On a threshold of desorption during the pumping of a nanofluid through porous medium

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Abstract. The results of direct numerical simulation are intended to describe the saturation process of a nanofluid through artificial porous medium. The calculations were fulfilled using the hypothesis, which presumed the adsorptive nature of nanoparticles adhesion to the solid boundaries of pores. Mathematical statement of the problem was based on the modified MIM-model and Darcy – Boussinesq equations. The dependence of the desorption intensity on the value of filtration velocity was taken into account in the course of theoretical investigation. It was shown that this factor for concentration redistribution of the immobile impurity led to the steepening of the wave front as a function of time. Phenomenological realization of novel physical assumptions made the results of numerical modeling closer to the experimental data.

1. Introduction

It is known that deposition of colloidal particles on the solid matrix of the medium complicates filtration of a suspension through a porous material [1]. This effect should be taken into account always during the impregnation of a porous medium with the suspension of nanoscale particles. In our case, we deal with the fine-dispersed powder to obtain a heat-resistant composite material. Technological process of the material production is carried out at a pressure difference on the inlet and outlet no more than one atmosphere [2]. Due to the pressure drop, the working nanofluid is pumped through a layer of artificial porous material with the thickness 1 – 2 cm. The particle size does not exceed 100 nm. The characteristic pore diameter of the material is about 10 microns. Experiments show that for about 20 minutes, the rate of liquid flow drops sharply to zero. In quantitative terms, the volume of liquid, pumped per unit time, decreases by almost two orders of magnitude. During this time, the particles cannot fill the pores along the entire thickness of the sample. They are located near the inlet in a thin stratum of settled particles, so that the penetration corresponds to about 1/10 of the total thickness of workpiece. After disappearance of the filtration flow, technological process was interrupted. Uniform saturation with nanoparticles throughout the sample volume was not achieved. Thus, the problem arises to construct theoretical model and to fulfill mathematical analysis of this phenomenon in order to develop the methods of control the technological process.

2. Problem formulation and system of basic equations

Let us consider a rectangular plate with thickness $L$ and height $H$. The sample is produced from a porous material. The medium is homogeneous at the initial moment of time. Due to the constant pressure
gradient on the wide faces of the workpiece, the nanosuspension is pumped in the transversal direction (Fig. 1). The layer is located in the gravity field, which implies consideration of the concentration-convective mechanism of impurity transport.

To describe the filtration process, we use a modified MIM model, which takes into account the nonlinear sorption response of the system on the pore velocity \([2, 3]\). In the framework of this model, it is assumed that the impurity is divided into two phases – mobile and immobile components. The first phase consists of particles drifting in the filtration flow, the second one settles on the boundaries of a solid matrix. In our case, the Kozeny–Carman mechanism determines pore blockage. Equations in the Darcy–Boussinesq approximation \([4]\) describe the dynamics of the filtration process. Thus, the Darcy law in terms of pore velocity, taking into account incompressibility of the liquid and the equations for concentrations of mobile and immobile phases has the form:

\[
\frac{\partial}{\partial t} (c_m + c_i) = -\left(\bar{u} \nabla\right) c_m + D \Delta c_m, \quad \frac{\partial}{\partial t} c_i = \alpha (c_m q_0 - c_i) - \gamma (u_e - u_c) c_i, \tag{1}
\]

\[
\frac{\eta \phi}{K(\phi)} \bar{u} + g c_m \rho_k \bar{k} = -\nabla P, \quad \nabla \bar{u} = 0, \tag{2}
\]

\[
\kappa(\phi) = \kappa_0 \phi^3 / (1 - \phi)^2, \phi = \phi_0 - c_i, \tag{3}
\]

where \(c_m, c_i\) – volume concentration of the heavy impurity in the mobile and immobile phases, respectively, \(\bar{u}\) – pore velocity of a liquid, \(\phi\) – porosity, \(D\) – diffusion coefficient, \(\kappa\) – permeability (function of porosity), \(P\) – additional term to hydrostatic pressure, \(\beta\) – coefficient of concentration expansion, \(\alpha\) – mass-transfer coefficient, \(\rho\) – liquid density, \(\kappa_0\) – Kozeny–Carman constant, \(\phi_0\) – porosity of a clean medium, \(\gamma\) – coefficient of the impurity distribution, \(g\) – gravity acceleration. Unit vector \(\bar{k}\) is oriented vertically upwards (Fig. 1). Parameter \(q_0\) is the concentration of saturation.

