substance C and the concentration of active substance sorbed in the rock Φ are equal to zero. Moreover, the general non-linear kinetics equation may then be approximated by means of the linear relation. The differential equation describing the migration process has been solved applying the Carson-Laplace integral transform method. The solution for the case when the diffusion-dispersion process may be neglected has been compared to the solution for a the situation in which the diffusion and dispersion influence the pattern of the migration phenomenon.

Key words: migration of contaminants, transfer of dissolved substances, diffusion, dispersion, sorption, flow through porous media, differential transport equations

W artykule rozważono jednowymiarową migrację chemicznie aktywnej substancji w porowatym górotworze. Zagadnienie migracji substancji aktywnych posiada zasadnicze znaczenie dla problematyki podziemnego składowania szkodliwych odpadów przemysłowych. Zawarte w składowisku substancje toksyczne, rozpuszczone następnie w postaci jonów i unoszone przez przepływające wody podziemne, mogą być rozpraszane na znacznym obszarze, prowadząc do zatrucia podziemnych zasobów wodnych. Z punktu widzenia ochrony zasobów wodnych informacja dotycząca migracji skażeń ma zasadnicze znaczenie.

W artykule przyjęto, że substancja rozpuszczona w wodzie przepływającej w skałach (zwana dalej substancją aktywną) podlega równocześnie procesom adwekcji, dyfuzji, dyspersji, sorpcji, wymiany

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jonowej i rozpadu chemicznego. Do opisu problemu zastosowane zostały równania różniczkowe bilansu i kinetyki.

Jako podstawowe równania opisujące ruch płynu unoszącego substancje aktywne przyjęto równanie ciągłości przepływu w ośrodku porowatym (2) oraz formułę Darcy'ego (1). Jednowymiarowa propagacja substancji aktywnej opisana jest równaniem transportu (7) uwzględniającej procesy wymienione uprzednio. W równaniu tym stężenie substancji w przepływającym płynie C oraz stężenie substancji zasorbowanej w skałach górotworu Φ są podstawowymi zmiennymi zależnymi od położenia i czasu.

Założono liniową kinetykę rozpadu substancji aktywnej daną wzorem (6), co z chemicznego punktu widzenia odpowiada reakcji I rzędu. Przyjęto, że procesy dyfuzji i dyspersji opisane są w wystarczajacym przybliżeniu prawem Ficka (4).

Rozważania ograniczono do początkowego stadium zjawiska migracji. Umożliwiło to przyjęcie założenia, że w chwili początkowej $t = 0$ koncentracja rozpuszczonej w wodzie substancji aktywnej C oraz koncentracja substancji aktywnej zasorbowanej w skałach Φ są równe zeru. Ponadto nieliniowe równanie kinetyki procesu sorpcji i wymiany jonowej (5) może być wówczas aproksymowane relacją linową (8). W rezultacie ogólne równanie transportu (7) upraszcza się do postaci (9).

Rozważono przypadek transportu jednowymiarowego, lecz uogólnienie równań na przypadki dwu- i trójwymiarowy nie stanonowi żadnego problemu. Przyjęto warunek początkowy, zgodnie z którym w chwili $t = 0$ koncentracja substancji aktywnej w przepływajacym płynie równa jest zeru, a dopływ tej substancji następuje poprzez brzeg $x = 0$. Odpowiada to warunkom początkowo-brzegowym (10)–(12).

W celu uniknięcia ewentualnych niejasności, w rozdziale 5 artykułu uściślono pojęcie początkowego stadium procesu migracji. Przyjmuje się, że proces migracji jest w stadium początkowym, jeśli nieliniowe równanie kinetyki procesu sorpcji i wymiany jonowej (5) może być aproksymowane relacją linową (8). Odpowiada to warunkowi (28), pokazanemu graficznie na rysunku 1.

Otrzymane równanie różniczkowe opisujące proces jednowymiarowej migracji (9) rozwiązano metodą transformacji Carsona-Laplace'a. Rozwiązanie fianlne w postaci całkowej (24) jest jednak niedogodne do przeprowadzania obliczeń i dlatego też skorzystno z numerycznych metod rozwiązywania równań różniczkowych cząstkowych.

Równanie transportu (9) rozwiązano metodą różnic skończonych. Zastosowano aproksymację typu semi-implicite (29), dzięki której problem sprowadzono do rozwiązania równania macierzowego (32) z macierzą współczynników $\mathbf{L}$ typu trójdiagonalnego. Analiza stabilności przyjętego schematu różnicowego (29), przeprowadzona szczegółowo w innej pracy autora (Sławomirski 2001) w oparciu o metodę analizy harmonicznej, prowadzi do warunku (30), który w obliczeniach efektywnych musi zawsze być spełniony.

Przykładowe obliczenia przeprowadzono na komputerze Digital AlphaStation typu RISC, wykorzystując specjalnie do tego celu napisany przez autora program obliczeniowy oparty na przyjętym schemacie różnicowym. Ze względu na duże możliwości obliczeniowe maszyny zastosowano siatkę obliczeniową zawierającą 6000 węzłów. Wyniki obliczeń przedstawiono na rysunkach 2–5.

