# MATHEMATICAL MODEL OF MASS TRANSFER IN THE CASE OF A BIDISPERSED POROUS MATERIAL 

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#### Abstract

Consideration is given to a model (suitable for description at large times) for analysis of the heat- and massexchange processes of a porous body with two types of pores. Specifically, we are dealing with impregnation (in a sense, with the process of extraction, its converse). The solution of the problem with the most typical supplementary conditions is obtained; the kinetic impregnation (withdrawal) function and the density of the substance flux from the body are found for this problem.


Keywords: two-component nature, mass exchange, porous body, impregnation, extraction.
Introduction. The bidispersion (two-component) model of heat and mass transfer is usually referred to when the more simple (traditional) one-component model yields a marked disagreement with experiment because of the too simplified representation of a medium as a homogeneous continuum. In particular, in mass transfer, peculiar volumes (cavities, pockets, stagnation zones, etc.) whose mass exchange with the environment may differ both quantitatively (other transfer coefficients) and qualitatively (other physical mechanisms of transfer) appear in a number of media. We note that, despite the difference in the transfer phenomena, in particular, sediment washing, heat transfer in a heterogeneous medium, filtration in bidispersion or cracked-porous media, adsorption, etc., the proposed models have many common mathematical properties, which enables researchers to use development results obtained in such (related) processes. Also, this leads to a mutual enrichment of different scientific trends related to two-component models. We can indicate certain works where the general theoretical issues of bidispersion models have been touched on and specific processes and limiting versions of two-component models have been investigated [1-6]. Here, to be specific, we will speak of the extraction (withdrawal) of a substance from a porous material and (or) its impregnation, although the results presented below are of a more general significance.

Diffusion models of withdrawal of the target component (TC) from a porous medium in extraction have predominantly been developed at present [7, 8], although here, too, the authors have used certain relations characteristic of the two-component models of TC withdrawal. In a number of cases, researchers, accepting the presence of the convective component of mass transfer, apply diffusion models to the description of extraction kinetics, replacing the mo-lecular-diffusion coefficients in them by effective-diffusion coefficients [9, 10]. However, such an approach takes no account of the actual regularities of the process, since the TC from small pores whose fraction may multiply exceed the fraction of large pores $[9,10]$ is withdrawn solely by molecular diffusion.

The features of hydrodynamics and chemical kinetics can frequently be explained with the model of a body containing different-scale pores (cracked-porous systems) [8].

Formulation of the Problem. We consider a system of channels in a semiinfinite body (Fig. 1). In the halfspace $x>0$, there are pores of two kinds: large pores emerging at $x=0$ and small pores connected to the large ones. Let us assume that at the initial instant of time $(t=0)$, the TC concentration is the same in all pores and is equal to $C_{0}$. Then a large pore "opens" and the process of extraction to the region $x<0$ begins; in this region, the TC concentration is taken to be zero not only at $t=0$ but at all instants of time that follow as well. It is necessary to find the TC flux in the large pore for $x=0$ as a function of time.

Such a formulation of the problem by no means assumes that the channels are straight. Both large and small pores can be as curved as is wished. The coordinate $x$ is the distance reckoned from the cross section $x=0$ along the large channel, whereas the coordinate $y$ is the distance from the corresponding point of the large channel (beginning of the small channel) along the small pore.

[^0]

Fig. 1. Diagram of pores in the semiinfinite body.
Instead of the problem formulated above, it is more convenient to solve the following, mathematically equivalent, problem. Let us assume that at the initial instant of time, the TC is in the region $x<0$ and has concentration $C_{0}$ and it is absent from the region $x>0$. Once the large pore has opened, the process of impregnation begins. By virtue of the linearity of transfer equations and since they involve only the derivatives of concentration with respect to coordinate and time, the time dependence of the TC flux in the cross section $x=0$ will be the same as that for the process of extraction. The difference is only in the direction of the flux.

In the equations of the process, we allow for the fractions of transport and stagnant channels $\varepsilon_{1}$ and $\varepsilon_{2}$ :

$$
\begin{equation*}
\varepsilon_{1}=V_{1} /\left(V_{1}+V_{2}\right), \quad \varepsilon_{2}=V_{2} /\left(V_{1}+V_{2}\right), \quad \varepsilon_{1}+\varepsilon_{2}=1 \tag{1}
\end{equation*}
$$

Let the channels have an arbitrary shape with cross-sectional areas $S_{1}$ and $S_{2}$ and lengths $l_{1}$ and $l_{2}$. Then we obtain the expression $\varepsilon=N S_{2} /\left(p_{1} l_{1}\right)$ for the quantity $\varepsilon$, i.e., for the fraction of the cross-sectional area of small pores at the boundary with large pores. In this case we have the dependence $\varphi=V_{2} / V_{1}=N S_{2} l_{2} /\left(S_{1} l_{1}\right)=\varepsilon p_{1} l_{2} / S_{1}$ for the ratio of the pore volumes, which reduces formulas (1) to the form

$$
\begin{equation*}
\varepsilon_{1}=1 /(1+\varphi), \quad \varepsilon_{2}=\varphi /(1+\varphi), \quad \varphi=\varepsilon p_{1} l_{2} / S_{1} \tag{2}
\end{equation*}
$$

The process of TC transfer in a large pore will be described by the system

$$
\begin{gather*}
\varepsilon_{1}\left(\frac{\partial}{\partial t}-D_{1} \frac{\partial^{2}}{\partial x^{2}}\right) C_{1}=-q(x, t),  \tag{3}\\
C_{1}=C_{1}(x, t), x \in(0, \infty), t \in(0, \infty), \quad C_{1}(0, t)=C_{0}=\mathrm{const}, \quad C_{1}(\infty, t)=0, \quad C_{1}(x, 0)=0 . \tag{4}
\end{gather*}
$$

At least in large pores, the transfer coefficient is not necessarily determined by molecular diffusion.
The term $q$ describing the "outflow" of a substance from large pores to small ones is involved in Eq. (3) in addition to the ordinary differential terms. The functional relationship between the quantity $q$ and the other parameters of the problem is generally dependent on the processes of mass transfer in the complete system of interconnected channels in the porous body and it is unlikely that we can determine this relationship. Therefore, one usually puts forward certain hypotheses of mass transfer in a heterogeneous medium [5, 6, 11]. Determination of the variable $q$ is an example of the closure problem arising in the physics of heterogeneous media [5, 6, 11]. Here we will formulate the dependence for $q$, suitable for description of the process at fairly high values of time.

We write the equation of evolution of the volume-average concentration of the TC in a small pore and the initial condition to it in the form

$$
\begin{equation*}
\varepsilon_{2} \partial C_{2} / \partial t=q, \quad C_{2}(x, 0)=0 \tag{5}
\end{equation*}
$$

The first relation of (5) has been obtained using integration of the one-dimensional equation of diffusion in a stagnant channel with respect to the variable $y$ with the impermeability condition for the TC flux at the "bottom" of the pore.

In the vicinity of the channel interface, the diffusion equations cannot be thought of as being one-dimensional. Adoption of one-dimensionality is a postulated simplification of the problem's formulation. Such actions are substantiated in certain heterogeneous media with the method of averaging over the ensemble of configurations of the system where diffusion processes in a continuum (in this case in a large channel in the vicinity of the interface) are much more rapid than those in a dispersion medium (in this case in small channels in the vicinity of the interface) [5].