![Figure 1. Geometry of the problem in Cartesian system of coordinate](image)

The simplest linear model is suitable for description of filtration processes in the case of low filtration rate. However, relatively high values of the applied pressure gradient are possible for considering technological process that lead to significant increase of the pumping speed. As a result, in order to extend the applicability of theoretical approach in the situation of extensive change of the filtration rate, Eq. (3) has been modified in comparison with idem in classical MIM model. Thus, there is an additional
non-linearity $\sim u_c c_i$ in Eq. (3) for the concentration of immobile component. Here $u_c$ is the component of pore velocity transversal to wide boundaries of the workpiece; $u_c$ is the material constant that has the meaning of a critical value for velocity. This term takes place only for condition $u_c > u_c$. It demonstrates that desorption is more intensive when the pore velocity is higher. In fact, the constant $u_c$ is a phenomenological characteristic of the porous material, i.e. if the pore velocity $u_c$ becomes equal to this value, the desorption stops. Namely, the blockage of the pores increases nonlinearly in dependence on diminution of velocity because of adsorption intensification with the time and its back action on medium permeability. The last term in Eq. (3) is taken into account in each grid node only for $u_c > u_c$, since the desorption can lead only to a decrease of concentration of the immobile component.

The system of the equations (1) – (4) has been converted into dimensionless form using next natural variables: $[\Delta x, \Delta y] = L, [\tau] = L^2/D, [\mathbf{u}] = D/L, [P] = P_2 - P_1, [c] = C_0, [q_0] = C_0$. Here $\Delta x$ and $\Delta y$ are the spatial intervals along the horizontal and vertical coordinates, respectively, and $C_0$ is the initial value of the particle concentration in the liquid at the left boundary. The inlet and outlet pressures are $P_2$ and $P_1$, respectively. After conversion into dimensionless form, the system looks like this:

\[
\begin{align*}
\partial_t (c_m + c_i) &= - (\mathbf{u} \nabla) c_m + \Delta c_m, \\
\frac{\partial}{\partial \tau} c_m + \text{Rd} \cdot c_m + = - Pe \nabla P, \quad \text{div} \mathbf{u} = 0, \\
\partial_x c_i &= ac_m (q_0 - c_i) - b (u_c - u_c) c_i, \\
\kappa(\phi) &= \kappa_0 \phi^3 (1 - \phi)^2, \quad \phi = \phi_0 - c_i,
\end{align*}
\]

These partial differential equations are supplemented by boundary conditions:

\[
\begin{align*}
u_c \big|_{x=0} &= - Pe k(\phi) \partial_x P \big|_{x=0}, \quad u_c \big|_{y=0,h} = 0, \quad (8) \\
c_m \big|_{x=0} &= C_0, \quad \partial_x c_m \big|_{x=1} = 0, \quad \partial_y c_m \big|_{y=0,h} = 0, \quad (9) \\
P \big|_{x=1} &= 1, \quad P \big|_{y=1} = 0, \quad \partial_y P \big|_{y=0,h} = - \frac{\text{Rd}}{Pe} c_m \big|_{y=0,h}. \quad (10)
\end{align*}
\]

The system of equations (5) – (8) and boundary conditions (9) – (11) include four dimensionless parameters. There are Peclet number $Pe$, which characterizes the pumping intensity, Rayleigh – Darcy number $Rd$, which is responsible for the gravitational influence on the liquid element, adsorption parameter $a$ and desorption one $b$:

\[
a = \alpha \frac{C_0 l^2}{D}, \quad b = \alpha \frac{\gamma L^2}{D}, \quad Pe = \frac{(P_2 - P_1) C_0}{D \eta \phi_0}, \quad \text{Rd} = \frac{g \rho \kappa L^2 \beta LC_0}{D \eta \phi_0}.
\]

The first expression in (9) and the last one in (11) are consequences of the Darcy – Boussinesq equation and appear as dynamic boundary conditions. In other words, the velocity, pressure, permeability at the input and concentration of the mobile component at the lower and upper boundaries of the calculated area depend on coordinates and time. The second condition in (10) for the mobile impurity concentration means that all impurity reaching the right boundary is carried out immediately along $x$ with the flow.