Rozwiązanie (34), (35) dla przypadku, gdy dyfuzja i dyspersja mogą być pominięte porównano z rozwiązaniem odpowiadającym sytuacji, gdy procesy dyfuzyjno-dyspersyjne mają istotny wpływ na finalny obraz zjawiska migracji. W przypadku gdy procesy dyfuzji i dyspersji są pominięte, rozwiązanie ma postać przesuwajacej się w czasie fali eksponencjalnej „obciętej" przez wyraźny front falowy. Matematycznie jest on reprezentowany przez funkcję Heaviside'a (rys. 6). Obecność procesów dyfuzji i dyspersji „wygładza" front falowy, powodując nawet przy odpowiednio dużych wartościach współczynnika dyfuzji-dyspersji jego zaniknięcie. Z matematycznego punktu widzenia odpowiada to zmianie typu równania z hiperbolicznego na paraboliczne, w którym żadne nieciągłości pierwszej pochodnej rozwiązania nie powinny mieć miejsca.

1. Subsurface flows

It is accepted commonly (cf., e.g., Bear 1972; Collins 1967; Peaceman 1977) that the subsurface water flow may be described by the well-known Darcy's formula according to which the specific discharge vector (i.e. the product of rock porosity φ and fluid velocity $\mathbf{u}$) is proportional to the pressure gradient grad P taken with the negative sign, and inversely proportional to the fluid viscosity μ, i.e.:

$$\varphi\mathbf{u} = -\frac{K}{\mu}\operatorname{grad}P \tag{1}$$

where the parameter K called permeability depends on the type of rock material, and is independent of flow conditions.

The substitution of Eq. (1) into the mass balance equation for the fluid flowing through porous medium (Bear 1972; Collins 1967; Peaceman 1977; Sławomirski et al. 1986, 1998, 1999, 2000)

$$\frac{\partial}{\partial t}(\rho\varphi\theta) + \operatorname{div}(\rho\varphi\mathbf{u}) + \rho q = 0 \tag{2}$$

gives

$$\operatorname{div}\left(\frac{K\rho}{\mu}\operatorname{grad}P\right) = \frac{\partial}{\partial t}(\rho\varphi\theta) + \rho(P)q \tag{3}$$

where ρ denotes fluid density, φ is rock porosity, θ is isotherm of sorption of fluid in rock material, q is intensity of external sources, and t is time.

For defined initial and boundary conditions, the solution of partial differential equation (3) gives the distribution of pressure P for each time moment t. The fluid flow velocity $\mathbf{u}$ may afterwards easily be determined from the Darcy's formula (1).

In the case when the intensities of external sources are constant the fluid velocity u varies in time so slightly, that one may consider it to be a "quasi-static" value. For one-dimensional flows the fluid velocity u may often be regarded as approximately constant.

2. Subsurface transfer of dissolved substances

Flowing water may dissolve various substances contained in the rock, and transfer them in the advection mode. The chemically active substances may be "nested" in the rock skeleton as the result of natural processes, or they may be deposited within the rock mass in an artificial manner.

The problem of propagation of dissolved substances is principal for the technology of the underground storage of toxic waste materials. Toxic substances may be leached out of a store by flowing subsurface water, and propagated in a considerable zone

as a result of the advection process. Such a situation may imply the intoxication of underground water resources located even far from a subsurface deposit of waste materials.

Generally, the advection of dissolved chemically active substances may be accompanied by the diffusion, dispersion, and sorption processes. For low concentrations the diffusion of an active substance may be described by the well-known Fick's law according to which the vector of density of a diffusion stream $\mathbf{J}$ is proportional to the concentration gradient grad C negated, i.e.:

$$\mathbf{J} = -\kappa \text{ grad } C \tag{4}$$

where κ is the diffusion coefficient.

The dispersion process is directly related to the random structure of channels in the porous medium. Taking into account that from the phenomenological standpoint the dispersion process may be described in the identical manner as the diffusion (i.e. by means of Eq. (4)), one my regard κ as the coefficient representing the superposition of diffusion and dispersion.

The sorption of an active substance already dissolved in water may be represented by the surface sorption (adsorption), volume sorption (absorption), or ion exchange (Grim 1953; Kelly 1948; Sławomirski et al. 1997, 1998, 1999, 2000, 2001; Stoch 1974). From the phenomenological standpoint various "types" of sorption of an active substance may be described as a combination. They are then represented by the sorption magnitude Φ which describes the amount of sorbed substance, expressed in mols (or alternatively in vals) per unit of volume of rock material. The sorption magnitude Φ cannot exceed a maximum value Φ_m which may be regarded as the maximum sorption capacity for a given rock material.