The problem will be considered further at fairly high values of time. By the high values of time we mean time intervals of the process that satisfy the inequality $t \geq O\left(T_{2}\right)$, where $T_{2}=l_{2}^{2} / D_{2}$ is the characteristic time of diffusion propagation of the TC in small channels. In this case, for the quantity $q$ in (3) and (5), the expression

$$
\begin{equation*}
q=\gamma\left(C_{1}-C_{2}\right) \tag{6}
\end{equation*}
$$

is frequently used. The coefficient $\gamma$ can be determined, in particular, as the least factor of time in the exponent of the Fourier expansion of the solution of the mass-transfer problem in a stagnant pore in the case of the impermeability of the channel "bottom" and with the condition of the first kind at the boundary of contact with a transport pore. Substituting expression (6) into system (3) and (5) and introducing dimensionless variables

$$
\begin{equation*}
G_{1}(z, \tau)=C_{1} / C_{0}, \quad G_{2}(z, \tau)=C_{2} / C_{0}, \quad \tau=t / T_{3}, \quad z=x / l_{3}, \tag{7}
\end{equation*}
$$

where $T_{3}=\gamma^{-1}$ and $l_{3}=\left(\varepsilon_{1} D_{1} / \gamma\right)^{1 / 2}$, we obtain the basic system of mass-transfer equations in the form

$$
\begin{equation*}
\varepsilon_{1} \frac{\partial G_{1}}{\partial \tau}-\frac{\partial^{2} G_{1}}{\partial z^{2}}=G_{2}-G_{1}, \quad \varepsilon_{2} \frac{\partial G_{2}}{\partial \tau}=G_{1}-G_{2} \tag{8}
\end{equation*}
$$

Supplementary conditions to Eqs. (8) will be written as follows:

$$
\begin{equation*}
G_{1}(0, \tau)=1, \quad G_{1}(\infty, \tau)<\infty, \quad G_{1}(z, 0)=G_{2}(z, 0)=0 \tag{9}
\end{equation*}
$$

Problem (8) and (9) is conveniently solved by the operational method (with respect to the variable $\tau$ ). Upon transformations, it has the form

$$
\begin{equation*}
d^{2} G_{1}^{*} / d z^{2}=\varepsilon_{1} p G_{1}^{*}+G_{2}^{*}-G_{1}^{*}, \quad \varepsilon_{2} p G_{2}^{*}=G_{1}^{*}-G_{2}^{*}, \quad G_{1}^{*}(0, p)=1 / p, \quad G_{1}^{*}(\infty, p)<0 \tag{10}
\end{equation*}
$$

The solution of problem (10) for the function $G_{1}^{*}(z, p)$ will be written as follows:

$$
\begin{equation*}
G_{1}^{*}=\frac{1}{p} \exp \left(-z \sqrt{\frac{\varepsilon_{1} \varepsilon_{2} p^{2}+p}{1+\varepsilon_{2} p}}\right) \tag{11}
\end{equation*}
$$

where we have selected the principal branch for the square root, i.e., in particular, we have $\sqrt{1}=1$. For the quantity $F_{\mathrm{S}}=-\partial G_{1} /\left.\partial z\right|_{z=0}$, the dimensionless density of the TC flux at the boundary of the porous body, we find, from (11), the Laplace-transformed value

$$
\begin{equation*}
F_{\mathrm{S}}^{*}(p)=\sqrt{\frac{1+\varepsilon_{1} \varepsilon_{2} p}{p\left(1+\varepsilon_{2} p\right)}} . \tag{12}
\end{equation*}
$$

In actual practice, it is difficult to directly measure the instantaneous value of the flux density $F_{\mathrm{S}}(\tau)$. It is only the integral curve $Q_{\mathrm{S}}(\tau)=\int_{0}^{\tau} F_{\mathrm{S}}(t) d t$ that is recorded directly. Here $Q_{\mathrm{S}}(\tau)$ is the variable (dimensionless) quantity equal to the
amount of the substance transmitted by a unit area of the boundary $x=0$ by the instant of time $t$. In what follows, for the sake of brevity (not quite correctly, omitting the last part of the previous sentence) we will call the functions $Q(\tau)$ with different subscripts the amount of the TC. According to (12), we have

$$
\begin{equation*}
Q_{\mathrm{s}}^{*}(p)=\frac{1}{p} \sqrt{\frac{1+\varepsilon_{1} \varepsilon_{2} p}{p\left(1+\varepsilon_{2} p\right)}} . \tag{13}
\end{equation*}
$$

To expand the function $Q_{\mathrm{S}}^{*}(p)$ in a series in powers $p^{-1 / 2}$ (for subsequent termwise inversion of the series) we use the existing formula [12]

$$
\begin{equation*}
\frac{1}{\sqrt{1-2 x t+t^{2}}}=\sum_{n=0}^{\infty} P_{n}(x) t^{n} \tag{14}
\end{equation*}
$$

where $P_{n}(x)$ are the Legendre polynomials for calculation of whose values there are convenient formulas [12, 13]. In particular, $P_{0}(x)=1, P_{1}(x)=x$, and $P_{2}(x)=\left(3 x^{2}-1\right) / 2$. The Legendre polynomials that follow can be found from the recurrence formula

$$
(n+1) P_{n+1}(x)-(2 n+1) x P_{n}(x)+n P_{n-1}(x)=0, \quad n=1,2, \ldots
$$

Also, we note that the radius of convergence of the power series in $t(14)$ is equal to unity for $|x| \leq 1$ but is dependent on $x$ for $|x| \geq 1$, as is the case in our formulas.

We multiply the numerator and the denominator of dependence (13) by $\left(\varepsilon_{1} \varepsilon_{2} p+1\right)^{1 / 2}$ and next, by introduction of the auxiliary variables

$$
\begin{equation*}
p=\alpha s, \quad \alpha=\frac{1}{\varepsilon_{2} \sqrt{\varepsilon_{1}}}, \quad \xi=\frac{1+\varepsilon_{1}}{2 \sqrt{\varepsilon_{1}}} \tag{15}
\end{equation*}
$$

reduce the expression in the denominator of (13) to a form allowing the use of relation (14). As a result we arrive at the expression

$$
\begin{equation*}
Q_{\mathrm{s}}^{*}(p)=\frac{1+\varepsilon_{1} \varepsilon_{2} p}{p \sqrt{p}} \frac{1}{\sqrt{1+2 \xi_{s}+s^{2}}} \tag{16}
\end{equation*}
$$

Let us split expression (16) into two terms determined by the numerator, allow for dependences (15) and for the formula $P_{n}(-x)=(-1)^{n} P_{n}(x)$ ( $n$ is the integer), and obtain expansion of $(16)$ in the sought series in powers $p^{-1 / 2}$ :

$$
\begin{equation*}
Q_{\mathrm{s}}^{*}(p)=\sum_{n=0}^{\infty}(-1)^{n} \alpha^{n+1} P_{n}(\xi)\left(\frac{1}{p^{n+5 / 2}}+\frac{\varepsilon_{1} \varepsilon_{2}}{p^{n+3 / 2}}\right) \tag{17}
\end{equation*}
$$

Next we use the correspondence of the transform $p^{-n}$ and the inverse transform $\tau^{n-1} / \Gamma(n)(n>0)$ [13] and obtain, from (17), the solution suitable for practical computations at fairly low values of time:

$$
\begin{gather*}
Q_{\mathrm{S}}(\tau)=R_{1}(\tau)+\varepsilon_{1} \varepsilon_{2} R_{2}(\tau)  \tag{18}\\
R_{1}(\tau)=\alpha \tau^{3 / 2} \sum_{n=0}^{\infty} P_{n}(\xi) \frac{(-1)^{n}(\alpha \tau)^{n}}{\Gamma\left(n+\frac{5}{2}\right)} ; \quad R_{2}(\tau)=\alpha \tau^{1 / 2} \sum_{n=0}^{\infty} P_{n}(\xi) \frac{(-1)^{n}(\alpha \tau)^{n}}{\Gamma\left(n+\frac{3}{2}\right)} \tag{19}
\end{gather*}
$$



Fig. 2. Amount of the TC in the porous body: 1) in the transport channel; 2) in lateral (small) pores; 3) in the total pore volume; 4) in the case of "diffusion" impregnation.

The series (19) have an infinite radius of convergence, which can be checked using the asymptotic formulas of gamma-function theory and the Legendre polynomials [12, 13]. A small number of their terms is necessary for calculating time values of practical significance for $\xi=O(1)$ (in our case $\xi \geq 1$ ). All the gamma functions involved in the series (19) can simply be expressed by factorials, etc. [12, 13]. The first term in the sum of (19) for $R_{2}(\tau)$ at $\mathrm{n}=0$ is the most substantial. This term corresponds to diffusion impregnation (without small channels). The physical meaning of the term is the absence of the influence of internal pores on the process at small times (it is necessary to pass to dimensional variables). The second term and the terms that follow give corrections to the first term; they are related to allowance for the TC withdrawal from internal channels. Also, it is noteworthy that upon simple (necessary) modernization, the expansion (17) enables us to write the solution of the problem on determination of the TC-flux density at the boundary of the region for a prescribed boundary function of the general form in terms of the fractional derivatives of this function.