3. Numerical method

The system of partial differential equations (4) – (7) with the boundary conditions (8) – (10) was solved numerically for definite values of dimensionless parameters (11) by the finite difference method using an explicit scheme of first-order accuracy by time and second-order accuracy by space [5]. The time step was chosen for the reason to obtain the stability of the numerical procedure (the Courant – Friedrichs –
Levy criterion). The author's computer code was implemented in the FORTRAN-90 programming language.

The problem was solved in a two-dimensional formulation, taking into account the uniformity of the system along \( z \) coordinate. We assume that the pressure field and the pore velocity component are equal to zero at the initial moment of time. The initial value of porosity \( \phi_0 \) was applied to be \( \phi_0 = 0.5 \). The pores of the sample are initially empty, which means that the concentration values of the mobile and immobile phases are equal to zero. There was used a numerical grid with the number of nodes along the axes 35:155. The ratio of the layer thickness \( L \) to the height \( H \) is taken as 1:5. All calculations were performed for the following dimensionless parameters: \( a = 600 \), \( b = 20 \), \( Rd = 30 \), \( Pe = 800 \), \( q_0 = 0.45 \). The Peclet and Rayleigh – Darcy numbers in (12) correspond to the parameters of water-alcohol solution, for which \( \nu = 2 \times 10^{-6} \) m\(^2\)/s, \( \rho = 10^3 \) kg/m\(^3\). Since the particles are quite heavy, we set the value for \( \beta = 3 \). The particle concentration in our suspension is not small and taken as 0.2 of the volume fraction. In addition, we use the rank values \( \kappa_0 = 10^{-14} \) m\(^2\), \( D = 10^{-10} \) m\(^2\)/s. For \( L = 10^{-2} \) m the Rayleigh – Darcy number can be estimated as \( Rd \approx 30 \). When the pressure difference is \( 1.6 \times 10^3 \) Pa, the Peclet number is \( Pe \approx 800 \). The non-dimensional parameters of adsorption and desorption for particles smaller than 100 nm are characterized by a wide spread, so they are selected to ensure agreement between the results of the calculation and the experimental data [2]. For the layer thickness and diffusion coefficient, mentioned above, in dimensional form we get a very small value of pores velocity \( 5 \times 10^{-3} \) mm/s. This estimation is in good agreement with the assumptions about the mechanism of separation, which occurs when the force of viscous stresses acting on the particle from the flow exceeds the force of the Van der Waals interaction with the wall. The value of critical stresses was estimated in the work [6]. The critical stresses for various combinations of particle sorts and wall materials are of the order of \( 10^{-2} \) Pa, which for a pore size of \( 10^{-5} \) m corresponds to the speed range of \( 10^{-2} \) – \( 10^{-1} \) mm/s.

4. Results and discussion

Preliminary numerical simulation of the filtration process in the framework of the proposed model for certain fixed set of control parameters was performed in the work [2]. The fields of velocity, admixture concentration in different phases, porosity and permeability are presented in this work. This study allows understanding the main features of the impurity concentration front motion into the depth of the sample. In addition, the qualitative comparison with the experiment is made. However, any variation of the parameter \( u_c \) is absent in this study. Critical velocity \( u_c \) determines the threshold of switching on/off the desorption mechanism. The variation of this parameter reveals a non-trivial response of the porous medium to its change. Thus, we present the results of calculations for the following values of this parameter: \( u_c = 210, 300, \) and \( 500 \). This choice depends on Peclet number, which is formed by the external pressure difference and gives the initial flow velocity \( u_c \approx Pe/2 = 400 \). The first and second values \( u_c \) are chosen so that the process of desorption works during the pumping at the initial stage. The value \( u_c = 500 \) is taken to study the behavior of the system in the absence of desorption from the outset of the filtration.
Figure 2. At the left the evolution of the front of immobile phase at $t = 0.001, 0.003, 0.1$. At the right the distribution of the concentration of mobile phase along the $x$-axis in different moments of time: $a) t = 0.001$, $b) t = 0.3$. The curve numbers in these figures correspond to: $1 - u_c = 210$, $2 - u_c = 300$, $3 - u_c = 500$. The dashed line describes the solution of linear one-wave equation (13).