The sorption process is described by sorption kinetics which expresses the relationship between the variation of sorption magnitude Φ in time t and the concentrations of the active substance in flowing water C. The sorption process is often accompanied by a reciprocal phenomenon, i.e. by a desorption process. One may assume that the sorption intensity is proportional to the concentration of an active substance in flowing water C, whereas the desorption intensity is proportional to the concentration of an active substance sorbed in the rock Φ. Since the sorption and desorption processes occur simultaneously, the general form of the sorption kinetics may be expressed in the following manner (Sławomirski 2001):

$$\frac{d\Phi}{dt} = \alpha C \left(1 - \frac{\Phi}{\Phi_m}\right) - \beta \frac{\Phi}{\Phi_m} \tag{5}$$

where α and β are the sorption and desorption coefficients respectively. The α and β coefficients are typical of a given rock material, and they may be determined by empirical measurements.

The active substance transferred by the flowing water may be subject to chemical transformations. If the substance is subject to decomposition, which may be regarded

as a first order reaction (in the chemical kinetics sense), then the reaction rate is proportional to the concentration of the substance, and we may write:

$$\left(\frac{dC}{dt}\right)_{\substack{\text{chemical}\\\text{reactions}}} = -\lambda C \tag{6}$$

where λ is the reaction constant.

Sorption, diffusion, and chemical decomposition may occur during the advection process, and imply extra variations in the concentration distribution for the active substance considered.

It should be noted that the chemically active substances, the propagation of which is described in this paper, are considered to be in the ionic form. Although the problem described here differs from the problem of transport of small grains of solid material by water through a porous medium, the equations of kinetics for both processes are almost identical. The latter phenomenon is related to the colmatage problem (i.e. the problem of sedimentation of small solid grains in the pore system of rocks), described in details by Litwiniszyn and Bodziony (1962, 1969), Trzaska (1966, 1970, 1972, 1989, 2000), et al.

3. Problem formulation

The purpose of this paper is to present an asymptotic solution which describes the distribution of concentration of an active substance transferred by water flowing through porous rock, and subjected to diffusion, dispersion, sorption, and chemical decomposition. The differential balance equation formulated recently by the author of this paper (Sławomirski 2000) will be applied. This equation describes simultaneous advection, diffusion, sorption, and chemical transformations of a dissolved active substance. In the case of one-dimensional flow the balance equation may be expressed in the following form:

$$\kappa\frac{\partial^2 C}{\partial x^2} = u\frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + \frac{\partial \Phi}{\partial t} + \left(\frac{\partial C}{\partial t}\right)_{\substack{\text{chemical}\\\text{reactions}}} \tag{7}$$

The equation written above contains two unknown functions: $C(x,t)$ and $\Phi(x,t)$. In order to obtain a close equations system the kinetics equation (5) may be taken into consideration. At the beginning of the migration process the concentration of a substance sorbed in the rock is very low, and the Φ/Φ_m is little more than zero. For such a situation one may apply the following approximation of Eq. (5):

$$\frac{d\Phi}{dt} = \alpha C \tag{8}$$

A detailed discussion of the validity of the approximation of non-linear kinetics equation (5) by linear relation (8) is presented in section 5 of this paper.

Substituting Eqs. (6) and (8) into Eq. (7) we receive the following second order differential equation involving only one unknown function $C(x,t)$:

$$\kappa \frac{\partial^2 C}{\partial x^2} = u \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + \alpha C + \lambda C \qquad (9)$$

In later sections of the paper the initial phase of the one-dimensional migration of a dissolved active substance in the zone $x \geq 0$ will be considered. We shall assume that at the initial time $t = 0$ the concentration of a dissolved and sorbed substance is equal to zero, and the active substance is introduced to the zone $x > 0$ across its boundary $x = 0$. Consequently, we may formulate the following initial and boundary conditions for Eq. (9):

$$C(x,t)\big|_{t=0} = 0 \qquad (10)$$

$$C(x,t)\big|_{x=0} = C_1(t) \qquad (11)$$

$$C(x,t)\big|_{t\to\infty} = 0 \qquad (12)$$

where $C_1(t)$ function is known.

The technique of solving the boundary value problem (9) to (12) will be elicited in the subsequent section of this paper.

It may be seen that the boundary value problem (9)–(12) has been formulated for an infinite migration zone. The analysis of a similar problem referring to a finite migration zone requires a separate discussion. In the later case one must be aware the problems in formulating the second boundary condition replacing the condition represented by Eq. (12). Moreover it should be taken into account that from the computational standpoint the migration problem is hyperbolic rather than parabolic.