At large times $\left(t \gg T_{3}\right)$, it is convenient to refer, for calculations, to the asymptotic (when $t \rightarrow \infty$ ) representation of the solution. We can obtain it, expanding expression (16) in a Taylor series in powers $p^{1 / 2}$ and inverting subsequently the resulting expression termwise. In so doing, we use the formula of correspondence of the transform $p^{-n}$ and the inverse transform $\tau^{n-1} / \Gamma(n)$ of the Laplace transformation for $n<0$. These formal calculations lead to the correct asymptotic expansion, since the algorithm of its search can be brought to the conditions of the corresponding theorems of operational calculus and asymptotic expansions [13, 14]. In fact, it is necessary to find asymptotic expansions for the functions $R_{1}(\tau)$ and $R_{2}(\tau)$. The above calculations yield ( $\tau \rightarrow \infty$ )

$$
\begin{equation*}
R_{1}(\tau)=-\frac{\sqrt{\tau}}{\pi} \sum_{n=0}^{\infty} P_{n}(\xi) \frac{\Gamma\left(n-\frac{1}{2}\right)}{(\alpha \tau)^{n}}, \quad R_{2}(\tau)=\frac{1}{\pi \sqrt{\tau}} \sum_{n=0}^{\infty} P_{n}(\xi) \frac{\Gamma\left(n+\frac{1}{2}\right)}{(\alpha \tau)^{n}} \tag{20}
\end{equation*}
$$

Formulas (19) and (20) show that $\alpha \tau$, not $\tau$, is a more natural dimensionless time in this problem.
To find the distribution of the substance in transport and stagnant pores separately first we integrate the first equation of (8) with account for the second term with respect to $z$ between the limits $(0, \infty)$ and then the resulting expression with respect to $\tau$ between the limits $(0, \tau)$. As a result we find

$$
\begin{equation*}
Q_{\mathrm{S}}(\tau)=Q_{1}(\tau)+Q_{2}(\tau), \quad Q_{1}(\tau)=\varepsilon_{1} I_{1}(\tau), \quad Q_{2}(\tau)=\varepsilon_{2} I_{2}(\tau) \tag{21}
\end{equation*}
$$

where $I_{j}(\tau)=\int_{0}^{\infty} G_{j}(z, \tau) d z\left(j=1\right.$ and 2), in particular, $I_{2}(\tau)=R_{1}(\tau)$. Allowing for formula (11) and for the previous calculations in deriving relations (18) and (19), we find, for $Q_{1}(\tau)$ and $Q_{2}(\tau)$, the dependences

$$
\begin{equation*}
Q_{1}(\tau)=\varepsilon_{1} R_{1}(\tau)+\varepsilon_{1} \varepsilon_{2} R_{2}(\tau), \quad Q_{2}(\tau)=\varepsilon_{2} R_{1}(\tau) \tag{22}
\end{equation*}
$$

Expressions (18)-(20) and (22) are quite sufficient to completely describe the kinetic impregnation curve throughout the time range of practical interest. It is noteworthy that we can infer from formulas (22), (18), and (20) that for fairly high values of time, when the first term of the expansion of (20) for the function $R_{1}(\tau)$ has a dominant role, impregnation occurs in the same manner as that in the diffusion version. The total volume of transport and stagnant pores participates in the process, which is in agreement with the result of [15]. The functions $Q_{1}(\tau), Q_{2}(\tau)$, and $Q_{\mathrm{s}}(\tau)$ for $\varepsilon_{1}=\varepsilon_{2}=0.5$ are plotted in Fig. 2 (curves 1, 2, and 3 respectively). For the sake of comparison this figure gives curve 4 corresponding to the diffusion impregnation regime.

Allowance for the Finite Length of Transport Pores. Let us assume that a large pore has a length $l_{1}$. At the boundary $x=l_{1}$, we must have the condition

$$
\begin{equation*}
\partial C_{1} / \partial x=0 \quad \text { at } \quad x=l_{1} \tag{23}
\end{equation*}
$$

which physically means that the substance does not enter via the cross section $x=l_{1}$. In this case we take $l_{1}$ as the characteristic length and introduce dimensionless variables and parameters

$$
\begin{equation*}
C_{1,2}=1-U_{1,2}, \quad \tau=D_{1} t /\left(l_{1}^{2} \varepsilon_{1}\right), \quad z=x / l_{1}, \quad n=\gamma l_{1}^{2} / D_{1}, \quad \varphi=\varepsilon_{2} / \varepsilon_{1} \tag{24}
\end{equation*}
$$

Equations (3), (5), and (6) in the variables (24) will be written as follows:

$$
\begin{equation*}
\frac{\partial U_{1}}{\partial \tau}=\frac{\partial^{2} U_{1}}{\partial z^{2}}+n\left(U_{2}-U_{1}\right), \quad \varphi \frac{\partial U_{2}}{\partial \tau}=n\left(U_{1}-U_{2}\right) \tag{25}
\end{equation*}
$$

It is noteworthy that the relationship between the dimensionless concentrations $C_{1,2}$ and $U_{1,2}$ (normalized to $C_{0}$ ) corresponds to the passage from the impregnation problem to the extraction problem. Supplementary conditions to system (25) will be written in the form

$$
\begin{equation*}
\partial U_{1} / \partial z=0 \quad \text { at } \quad z=1,\left.\quad U_{1}\right|_{z=0}=0,\left.\quad U_{j}\right|_{\tau=0}=1, \quad j=1,2 . \tag{26}
\end{equation*}
$$

We will seek the solution of problem (25) and (26) in the form of Fourier series

$$
\begin{equation*}
U_{i}(\tau, z)=\sum_{k=0}^{\infty} \vartheta_{i}^{k}(\tau) \sin \left(\lambda_{k} z\right), \quad i=1,2 \tag{27}
\end{equation*}
$$

where $\lambda_{k}=\pi(1 / 2+k), k=0,1,2, \ldots$. Conditions (26) in the variable $z$ for the function $U_{1}$ are fulfilled. Substituting expressions (27) into system (25) and using the completeness of the system of functions $\sin \left(z \lambda_{k}\right)$ in the interval $(0,1)$, we obtain equations for the functions $\vartheta_{i}^{k}$ :

$$
\begin{equation*}
\frac{d \vartheta_{1}^{k}}{d \tau}+\lambda_{k}^{2} \vartheta_{1}^{k}=n\left(\vartheta_{2}^{k}-\vartheta_{1}^{k}\right), \quad \varphi \frac{d \vartheta_{2}^{k}}{d \tau}=n\left(\vartheta_{1}^{k}-\vartheta_{2}^{k}\right) \tag{28}
\end{equation*}
$$

The initial conditions for this system are determined from a comparison of formulas (27) for $\tau=0$ and initial conditions (26) and, by virtue of the orthogonality of the functions $\sin \left(z \lambda_{k}\right)$ in the interval $(0,1)$, have the form

$$
\begin{equation*}
\vartheta_{j}^{k}(0)=2 / \lambda_{k}, \quad j=1,2 . \tag{29}
\end{equation*}
$$

The solution of system (28) with conditions (29) is represented in the form

$$
\vartheta_{1}^{k}(\tau)=\frac{2}{\lambda_{k}\left(p_{k}^{+}-p_{k}\right)}\left[\left(p_{k}^{+}+\frac{n}{\varepsilon_{2}}\right) \exp \left(p_{k}^{+} \tau\right)-\left(p_{k}^{-}+\frac{n}{\varepsilon_{2}}\right) \exp \left(p_{k}^{-} \tau\right)\right]
$$

$$
\begin{gather*}
\vartheta_{2}^{k}(\tau)=\frac{2}{\lambda_{k}\left(p_{k}^{+}-\overline{p_{k}}\right)}\left[\left(p_{k}^{+}+\frac{n}{\varepsilon_{2}}+\lambda_{k}^{2}\right) \exp \left(p_{k}^{+} \tau\right)-\left(p_{k}^{-}+\frac{n}{\varepsilon_{2}}+\lambda_{k}^{2}\right) \exp \left(p_{k}^{-} \tau\right)\right]  \tag{30}\\
p_{k}^{ \pm}=\left(-n / \varepsilon_{1}-\varphi \lambda_{k}^{2} \pm \sqrt{E_{k}}\right) /(2 \varphi), \quad E_{k}=\left(n / \varepsilon_{1}+\varphi \lambda_{k}^{2}\right)^{2}-4 \varphi n \lambda_{k}^{2}=\left(n / \varepsilon_{1}-\varphi \lambda_{k}^{2}\right)^{2}+4 \varphi^{2} n \lambda_{k}^{2} . \tag{31}
\end{gather*}
$$

From the two expressions for the function $E_{k}$, it is seen that $E_{k}$ is more than 0 ; furthermore, the absolute value of $\sqrt{E_{k}}$ is less than $n / \varepsilon_{1}+\varphi \lambda_{k}^{2}$ and consequently $p_{k}^{ \pm}$is always less than 0 , i.e., the solution of problem (25) and (26) will decrease with time.