4. Direct solution of the boundary value problem

The initial/boundary value problem formulated in the previous section of will be solved applying the integral transform method (cf., e.g., Carslaw and Jaeger 1968; Osiowski 1965, 1971; Sneddon 1955; Tranter, 1959; Wagner, 1940, 1960). The Carson-Laplace transform $\overline{C}(x)$ of the function $C(x,t)$, representing the active substance concentration, is defined by:

$$\overline{C}(x) = T_{p,t}[C(x,t)] \overset{\mathrm{df}}{=} p \int_0^\infty C(x,t)\exp(-pt)dt \qquad (13)$$

where p is a complex parameter. The function $C(x,t)$ may be determined from its transform $\overline{C}(x)$ applying the following inversion formula:

$$C(x,t) = T_{p,t}^{-1}[\overline{C}(x,p)] = \frac{1}{2\pi i} \int\limits_{\alpha - i\infty}^{\alpha + i\infty} \frac{\overline{C}(p)\exp(pt)}{p} dp \tag{14}$$

where the real value a must be appointed in such a manner that all singular or branch points of the integrand are located on the left hand side with respect to the straight line $\text{Re}\{p\} = a$.

Multiplying both sides of Eq. (9) by e^{-pt}, integrating them with respect to t in the interval $[0; \infty]$, and taking into account the theorem about the differentiation of derivatives we obtain:

$$\kappa \frac{d^2 \overline{C}}{dx^2} = u \frac{d\overline{C}}{dx} + p\overline{C} + (\alpha + \lambda)\overline{C} \tag{15}$$

The general solution of Eq. (15) is as follows:

$$\overline{C}(x) = A\exp\left[\frac{1}{2\kappa}\left(u - \sqrt{u^2 + 4\kappa(p + \alpha + \lambda)}\right)x\right] \tag{16}$$

$$+ B\exp\left[\frac{1}{2\kappa}\left(u + \sqrt{u^2 + 4\kappa(p + \alpha + \lambda)}\right)x\right]$$

where A and B are arbitrary constants. The second term in solution (16) is unbounded when $p \to \infty$, and therefore we must assume $B = 0$. Consequently, solution (16) is reduced to the following form:

$$\overline{C}(x) = A\exp\left[\left(\frac{u}{2\kappa} - \frac{1}{\sqrt{\kappa}}\sqrt{p + \alpha + \lambda + \frac{u^2}{4\kappa}}\right)x\right] \tag{17}$$

The A constant may easily be determined from boundary condition (11). We obtain:

$$\overline{C}(x) = \overline{C}_1(p)\exp\left[\left(\frac{u}{2\kappa} - \frac{1}{\sqrt{\kappa}}\sqrt{p + \alpha + \lambda + \frac{u^2}{4\kappa}}\right)x\right] \tag{18}$$

or

$$\overline{C}(x) = \overline{C}_1(p)\exp\left[-\sqrt{p + \left(\alpha + \lambda + \frac{u^2}{4\kappa}\right)}\frac{1}{\sqrt{\kappa}}\right]\exp\left(\frac{ux}{2\kappa}\right) \tag{19}$$

where

$$\overline{C}_1(p) = T_{p,t}[C_1(t)] \tag{20}$$

The expression written above ma also be expressed in the following form:

$$\overline{C}(x) = \frac{1}{p}\overline{C}_1(p)\frac{p}{p+\left(\alpha+\lambda+\frac{u^2}{4\kappa}\right)}\left[p+\left(\alpha+\lambda+\frac{u^2}{4\kappa}\right)\right] \tag{21}$$

$$\times\exp\left[-\sqrt{p+\left(\alpha+\lambda+\frac{u^2}{4\kappa}\right)}\frac{x}{\sqrt{\kappa}}\right]\exp\left(\frac{ux}{2\kappa}\right)$$

Taking into account that according to the tables of integral transforms presented in monographs by Bateman and Erdelyi (1954), Wagner (1940, 1960), and Osiowski (1965, 1971) we have:

$$T_{p,t}\left[\frac{b}{2\sqrt{\pi}t^{3/2}}\exp\left(-\frac{b^2}{4t}\right)\right] = p\exp(-b\sqrt{p}) \tag{22}$$

and bearing in mind the theorem about translation, and theorem about convolution one may express the original function for the transform (21) in the following form:

$$C(x,t) = \int_0^t C_1(t-\tau)\frac{x/\sqrt{\kappa}}{2\sqrt{\pi}\tau^{3/2}}\exp\left(-\frac{x^2/\kappa}{4\tau}\right) \tag{23}$$

$$\times\exp\left[-\left(\alpha+\lambda+\frac{u^2}{4\kappa}\right)\tau\right]d\tau\exp\left(\frac{ux}{2\kappa}\right)$$

and finally:

$$. C(x,t) = \frac{x}{2\sqrt{\pi\kappa}}\exp\left(\frac{ux}{2\kappa}\right)\int_0^t\frac{C_1(t-\tau)}{\tau^{3/2}}\exp\left(\frac{x^2}{4\kappa\tau}\right)\exp\left[-\left(\alpha+\lambda+\frac{u^2}{4\kappa}\right)\tau\right]d\tau \tag{24}$$

Formula (24) expresses the distribution of concentrations of the dissolved active substance in space and time when the superposition of the advection, sorption, and diffusion-dispersion processes occur. Referring back to earlier comments it will be realised that the solution (24) refers only to the initial phase of the substance migration process.

5. Initial phase of the migration process

In order to avoid misunderstanding it is necessary to define the term 'initial phase of the migration process' encountered in the previous sections of this paper.

According to the remarks presented in section 3 for the initial phase of the migration process the general sorption kinetics (5) may be approximated by the linear sorption kinetics (8). For the general case the concentration of dissolved substances C at a particular point of the flow zone is variable in time. On the other hand, if the concentration C_1 at the boundary is constant, and the point is located not far from the boundary, then after certain time the magnitude of C at this point is 'stablized', and it may be regarded as a constant for the purposes of calculations.

For $C_1 = \text{const.}$ and initial condition $\Phi(t)|_{t=0} = 0$ the solution of the general sorption kinetics equation (5) is:

$$\Phi_{general}(t) = \frac{\alpha C \Phi_m}{\alpha C - \beta}\left[1 - \exp\left(\frac{\alpha C - \beta}{\Phi_m}t\right)\right] \tag{25}$$

whereas the solution of the linear sorption kinetics equation (8) is:

$$\Phi_{linear}(t) = \alpha C t \tag{26}$$

Note that both kinetics lines start from the point ($t = 0$, $\Phi = 0$), and the derivatives $d\Phi/dt$ are the same for $t = 0$ (cf. Fig. 1).

For the initial phase of the migration process the general sorption kinetics may be approximated by the linear sorption kinetics, i.e. the relative approximation error is small. Consequently, it may be written:

$$\left|\frac{\Phi_{general}(t) - \Phi_{linear}(t)}{\Phi_{general}}\right| \ll 1 \tag{27}$$

or, substituting expressions (25) and (26) into inequality (27):
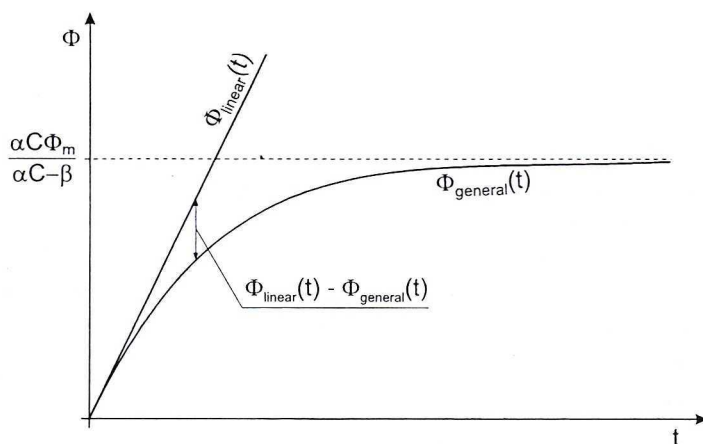

Fig. 1. Linear and non-linear kinetics images for the sorption of an active substance

Fig. 1. Graficzny obraz liniowej i nieliniowej kinetyki sorpcji substancji aktywnej

$$\left| \frac{\Phi_m \left[1 - \exp\left(-\frac{\alpha C - \beta}{\Phi_m} t \right) \right] - (\alpha C - \beta)t}{\Phi_m \left[1 - \exp\left(-\frac{\alpha C - \beta}{\Phi_m} t \right) \right]} \right| \ll 1 \tag{28}$$

In this paper the author has assumed that the initial phase of the migration process occurs in time period $t \in [0; T]$ for which inequality (28) is satisfied for all magnitudes of t. When the concentration of the dissolved substance C is variable, then the upper limit of the $C(t)$ function should be substituted as the C value in inequality (28).

6. Numerical solution of the boundary value problem

The direct solution (24) of the boundary value problem (9) to (12) expressed in the form of the parameter dependent integral is not convenient for efficient computation. Fortunately, the numerical solution of the problem may be applied, and computations may be performed by means of computers.

The finite difference technique has been applied to solve the boundary value problem (9) to (12) (cf. e.g. Collatz 1951; Richtmyer and Morton 1967; Sławomirski 1986). The following semi-implicit finite difference approximation has successfully been applied by the author with respect to differential equation (9):

$$\frac{\kappa_{j-1/2}C_{j-1}^{n+1} - (\kappa_{j-1/2} + \kappa_{j+1/2})C_j^{n+1} + \kappa_{j+1/2}C_{j+1}^{n+1}}{(\delta x)^2} = \frac{C_j^{n+1} - C_j^n}{\delta t} + (\alpha + \lambda)C_j^{n+1} \tag{29}$$

$$+ u_{j-1/2} \frac{C_j^n - C_{j-1}^n}{\delta x}$$

where j refers to the node in the computational grid, n determines time level, δx is the length of a computational block, and δt is a time increment.