We find the amount of the TC (accurate to the factor) in the transport and stagnant channels, integrating dependences (27) with respect to $z$ between the limits ( 0,1 ). As a result we obtain

$$
\begin{equation*}
Q_{i}(\tau)=\int_{0}^{1} U_{i}(\tau, z) d z=\sum_{k=0}^{\infty} \vartheta_{i}^{k}(\tau) / \lambda_{k}, \quad i=1,2 \tag{32}
\end{equation*}
$$

Only one term "survives" in formulas (32), when the values of time are fairly high. We see that the asymptotic behavior of the withdrawn-TC volume is determined by the most slowly decreasing exponent in dependence (30) for $k=0$ :

$$
\begin{equation*}
Q_{1}(\tau)=\frac{2\left(p_{0}^{+}+\frac{n}{\varepsilon_{2}}\right) \exp \left(p_{0}^{+} \tau\right)}{\lambda_{0}^{2}\left(p_{0}^{+}-p_{0}^{-}\right)}, \quad Q_{2}(\tau)=\frac{2\left(p_{0}^{+}+\frac{n}{\varepsilon_{2}}+\lambda_{0}^{2}\right) \exp \left(p_{0}^{+} \tau\right)}{\lambda_{0}^{2}\left(p_{0}^{+}-p_{0}^{-}\right)} \tag{33}
\end{equation*}
$$

Determination of the Density of the TC Flux at the Boundary of a Porous Sediment for a Semiinfinite
Body. This quantity is most simply determined after the differentiation of formula (18), i.e., the series (19) with respect to time, which is legitimate by virtue of the convergence of these power series. We have

$$
\begin{gather*}
F_{\mathrm{s}}(\tau)=R_{2}(\tau)+\varepsilon_{1} \varepsilon_{2} R_{3}(\tau)  \tag{34}\\
R_{3}(\tau)=\frac{\alpha}{\tau^{1 / 2}} \sum_{n=0}^{\infty} P_{n}(\xi) \frac{(-1)^{n}(\alpha \tau)^{n}}{\Gamma\left(n+\frac{1}{2}\right)} \cong \frac{-1}{\pi \tau^{3 / 2}} \sum_{n=0}^{\infty} P_{n}(\xi) \frac{\Gamma\left(n+\frac{3}{2}\right)}{(\alpha \tau)^{n}} \tag{35}
\end{gather*}
$$

where the last series is asymptotic when $\tau \rightarrow \infty$, which is found analogously to formulas (20). Thus, we have obtained that at large times, we can use, for the function $F_{\mathrm{s}}(\tau)$, the asymptotic expansion

$$
\begin{equation*}
F_{\mathrm{S}}(\tau)=\frac{1}{\pi \sqrt{\tau}} \sum_{n=0}^{\infty} P_{n}(\xi) \frac{\Gamma\left(n+\frac{1}{2}\right)}{(\alpha \tau)^{n}}-\frac{\varepsilon_{1} \varepsilon_{2}}{\pi \tau \sqrt{\tau}} \sum_{n=0}^{\infty} P_{n}(\xi) \frac{\Gamma\left(n+\frac{3}{2}\right)}{(\alpha \tau)^{n}} \tag{36}
\end{equation*}
$$

It is noteworthy that the introduced functions $R_{j}(\tau)\left(j=1,2\right.$, and 3) are related by $R_{2}(\tau)=R_{1}^{\prime}(\tau)$ and $R_{3}(\tau)=R_{2}^{\prime}(\tau)$. The minus sign before the asymptotic formula (35) must not confuse anyone, since the function $R_{3}(\tau)$ takes on first positive values (for $\alpha \tau \in(0,0.8378)$ and then negative ones (for $\alpha \tau>0.8378$ ). Therefore, it is clear that the asymptotic formula (35) can describe only the negative part of the function $R_{3}(\tau)$ and, what is more, from a certain value of the argument.

The problem on determination of the flux density at the boundary of the region for the system of equations of the form (8) has been considered in [16, 17] with operator product expansions using fractional derivatives. In these
works, it was erroneously derived that the variable $G_{1}(z, \tau)$ (in our notation) at the boundary of the region $z=0$ undergoes an abrupt change

$$
\begin{equation*}
G_{1}(-0, \tau)=1, \quad G_{1}(+0, \tau)=1-\exp \left(-\tau / \varepsilon_{2}\right), \tag{37}
\end{equation*}
$$

which has led to a distorted picture of mass exchange. In [16, 17], it has been assumed that condition (9) which is written in (37) (and in $[16,17]$ ) at the point $z=-0$ (displaced from zero to the left by an infinitesimal quantity) is fulfilled. In the present work, we take into account that here the value of the parameter $\gamma$ differs $\varepsilon_{2}$ times from that in [16]. In [16], a detailed solution has been given only for the partial version $\varepsilon_{1}=\varepsilon_{2}=1 / 2$. We obtain the solution of the problem of [16] in the general case for any value of $\varepsilon_{1}$.

With the law of variation in the TC at entry into the porous body according to dependence (37), we replace the formula for the flux density (12) by the following one:

$$
\begin{equation*}
F_{\mathrm{s}}^{*}(p)=\frac{\left(\frac{1}{p}+\varepsilon_{1} \varepsilon_{2}\right)^{1 / 2}}{\left(1+\varepsilon_{2} p\right)^{3 / 2}} \tag{38}
\end{equation*}
$$

To obtain an expansion analogous to $[16,17]$ we use the theorem of parametric shift of the Laplace transformation [13, 14] $p \rightarrow p+1 / \varepsilon_{2}$. In inverting the function of the new parameter, the result, according to [13, 14], should be multiplied by $\exp \left(-\tau / \varepsilon_{2}\right)$. Instead of (38), we will invert the expression

$$
\begin{equation*}
f_{\mathrm{S}}^{*}(p)=\frac{1}{p \sqrt{p \varepsilon_{2}}} \sqrt{\frac{\varepsilon_{1} p+1}{\varepsilon_{2} p-1}} \tag{39}
\end{equation*}
$$

Introducing the variables $p=i s / \sqrt{\varepsilon_{1} \varepsilon_{2}}$ and $\xi=\left(\varepsilon_{2}-\varepsilon_{1}\right) / 2 \sqrt{\varepsilon_{1} \varepsilon_{2}}$, we obtain

$$
\begin{equation*}
\sqrt{\frac{\varepsilon_{1} p+1}{\varepsilon_{2} p-1}}=\frac{s \sqrt{\varepsilon_{1} / \varepsilon_{2}}-i}{\sqrt{1-2 i \xi_{s}+s^{2}}} \tag{40}
\end{equation*}
$$

which enables us to use relation (14). Passing from the variable $s$ to $p$, we apply formula (40) to expansion of (39) in negative powers of $p$. As a result we have

$$
\begin{equation*}
f_{\mathrm{S}}^{*}(p)=\frac{1}{\varepsilon_{2}}\left(\sqrt{\varepsilon_{1}}+\frac{1}{p \sqrt{\varepsilon_{1}}}\right)_{n=0}^{\infty} \frac{i^{n} P_{n}(i \xi)}{\left(\varepsilon_{1} \varepsilon_{2}\right)^{n / 2}} \frac{1}{p^{n+3 / 2}} \tag{41}
\end{equation*}
$$