The stability requirements for the semi-implicit approximation (29) of differential equation (9) have been discussed by Sławomirski (2001). He applied the von Neumann stability investigation technique based on harmonic analysis. It has been proved that the semi-implicit difference scheme (29) is locally stable if the following requirement for the time step δt is satisfied:

$$\delta t \leq \underset{j=1,2,3,\dots}{\text{Max}} \left\{ \frac{u_{j-1/2}\delta x + \frac{1}{2}\lambda_j(\delta x)^2 + 2\kappa_{j-1/2}}{(u_{j-1/2})^2 - \frac{1}{4}(\lambda_j)^2(\delta x)^2 - 2\lambda_j\kappa_{j-1/2}} \right\} \tag{30}$$

The difference equation (29) may briefly be rewritten as:

$$U_j C_{j-1}^{n+1} + V_j C_j^{n+1} + W_j C_{j+1}^{n+1} = R_j^n \tag{31}$$

where U_j, V_j and W_j represent terms accompanying unknown values of concentration, and R_j^n represents right hand side terms assumed to be known at n-th time level. The system of linear equations (31) may equivalently be written as the following matrix equation:

$$\mathbf{L}\,\mathbf{C}^{n+1} = \mathbf{R}^n \tag{32}$$

where $\mathbf{C}^{n+1}$ is vector of unknown values C_j^{n+1}, $\mathbf{L}$ is a three-diagonal matrix of coefficients, and $\mathbf{R}^n$ is the known right hand side vector.

The matrix equation (32) may be solved by means of the Thomas algorithm based on the factorisation of a three-diagonal matrix of coefficients. The realisation of computations step by step for successive time levels gives the solution of the problem in space and time.

7. Examples of computational results

The algorithm outlined above has been embedded within the program prepared by the author for an RISC type computer. Computations have been realised by means of a Digital AlphaStation.

The computational results are presented in Figs. 2–5. It has been assumed that at the initial time ($t = 0$) the concentration of the active substance in the flowing fluid C, and the concentration of the active substance sorbed in the rock Φ were equal to zero. At the boundary of flow zone (i.e. at point $x = 0$) the concentration of transported substance is equal to 2.0×10^{-6}. In other words, boundary conditions (10) to (12) are satisfied, and $C_1 = 2.0 \times 10^{-6} = \text{const}$. The velocity of advection was assigned to be 1 m/day. Figs. 2–5 show the influence of the magnitudes of various parameters on the form of the solution of the problem.

Fig. 2 illustrates the influence of the magnitude of the diffusion and dispersion coefficient κ on the spatial distribution of the concentrations of the active substance 200 days after the beginning of the migration process. It is assumed that sorption and chemical disintegration of the active substance do not occur, i.e. the α and λ parameters are assumed to be zero.

Fig. 3 presents the influence of sorption and chemical disintegration (represented by α and λ parameters) on the spatial distribution of the concentration of the active substance 200 days after the beginning of the migration process. It is assumed that diffusion and dispersion do not occur, i.e. the κ coefficient is assumed to be zero.

Fig. 4 shows the simultaneous influence of diffusion, dispersion, sorption, and chemical disintegration on the concentration of the active substance 200 days after the beginning of the migration process. It is assumed that the diffusion-dispersion coefficient $\kappa = 10^{-7}$. The curves refer to various magnitudes of α and λ parameters.
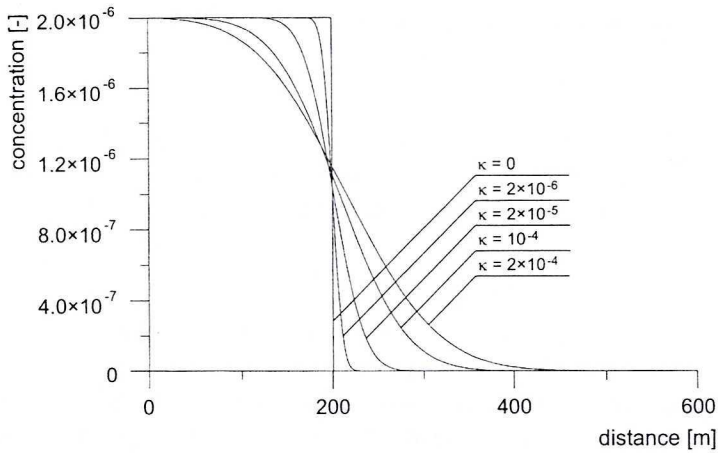
Fig. 2. The influence of the magnitude of the diffusion-dispersion coefficient κ on the spatial distribution of the concentration of the active substance 200 days after the beginning of the migration process, in the case when sorption and chemical disintegration of the active substance do not occur

Fig. 2. Wpływ wielkości współczynnika dyfuzji-dyspersji κ na rozkład przestrzenny koncentracji substancji aktywnej po 200 dniach od rozpoczęcia procesu migracji w przypadku, gdy nie uwzględnia się procesów sorpcji i rozpadu chemicznego
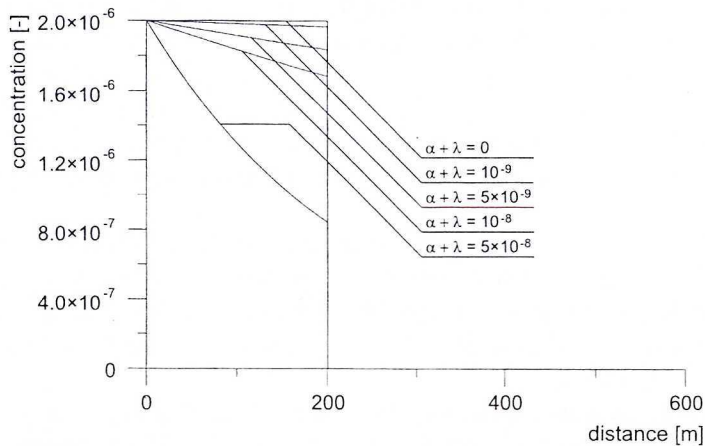

Fig. 3. The influence of sorption and chemical disintegration (represented by α and λ parameters) on spatial distribution of the concentration of the active substance 200 days after the beginning of the migration process, in the case when diffusion and dispersion do not occur

Fig. 3. Wpływ intensywności zjawisk sorpcji i rozpadu chemicznego (reprezentowanych odpowiednio przez parametry α i λ) na rozkład przestrzenny koncentracji substancji aktywnej po 200 dniach od rozpoczęcia procesu migracji w przypadku, gdy nie uwzględnia się efektów dyfuzji i dyspersji
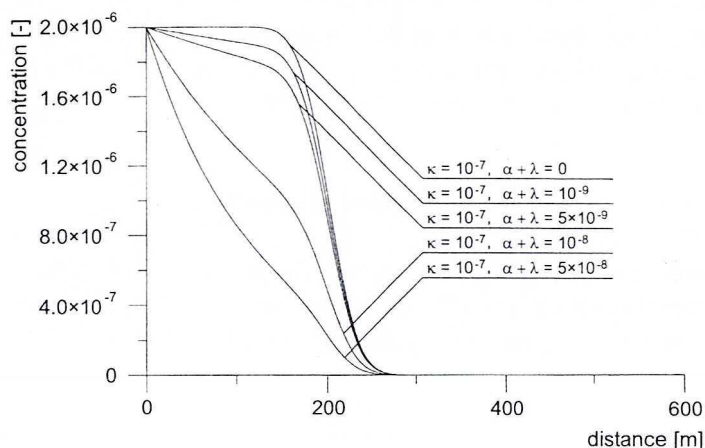
Fig. 4. The influence of diffusion, dispersion, sorption and chemical disintegration on the concentration of the active substance 200 days after the beginning of the migration process. It is assumed that the diffusion-dispersion coefficient $\kappa = 10^{-7}$. The curves refer to various magnitudes of α and λ parameters

Fig. 4. Wpływ intensywności zjawisk dyfuzji, dyspersji, sorpcji i rozpadu chemicznego na rozkład przestrzenny koncentracji substancji aktywnej po 200 dniach od rozpoczęcia procesu migracji. Jako wartość współczynnika dyfuzji-dyspersji przyjęto $\kappa = 10^{-7}$. Poszczególne krzywe odnoszą się do rozmaitych wartości parametrów α i λ
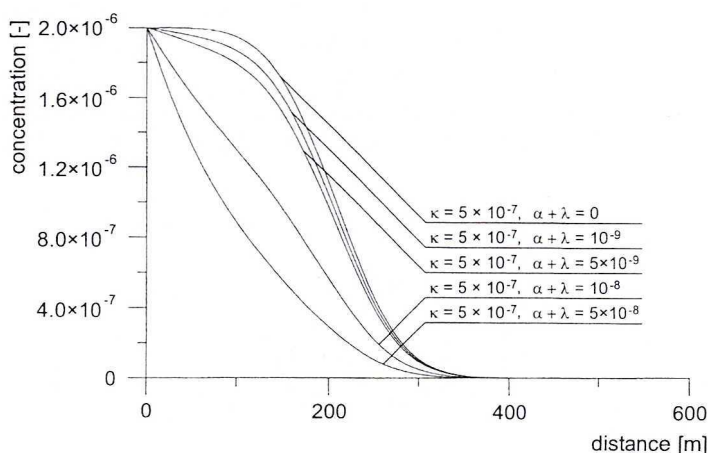

Fig. 5. The influence of diffusion, dispersion, sorption and chemical disintegration on the concentration of the active substance 200 days after the beginning of the migration process. The diffusion-dispersion coefficient κ here is five times greater in comparison to the magnitude of the coefficient applied to obtain Fig. 4

Fig. 5. Wpływ intensywności zjawisk dyfuzji, dyspersji, sorpcji i rozpadu chemicznego na rozkład przestrzenny koncentracji substancji aktywnej po 200 dniach od rozpoczęcia procesu migracji. Wartość współczynnika dyfuzji-dyspersji κ przyjęto tutaj pięć razy większą w porównaniu z wartością zastosowaną do otrzymania Fig. 4

Fig. 5 depicts a similar situation to that shown in Fig. 4. The diffusion-dispersion coefficient here is five times greater in comparison to the magnitude of the coefficient applied to obtain Fig. 4, i.e. we have $\kappa = 5.0 \times 10^{-7}$.