Let us introduce the notation $\Phi_{k}(\xi)=i^{k} P_{k}(i \xi)$. We emphasize that $\Phi_{k}(\xi)$ is the real polynomial for the real argument. Numerous [12,13] formulas for Legendre polynomials can be used for derivation of the corresponding formulas for the function $\Phi_{k}(\xi)$. For example, it is easy to obtain the relation

$$
\begin{equation*}
\Phi_{n}(x)=\frac{(-1)^{n}}{\pi} \int_{0}^{\pi}\left[x+\cos \varphi \sqrt{1+x^{2}}\right]^{n} d \varphi \tag{42}
\end{equation*}
$$

Termwise inversion of the series (41) yields the following expression for the flux density $F_{\mathrm{s}}$ :

$$
\begin{equation*}
F_{\mathrm{S}}(\tau)=\frac{\exp \left(-\tau / \varepsilon_{2}\right) \sqrt{\tau}}{\varepsilon_{2}}\left\{\sum_{n=0}^{\infty} \frac{\tau^{n} \Phi_{n}(\xi)}{\left(\varepsilon_{1} \varepsilon_{2}\right)^{n / 2}}\left[\frac{\sqrt{\varepsilon_{1}}}{\Gamma\left(n+\frac{3}{2}\right)}+\frac{\tau}{\Gamma\left(n+\frac{5}{2}\right) \sqrt{\varepsilon_{1}}}\right]\right\} \tag{43}
\end{equation*}
$$



Fig. 3. Density of the TC flux at the boundary of the porous body: 1) formula (34) for $\varepsilon_{1}=1 / 2 ; 2$ ) formula (46).

When $x$ is real, formula (42) enables us to roughly evaluate the function $\Phi_{n}(x)$ :

$$
\left|\Phi_{n}(x)\right| \leq\left(|x|+\sqrt{1+x^{2}}\right)^{n}
$$

this evaluation is sufficient to establish the absolute convergence of the series (43) with allowance for the asymptotic behavior of the gamma function for high values of the argument [12, 13].

The principal term determining the inertial stage of impregnation of the sediment has the form

$$
\begin{equation*}
F_{\mathrm{S}}(\tau)=\frac{2 \sqrt{\tau \varepsilon_{1}}}{\varepsilon_{2} \sqrt{\pi}}, \quad \tau \rightarrow 0 \tag{44}
\end{equation*}
$$

as follows from dependence (43). This dependence is caused by the law of variation in the TC concentration at the boundary, which is linear in time for $\tau \rightarrow 0$ and has been used in the formulation of the problem, not by the mass exchange between the zones (in the opinion of Babenko et al. [16]). Dependence (44) "works" at such small times that mass exchange between the zones has yet to manifest itself.

To obtain the formula describing the behavior of the heat flux at large times we can use dependence (38), expand it is positive powers of the parameter $p$, and then invert the resulting expression. Inversion of the first three terms yields a trinomial asymptotic expansion of the function $F_{\mathrm{s}}$ :

$$
\begin{equation*}
F_{\mathrm{s}}(\tau)=\frac{1}{\sqrt{\pi \tau}}\left[1+\frac{\varepsilon_{2}\left(3-\varepsilon_{1}\right)}{4 \tau}+\frac{3 \varepsilon_{2}^{2}\left(15-\varepsilon_{1}^{2}-6 \varepsilon_{1}\right)}{32 \tau^{2}}+O\left(\frac{1}{\tau^{3}}\right)\right], \quad \tau \rightarrow \infty \tag{45}
\end{equation*}
$$

In the problem considered in [16], we have $\varepsilon_{1}=\varepsilon_{2}=1 / 2$, with $\xi$ being equal to zero. Using the existing [12] formula for Legendre polynomials for the zero argument, we obtain $\Phi_{2 n+1}(0)=0$ and $\Phi_{2 n}(0)=(-1)^{n} P_{2 n}(0)=$ $\Gamma(n+1 / 2) /[\Gamma(1 / 2) n!], n=0,1,2, \ldots$. Expression (43) is simplified and takes the form

$$
\begin{equation*}
F_{\mathrm{S}}(\tau)=\sqrt{\frac{2 \tau}{\pi}} \exp (-2 \tau)\left\{\sum_{n=0}^{\infty} \frac{\Gamma\left(n+\frac{1}{2}\right)}{\Gamma\left(2 n+\frac{3}{2}\right)} \frac{(2 \tau)^{2 n}}{n!}+2 \tau \sum_{n=0}^{\infty} \frac{\Gamma\left(n+\frac{1}{2}\right)}{\Gamma\left(2 n+\frac{5}{2}\right)} \frac{(2 \tau)^{2 n}}{n!}\right\} \tag{46}
\end{equation*}
$$

The first (in the power of $\tau$ ) term of dependence (46) (in the braces with allowance for the factor $\tau^{1 / 2}$ ) is coincident with that from [16], whereas the second term (of the order of $\tau^{3 / 2}$ ) in [16] is zero, unlike that given in the present work.

Certain functions describing the behavior of the TC-flux density are given as an illustration in Fig. 3. In particular, this figure plots the function $F_{\mathrm{s}}(\tau)$; the plot is determined by relation (34) for $\varepsilon_{1}=\varepsilon_{2}=1 / 2$ (curve 1). The curves for other values of the parameter $\varepsilon_{1}$ are close to curve 1 shown in Fig. 3; therefore, we do not give them.

The function $F_{\mathrm{s}}(\tau)$ plotted from formula (46) is shown in Fig. 3 (curve 2). It is seen that curves 1 and 2 approach each other with increase in the time, as they must, since both functions presented in Fig. 3 tend to zero and have the same (monomial) behavior asymptotic for $\tau \rightarrow \infty$. Formula (37) may be considered as a particular case of a relaxation relation, bringing the function in the boundary condition of the first kind for $z=0$ to a constant (unit) value. This is the reason for the proximity of these curves at large times. It should be expected that if a limiting value of unity in formula (37) were reached faster, more precisely, if a larger constant were present in it instead of $\varepsilon_{2}$, the maximum of the function $F_{\mathrm{s}}(\tau)=0.7723$ (curve 2 ) would shift from the point $\tau=0.5998$ closer to the origin of coordinates, and the maximum itself would be larger, i.e., the new curve 2 on a larger $\tau$ interval would fit curve 1 more tightly. At the same time, a behavior characteristic of the boundary layer would be observed in the vicinity of the point $\tau=0$.

To obtain expansions representing the solution of the functions in power series of the time $\tau$, one first finds series expansions in the Laplace transform space, i.e., in powers of the parameter $p$. Thereafter, the resulting series is inverted termwise. When expressions containing square roots (of the (13) and (38) type) are present, series of formulas of the binomial type are to be multiplied. This is not always convenient. Here we seek to express the expansion coefficients by certain polynomials (in this case by Legendre polynomials). Numerous convenient formulas are usually available for calculation of the values of such polynomials. The above procedure can be performed for relation (38) if we use, instead of (14), the following formula:

$$
\begin{equation*}
\frac{a z}{(1+a z) \sqrt{(1+a z)(1+b z)}}=\frac{b-a}{2 \sqrt{a b}} \sum_{n=1}^{\infty}(-1)^{n} P_{n}^{\prime}(\xi) z^{n}(a b)^{n / 2}-\sum_{n=1}^{\infty}(-1)^{n} n P_{n}(\xi) z^{n}(a b)^{n / 2}, \quad \xi=\frac{a+b}{2 \sqrt{a b}} \tag{47}
\end{equation*}
$$