8. Discussion of results

The solutions presented in Fig. 3–5 may easily be compared to the solution of the same problem for a situation when the diffusion and dispersion effects are so weak that they may be neglected. The transfer equation (9) may then be reduced to the following form:

$$u \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + (\alpha + \lambda)C = 0 \tag{33}$$

For the constant boundary condition $C(x,t)|_{x=0} = C_1 = $ const. the solution of Eq. (33) may then be expressed in the following form (Sławomirski 2000):

$$C(x,t) = C_1 \exp\left(\frac{(\alpha + \lambda)}{u} x\right) H\left(t - \frac{x}{u}\right) \tag{34}$$

where $H(\xi - \xi_o)$ is the Heaviside function defined by:

$$H(\xi - \xi_o) = \begin{cases} 1 & \text{for} \quad \xi > \xi_o \\ 0 & \text{for} \quad \xi < \xi_o \end{cases} \tag{35}$$

The solution (34) referring to a situation when the diffusion-dispersion process is neglible is presented in Fig. 3 and 6. The figures show that the concentration of the active
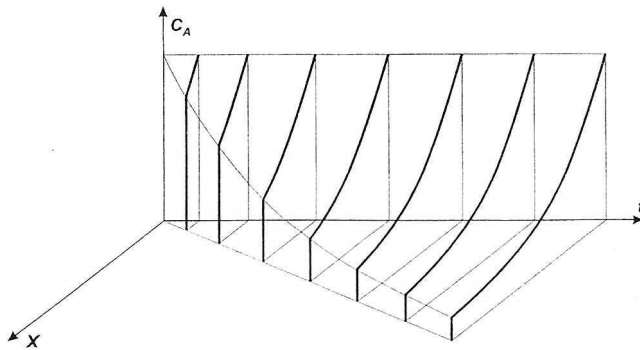

Fig. 6. Space and time spatial distribution of the concentration of the active substance dissolved in flowing water and subjected to advection, sorption and chemical disintegration processes. Diffusion and dispersion are assumed to be absent

Fig. 6. Czasowo-przestrzenny rozkład koncentracji substancji aktywnej rozpuszczonej w wodzie i poddanej procesom adwekcji, sorpcji i rozpadu chemicznego, otrzymany przy założeniu nieobecności zjawisk dyfuzji i dyspersji

substance $C(x,t)$ decreases exponentally with distance. The exponental function is 'cut' by a 'wave front' which starting from point $x = 0$ translates according to the direction of the x-axis. The front translation rate is identical with the fluid velocity u. From the mathematical standpoint the wave front is represented by the Heaviside function $H(t - x/u)$. If after time t the fluid transporting the dissolved substance reaches point x (i.e. if $ut \geq x$), then the concentration of the substance at point x and time t is given by the exponential function (34). If this does not occur (i.e. if $ut < x$) the concentration of the substance at point x and time t is equal to zero.

The presence of the diffusion and dispersion processes flattens the wave front. The hyperbolic-type solution (34) is replaced by a parabolic-type solution (24) in which any sharp 'jump' cannot exist. The wave front is flattened, and its 'corners' are rounded (cf. Figs. 2, 4, 5). Consequently, for $ut < x$ the concentration of the substance at point x and time t is greater than zero owing to the diffusion and dispersion phenomena. The 'intensity of damping' of the wave front depends on the magnitude of the diffusion-dispersion coefficient κ. The concentration of the active substance given by formula (24) decreases with distance, i.e. we have $\partial C / \partial x < 0$ but the condition $\partial^2 C / \partial x^2 < 0$ is not generally satisfied.

For high magnitudes of the diffusion-dispersion coefficient κ and a small fluid flow velocity u the diffusion type transport of an active substance dominates the advection type transport. The solution of the problem in such a case may easily be obtained from formula (24) assuming $u = 0$, i.e.:

$$C(x,t) = \frac{x}{2\sqrt{\pi\kappa}} \int\limits_0^t \frac{C_1(t-\tau)}{\tau^{3/2}} \exp\left(-\frac{x^2}{4\pi\kappa}\right) \exp[-(\alpha + \lambda)\tau]d\tau \qquad (36)$$

The image of solution (36) is represented by a function monotonically decreasing with distance.

Note that the results presented above refer to the initial period of propagation of an active substance in the sense discussed in section 5. For this phase the approximation of the general sorption kinetics (5) by Eq. (8) is sufficient for the description of the problem. On the other hand, for later periods of migration of the active substance the approximation mentioned here is inadequate.

Consequently, the results presented in this paper should only be regarded as an asymptotic solution of the migration problem. Such a solution is adequate for the description of the migration problem when condition (28) is satisfied.

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