The derivative of the Legendre polynomial involved in the first series of (47) can be expressed by Legendre polynomials with other numbers, e.g., using the well-known recurrence relation

$$
\left(1-z^{2}\right) P_{n}^{\prime}(z)=n P_{n-1}(z)-n z P_{n}(z), \quad n=1,2, \ldots
$$

appropriate when $z \neq 1$, which is sufficient for our purposes. This follows from the fact that we do not need the value of $d P_{n} /\left.d z\right|_{z=1}=n(n+1) / 2$ for $z=1$, since we have $b=a(\xi=1)$ and the first series (containing the derivatives of the Legendre polynomials) disappears. However, the polynomials $d P_{n} / d z$ can be considered as independent objects satisfying the recurrence relation

$$
n P_{n+1}^{\prime}(z)-(2 n+1) z P_{n}^{\prime}(z)+(n+1) P_{n-1}^{\prime}(z)=0, \quad n=1,2, \ldots
$$

and a number of other dependences related to Legendre polynomials.
Comparison to a Diffusion Regime. As is seen from system (8), the diffusion version of impregnation will be obtained if we set $\varepsilon_{2}=0\left(\varepsilon_{1}=1\right)$ in the system. System (8) will be reduced to the diffusion equation for the function $G_{1}(z, \tau)$ and to the relation $G_{2}(z, \tau)=G_{1}(z, \tau)$. Thus, for the formula of "diffusion impregnation" to be obtained, it is sufficient to pass to the limit $\varepsilon_{2} \rightarrow 0$ in the found solution (18), which also leads to the limiting equalities $\varepsilon_{1} \rightarrow 1$ and $\alpha \rightarrow \infty$. As a result, expression (18) with account for the asymptotic formulas (20) yields the "diffusion" relation $Q_{\mathrm{s}}(\tau)=2(\tau / \pi)^{1 / 2}$. This dependence corresponds to curve 4 in Fig. 2. From physical considerations, it is clear that the presence of internal pores offers additional possibilities for the TC to penetrate into a porous body compared to the diffusion version, creating the "rarefaction" of the concentration at entry into the body and thereby increasing the substance flux. Here we are dealing with the specific boundary condition (9) at entry into the porous body. The general case where the substance can both enter the sediment and come out from it, which is caused by the external situation (boundary condition for $z=0$, which is not necessarily of the first kind), is not considered now. The corresponding more complex problem for a general-type boundary condition of the first kind will be discussed below.

Also, the proposed model must reflect the fact that a greater amount of the TC penetrates into the sample with internal pores over a given period $\tau>0$ than the amount in the case of their absence. This is not evident from the obtained formulas (18)-(22). A comparison of the plots (curves 3 and 4 in Fig. 2) of the corresponding dependences can be an illustrative (but not mathematical) proof of the increase in the amount of the TC in the body. We


Fig. 4. Integration contour.
prove this property mathematically as follows. We will rely on formula (12) for the TC-flux density at the boundary of the region and will take into account that this formula must be divided by $\sqrt{\varepsilon_{1}}$ in comparing it to the corresponding formula of the diffusion regime because of the selected scale of variables (see (7)). We have

$$
\begin{equation*}
F_{\mathrm{s}}^{*}(p)=\sqrt{\frac{1+\varepsilon_{1} \varepsilon_{2} p}{\varepsilon_{1} p\left(1+\varepsilon_{2} p\right)}} . \tag{48}
\end{equation*}
$$

Next, we use the Riemann-Mellin formula. We make two cuts in the plane $p$ along the negative part of the real axis to separate the single-valued branch of the function $F_{\text {sup }} *(p)$ (see Fig. 4). Using the Riemann-Mellin formula, the Jordan lemma [13, 14], the property of regularity of the function $F_{\text {sup }}{ }^{*}(p)$ in the $p$ plane with the noted cut, the Cauchy theorem, and an analysis of the behavior of the function $F_{\text {sup }}{ }^{*}(p)$ in the vicinity of the branching points $p=0, p=$ $-a$, and $p=-b$, we reduce the integral in the Riemann-Mellin formula along the straight line $L$ ( $\operatorname{Re} p=$ const $>0$ ) to the sum of two integrals along the edges of the cut. For this purpose we must pass to the limit $R \rightarrow \infty$ and let the radii of the circles bypassing the branching points $p=0, p=-a$, and $p=-b$ tend to zero. Finally, we obtain

$$
\begin{equation*}
F_{\mathrm{S}}(\tau, b)=\frac{1}{\pi} \int_{0}^{a} \frac{\exp (-r \tau)}{\sqrt{r}} \sqrt{\frac{b-r}{a-r}} d r+\frac{1}{\pi} \int_{b}^{\infty} \frac{\exp (-r \tau)}{\sqrt{r}} \sqrt{\frac{r-b}{r-a}} d r, \tag{49}
\end{equation*}
$$

where $a=1 / \varepsilon_{2}$ and $b=a / \varepsilon_{1}(b>a)$. In the following discussion, in comparing our solution and the diffusion regime, we will assume the parameters $\varepsilon_{1}$ and $\varepsilon_{2}$ to be free (which does not affect the result), i.e., to be not related by the dependence $\varepsilon_{1}+\varepsilon_{2}=1$. This results in the independence of the parameters $a$ and $b(b \geq a)$.

From formula (49), it is seen that for $a=b$ the function $F_{\mathrm{s}}(\tau, b)$ is represented by one integral taken between the limits $(0, \infty)$ and whose value is expressed by the function $1 /(\pi \tau)^{1 / 2}$ coincident with the dependence for the flux density of the diffusion version of impregnation. For the derivative of the function $F_{\mathrm{s}}(\tau, b)$ with respect to the parameter $b$, we have

$$
\begin{equation*}
\pi \frac{\partial F_{\mathrm{s}}}{\partial b}=\int_{0}^{a} \frac{\exp (-r \tau) d r}{\sqrt{r(b-r)(a-r)}}-\int_{b}^{\infty} \frac{\exp (-r \tau) d r}{\sqrt{r(r-b)(r-a)}} . \tag{50}
\end{equation*}
$$

When $\tau=0$ it is easily checked that the value of this derivative is equal to zero (the integrals in formula (50) are equal). When $\tau>0$, according to the mean-value theorem, we have for the integrals

$$
\begin{equation*}
\pi \frac{\partial F_{\mathrm{s}}}{\partial b}=\left[\exp \left(-r_{1} \tau\right)-\exp \left(-r_{2} \tau\right)\right] \int_{0}^{a} \frac{d r}{\sqrt{r(b-r)(a-r)}}, \tag{51}
\end{equation*}
$$

where $r_{1} \in(0, a)$ and $r_{2} \in(b, \infty)$, because of which (the exponential function exp $(-r \tau)$ monotonically decreases for $r>0$ ) the value of the derivative $\partial F_{\mathrm{S}} / \partial b$ is positive. Therefore, when $b>a$, we obtain $F_{\mathrm{S}}(\tau)>1 /(\pi \tau)^{1 / 2}(\tau>0)$. This means that the TC-flux density in our problem exceeds the flux density in the diffusion model, which is the required result. After termwise integration between the limits $(0, \tau)$, it follows that $Q_{\mathrm{s}}(\tau)>2(\tau / \pi)^{1 / 2}$, i.e., the total amount of the TC in the porous body in the model in question exceeds the corresponding quantity in the diffusion case.

With allowance for the obtained results the solution of the general problem on determination of the amount of the TC that has entered the porous body with the boundary condition $G(0, \tau)=f(\tau) \geq 0$ (the function $f(\tau)$ cannot be negative, since it expresses the concentration of the substance) can be represented as the integral of convolution of the functions

$$
\begin{equation*}
Q_{\mathrm{s}}(\tau)=\int_{0}^{\tau} f(\tau-\xi) F_{\mathrm{s}}(\xi) d \xi \tag{52}
\end{equation*}
$$

The integral of (52) for low $\tau$ values is easily calculated numerically, e.g., using the trapezoidal rule. The singularity of the function $F_{\mathrm{S}}(\tau)$ for $\tau \rightarrow 0$ is easily overcome in calculating the integral in (52) after the replacement of the integration variable $\xi=x^{2}$. Also, the expansion of the function $F_{\mathrm{s}}(\tau)$, asymptotic for $\tau \rightarrow \infty-(36)$ - can turn out to be useful.

We note that the total growth in the TC in this model always exceeds that in the diffusion version. This is quite evident from formula (52), when we apply to it the same procedure as that in the above proof of the inequality of the values of the flux densities in the noted models. The nonnegative character of the function $f(\tau) \geq 0$ under the integration sign in expression (52) is of importance.

Distribution of the TC in the Semiinfinite Porous Body. The above results are sufficient for practical purposes. However, it is expedient to discuss the TC concentration in the sediment within the framework of this model to fully understand the process of impregnation (extraction). The solution of problem (8) and (9) can be found by the Fourier method analogously to the solution of problem (25) and (26) or by passage to the limit $l_{2} / l_{3} \rightarrow \infty$ in (25) and (26). As a result, we obtain

$$
\begin{gather*}
G_{i}(\tau, z)=1-\frac{2}{\pi} \int_{0}^{\infty} \sin (\lambda z) \vartheta_{i}(\lambda, \tau) \frac{d \lambda}{\lambda}, \quad i=1,2,  \tag{53}\\
\vartheta_{1}(\lambda, \tau)=\frac{\left(p^{+}+\varepsilon_{2}^{-1}\right) \exp \left(p^{+} \tau / \varepsilon_{1}\right)-\left(p^{-}+\varepsilon_{2}^{-1}\right) \exp \left(p^{-} \tau / \varepsilon_{1}\right)}{p^{+}-p^{-}} ; \\
\vartheta_{2}(\lambda, \tau)=\frac{\left(p^{+}+\lambda^{2}+\varepsilon_{2}^{-1}\right) \exp \left(p^{+} \tau / \varepsilon_{1}\right)-\left(p^{-}+\lambda^{2}+\varepsilon_{2}^{-1}\right) \exp \left(p^{-} \tau / \varepsilon_{1}\right)}{p^{+}-p^{-}} ;  \tag{54}\\
E=\left(\varepsilon_{1}^{-1}+\varphi \lambda^{2}\right)^{2}-4 \varphi \lambda^{2}=\left(\varepsilon_{1}^{-1}-\varphi \lambda^{2}\right)^{2}+4 \varphi^{2} \lambda^{2} ; p^{ \pm}=\left[-\varepsilon_{1}^{-1}-\varphi \lambda^{2} \pm E^{1 / 2}\right] /(2 \varphi) .
\end{gather*}
$$

From the last two relations of (54) for the function $E$, it is seen that $E>0$; furthermore, the absolute value of $E^{1 / 2}$ is less than $\varphi \lambda^{2}+1 / \varepsilon_{1}$ and consequently we always have $p^{-}<0$ and $p^{+} \leq 0$. The possibility of $p^{+}$vanishing at the boundary of the integration region $(\lambda=0)$ in formulas (53) leads to a change in the asymptotics (for $\tau \rightarrow \infty$ ) of the integral characteristics of the solution from the exponential tendency to unity for the body of a finite dimension (33) $\left(G_{j}=1-U_{j}\right)$ to an algebraic growth in (22), (20) in the approximation of a semiinfinite body.

For fairly high values of time and finite $z$ values, the asymptotics in the integrals of (53) is determined in the vicinity of the points $\lambda$, where the values of the exponents in the functions $\vartheta_{j}(\lambda, \tau)$ are maximum. It is easily checked that the functions $p^{ \pm}(\lambda)$ are monotonically decreasing and consequently the point $\lambda=0$ is of asymptotic interest. In the vicinity of this point, we have the expansions

$$
\begin{equation*}
p^{+} \cong-\varepsilon_{1} \lambda^{2}+O\left(\lambda^{4}\right), \quad p^{-} \cong \frac{1}{\varepsilon_{2}}+O\left(\lambda^{2}\right) \tag{55}
\end{equation*}
$$

Hence it is clear that only the exponent containing $p^{+}$should be allowed for in the integrals of (53) in accordance with the Laplace method [13]. When $\lambda \rightarrow 0$ the functions $\vartheta_{1}$ and $\vartheta_{2}$ in the principal asymptotic approximation are coincident, which follows from relations (54). Expanding the corresponding functions in the vicinity of the point $\lambda=$ 0 , we obtain

$$
\begin{equation*}
G_{i}(z, \tau) \cong 1-\frac{2 z}{\pi} \int_{0}^{\infty} \exp \left(-\lambda^{2} \tau\right) d \lambda=1-\frac{z}{\sqrt{\pi \tau}}, \quad \tau \rightarrow \infty, \quad z=O(1), \quad i=1,2 \tag{56}
\end{equation*}
$$

It follows from dependences (56) that the TC concentrations in both zones change in synchronism at large times within the framework of this model. Also, it is noteworthy that the law (56) corresponds to the solution (asymptotic for $\tau \rightarrow \infty$ and $z=O(1)$ ) of the diffusion problem with the same (our) supplementary conditions. Clearly, expression (56) is appropriate only for a low (compared to unity) value of the second term.

Also, the behavior of the TC concentration for high values of $z$ and $\tau$ is of interest. This asymptotics is most simply found at points moving with a certain velocity $v$ at large times, i.e., at $z=v \tau(z$ and $\tau \rightarrow \infty$ and $v=$ const $=$ $O(1))$. In this case it is convenient to use the Riemann-Mellin integral written for the function $G_{1}(z, \tau)$ :

$$
\begin{equation*}
G_{1}(z, \tau)=\frac{1}{2 \pi i} \int_{L} \exp \left[\tau\left(p-v \sqrt{\frac{\varepsilon_{1} \varepsilon_{2} p^{2}+p}{1+\varepsilon_{2} p}}\right)\right] \frac{d p}{p} \tag{57}
\end{equation*}
$$

which can approximately be found using the saddle-point approximation (method of steepest descents) [13, 18]. To determine the stationary point $p_{*}$ (saddle point) we have, setting the derivative with respect to $p$ in the expression under the exponent $\operatorname{sign}\left\{\mu(p)=p-v\left[\left(p+\varepsilon_{1} \varepsilon_{2} p^{2}\right) /\left(1+\varepsilon_{2} p\right)\right]^{1 / 2}\right\}$ equal to zero, the equation

$$
\begin{equation*}
v=\frac{2 \sqrt{p_{*}\left(1+\varepsilon_{1} \varepsilon_{2} p_{*}\right)\left(1+\varepsilon_{2} p_{*}\right)^{3}}}{1+2 \varepsilon_{1} \varepsilon_{2} p_{*}+\varepsilon_{1} \varepsilon_{2}^{2} p_{*}^{2}} . \tag{58}
\end{equation*}
$$

Since $v$ is more than 0 , we easily note that Eq. (58) has the unique real root $p_{*}, p_{*} \in(0, \infty)$. This yields the stationary point $p_{*}>0$. The functions $v\left(p_{*}\right)$ are plotted in Fig. 5 (curves $1-3$ for the values $\varepsilon_{1}=0.25,0.5$, and 0.75 respectively). Computation of the second derivative of the function $\mu(p)$ at the stationary point yields

$$
\begin{equation*}
\mu^{\prime \prime}\left(p_{*}\right)=\psi\left(p_{*}\right)=\frac{v\left[\left(1+2 \varepsilon_{1} \varepsilon_{2} p_{*}+\varepsilon_{1} \varepsilon_{2}^{2} p_{*}^{2}\right)^{2}+4 \varepsilon_{2}^{2} p_{*}\left(1+\varepsilon_{1} \varepsilon_{2} p_{*}\right)\right]}{4 p_{*}^{3 / 2}\left(1+\varepsilon_{1} \varepsilon_{2} p_{*}\right)^{3 / 2}\left(1+\varepsilon_{2} p_{*}\right)^{5 / 2}}, \tag{59}
\end{equation*}
$$

and the value of the function $\mu\left(p_{*}\right)$ itself is equal to

$$
\begin{equation*}
\mu\left(p_{*}\right)=\frac{-p_{*}\left(1+2 \varepsilon_{2} p_{*}+\varepsilon_{1} \varepsilon_{2}^{2} p_{*}^{2}\right)}{1+2 \varepsilon_{1} \varepsilon_{2} p_{*}+\varepsilon_{1} \varepsilon_{2}^{2} p_{*}^{2}} . \tag{60}
\end{equation*}
$$

The functions $\mu\left(p_{*}\right)$ and $10 \times \psi\left(p_{*}\right)$ are plotted in Fig. 5 (curves $4-6$ for $\mu\left(p_{*}\right)$ and $7-9$ for $10 \times \psi\left(p_{*}\right)$ for the values $\varepsilon_{1}=0.25,0.5$, and 0.75 respectively.)

The line of steepest descent intersects the real axis of the plane $p$ at the saddle point $p_{*}$ at a right angle. Therefore, we can use the line $L$ passing through the point $p_{*}$ in the Riemann-Mellin integral (57) to construct the principal term of the asymptotics of the function $G_{1}(z, \tau)$. Performing the standard procedure of saddle-point approximation [13, 18], we arrive at the following asymptotic expression (principal part) for the solution:


Fig. 5. Plots of the functions determining the asymptotic formula (61) for the values $\varepsilon_{1}=0.25,0.5$, and 0.75 .

$$
\begin{equation*}
G_{1}(z, \tau) \cong \frac{\exp \left[\tau \mu\left(p_{*}\right)\right]}{p_{*} \sqrt{2 \pi \tau \psi\left(p_{*}\right)}}, \quad \tau \rightarrow \infty, \quad p_{*} \geq O(1) \tag{61}
\end{equation*}
$$

For fairly high values of the parameter $p_{*}$, we have $\mu\left(p_{*}\right) \approx-p_{*}, \psi\left(p_{*}\right) \approx 1 /\left(2\left(p_{*}\right)\right.$, and $v=z / \tau \approx 2\left(p_{*} / \varepsilon_{1}\right)^{1 / 2}$. Substituting these expressions into (61), we find

$$
\begin{equation*}
G_{1}(z, \tau) \cong \frac{2 \sqrt{\tau}}{z \sqrt{\pi \varepsilon_{1}}} \exp \left(-\frac{\varepsilon_{1} z^{2}}{4 \tau}\right), \quad \tau \rightarrow \infty, \quad z \gg \tau \tag{62}
\end{equation*}
$$

Precisely the same expression is obtained when we consider the diffusion problem with our supplementary conditions. In this case we have

$$
G_{D}(z, \tau)=\operatorname{erfc}\left(\frac{z \sqrt{\varepsilon_{1}}}{2 \sqrt{\tau}}\right), \quad \operatorname{erfc}(x)=\frac{2}{\sqrt{\pi}} \int_{x}^{\infty} \exp \left(-t^{2}\right) d t
$$

where erfc $(x)$ is the supplementary probability integral.
Using formula (10) relating the functions $G_{1}^{*}$ and $G_{2}^{*}$ and the relation $G_{\mathrm{S}}=\varepsilon_{1} G_{1}+\varepsilon_{2} G_{2}$, we obtain, analogously to the derivation of (61), the dependences for the quantities $G_{2}$ and $G_{\mathrm{s}}$ :

$$
\begin{equation*}
G_{2}(z, \tau) \cong \frac{\exp \left[\tau \mu\left(p_{*}\right)\right]}{p_{*}\left(1+\varepsilon_{2} p_{*}\right) \sqrt{2 \pi \tau \psi\left(p_{*}\right)}}, \quad G_{\mathrm{S}}(z, \tau) \cong \frac{\left(1+\varepsilon_{1} \varepsilon_{2} p_{*}\right) \exp \left[\tau \mu\left(p_{*}\right)\right]}{p_{*}\left(1+\varepsilon_{2} p_{*}\right) \sqrt{2 \pi \tau \psi\left(p_{*}\right)}}, \tau \rightarrow \infty, \quad p_{*} \geq O(1) . \tag{63}
\end{equation*}
$$

Solution in the form (61) and (63) is somewhat inconvenient because of dependence (58) unsolved for $v=$ $z / \tau$, i.e., it is desirable to have the explicit formula of the form $p_{*}=p_{*}(v)$ instead of (58). If we do this, the asymptotic formulas (61) and (63) will explicitly be dependent on $z$ and $\tau$. For practical purposes, we can propose when $\varepsilon_{1}>0.4$ the simple approximate formula

$$
p_{*}(v)=\frac{v^{2}\left(1+\varepsilon_{1} \varepsilon_{2} v^{2}\right)}{4\left(1+\varepsilon_{2} v^{2}\right)},
$$

having the asymptotic behavior identical to (58) for both $v \rightarrow \infty$ and $v \rightarrow 0$.
Conclusions. We have investigated several problems on impregnation of a porous body with two types of TC pores on the basis of a two-component mass-transfer model suitable for description of the process at fairly large times. We have analyzed the versions of approximation of a semiinfinite body and a body of a finite length. In the first case, we have constructed expansions of the solution in power series in dimensionless time, which are suitable for calcula-
tion of the TC flux and the total amount of the TC in the body. The principal terms of the asymptotic representation of the solution are the power time functions.

In the case of a finite body the functions characterizing the solution are expressed by the series in exponential functions (decreasing when $\tau \rightarrow \infty$ ). In withdrawing the TC from the porous system, the total amount of the TC in this version exponentially tends to zero for $\tau \rightarrow \infty$ with determined parameters for the factor of time in the exponent and the preexponential factor (see dependence (33)). We have obtained the asymptotic formulas determining the TC distribution in the semiinfinite porous body.

## NOTATION

$a$ and $b$, parameters in relation (47); $C_{1}$ and $C_{2}$, concentration of the target product in the transport and stagnant channels respectively, $\mathrm{kg} / \mathrm{m}^{3} ; C_{0}$, value of the concentration at entry into the system (for impregnation), $\mathrm{kg} / \mathrm{m}^{3}$; $D$, diffusion coefficient, $\mathrm{m}^{2} / \mathrm{sec} ; E$ and $p^{ \pm}$, auxiliary variables, see (31) and (54); $F_{\mathrm{s}}$, density of the target-product flux, $\mathrm{kg} /\left(\mathrm{m}^{2} \cdot \mathrm{sec}\right) ; f(z)$, boundary function in relation $(52) ; G_{1}$ and $G_{2}$, dimensionless concentration of the target product in the transport and stagnant channels respectively; $I_{1}(\tau)$ and $I_{2}(\tau)$, integral characteristics of the process, see (21); $i$, imaginary unit; $L$, straight line of integration in the Riemann-Mellin formula; $l_{1}$, length of a transport channel, m ; $l_{2}$, length of a stagnant pore, $\mathrm{m} ; l_{3}$, characteristic length scale, $\mathrm{m} ; N$, average number of the stagnant channels in contact with one transport channel; $n$, auxiliary dimensionless variable, see (24); $P_{n}(x)$, Legendre polynomials of $n$th order; $p$, parameter of the Laplace transformation; $p_{1}$, perimeter of a transport pore, $\mathrm{m} ; Q$, amount of the substance transmitted by the cross section over the period $t, \mathrm{~kg} / \mathrm{m}^{2} ; p_{*}$, root of Eq. (58); $q$, term describing the exchange of the substance between the principal channel and the secondary channels, $\mathrm{kg} /\left(\mathrm{m}^{3} \cdot \mathrm{sec}\right) ; R$, radius of the circular arc in Fig. 4; $R_{1}(\tau), R_{2}(\tau)$, and $R_{3}(\tau)$, auxiliary functions, see (19) and (35); $r_{1}$ and $r_{2}$, parameters in formula (51); $S_{1}$ and $S_{2}$, crosssectional areas of the transport and stagnant channels respectively, $\mathrm{m}^{2} ; s$, auxiliary variable replacing $p$, see (15); $T_{2}$ and $T_{3}$, time scales, sec; t, time, sec; $U_{1}$ and $U_{2}$, new sought functions, see (24); $V_{1}$ and $V_{2}$, volumes of the transport and stagnant pores in the porous system, $\mathrm{m}^{3} ; v$, dimensionless velocity; $x$, coordinate matched to the principal channel, $\mathrm{m} ; y$, coordinate along the small channel, $\mathrm{m} ; z$, dimensionless coordinate; $\alpha$, auxiliary variable, see ( 15 ); $\Gamma(z)$, gamma function; $\gamma$, constant coefficient of mass exchange between channels of different types, $\sec ^{-1} ; \varepsilon$, fraction of the crosssectional area of small pores at the boundary with large ones; $\varepsilon_{1}$ and $\varepsilon_{2}$, volume fractions of the transport and stagnation zones respectively; $\vartheta_{i}^{k}$, functions in Fourier series, see (27); $\lambda_{k}$, eigenvalues; $\mu$ and $\psi$, functions of $p_{*}$, determined in (59) and (60); $\xi$, dimensionless parameter, see (15), (40), and (47); $\tau$, dimensionless time; $\Phi_{k}(\xi)=i^{k} P_{k}(i \xi) ; \varphi$, auxiliary variable, see (2) and (24). Subscripts and superscripts: 1, large pores; 2, small pores; $D$, diffusion problem; s, phase interface; *, Laplace-transformed quantities.

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