Ultimately, the concentration front for lower $u_c$ eventually moves faster than one for the large values of this parameter. The family of lines for the distributions of immobile component in Fig. 2, corresponding to the time $t = 0.1$, shows that pore filling is quicker for small values of the critical velocity. At lower $u_c$ the process of desorption in the system continues longer. This leads to the situation, when the concentration of the mobile component in each point across the layer is greater for every moment of time (Fig. 2, right fragments $a, b$). The curves 1, 2, and 3 are arranged one after another so that a lower $u_c$ value corresponds to higher concentration of the mobile component.

Figure 3. Time dependence of $x$-component of the pore velocity at the point with coordinates $x = 0.5, y = 2.5$ (the middle of the sample); $b)$ on the fragment the function $u_x(t)$ at the initial stage: $1 - u_c = 210$, $2 - u_c = 300$, $3 - u_c = 500$. 
The immobile component behaves otherwise in comparison with mobile phase. It does not follow the concentration of the mobile component synchronously because its distribution depends on the porous velocity. Calculations show (Fig. 3) that the velocity falls monotonically very quickly over the time. In the interval $\Delta t = 0.001 \div 0.003$ it decreases by almost two orders of magnitude, and then at a long time it reaches a small constant value. Initially, the concentration of the immobile component at the input is less for $u_c = 210$ (Fig. 3). However, the impurity penetrates into the workpiece more intensively and the concentration of the mobile component at this value $u_c$ has a greater numerical value everywhere along $x$. In other words, the concentration of the mobile component increases in the depth of the sample due to desorption at the inlet and convective transport.

![Figure 4. Evolution of porosity (left) and permeability (right) in cross-section for time points: $t = 0.001$, 0.003, 0.1. Curve numbers in both figures correspond to: 1 – $u_c = 210$, 2 – $u_c = 300$, 3 – $u_c = 500$.]

It leads to the increase of the immobile component concentration inside porous medium, since $\delta c_i \sim c_m$. As a result, the concentration front of the immobile component for small $u_c$ outruns one for high value of this parameter. The porosity and permeability distributions follow the concentration of immobile impurity field synchronously (Fig. 4) and describe a complex competition between adsorption and convective transport. Curves 1 and 3 (Fig.4) change places over time due to the fact that at lower $u_c$ at the initial stage, the impurity penetrates deeper into the array and settles on the solid walls of the pores. Later on, the desorption stops in all three cases, and the concentration front at a lower $u_c$ becomes the first. It indicates shorter impregnation time of the sample at smaller $u_c$.

5. Analytical solution of a linearized problem

For more deep consideration of this phenomenon, we attempt to obtain an analytical solution at a most simple statement of the problem. Let us return to the system of equations (4) – (7). To realize analytical approach, one-dimensional approximation should be used that permits to ignore influence of the gravity. Since one-dimensional problem is considered, the velocity does not depend on the coordinates. It is a function of only time. However, the pressure, porosity, permeability, and concentration fields are function of $x$ coordinate and time. Then we consider the limiting case in which the velocity $u$ tends to value of high infinitesimal order, which corresponds to the stage of a long time in experiment. The important
objective, concerning the field of mobile concentration is to determine the main mechanism of motion in principal order. Two limiting cases follow after a global linearization of the problem:

$$\frac{u \partial c_m}{\partial x} \gg \frac{\partial^2 c_m}{\partial x^2}, \quad \dot{c} = -uc_x + f(x), \quad (12)$$

$$\frac{u \partial c_m}{\partial x} \ll \frac{\partial^2 c_m}{\partial x^2}, \quad ac_0^2 c + c = c_{xx} + f(x), \quad (13)$$

where $f(x)$ is the piecewise function to satisfy the step initial conditions. According to equation (12), the main mechanism of transport is connected with convective transfer; otherwise, the equation (13) corresponds to penetration of an impurity due to diffusion. Thus, two linear evolutional equations are obtained that describe the distribution of the concentration of immobile component by means of respective mechanism. The solution of these equations in the limit of large time and comparison with the complete problem in the main order show, that the predominant mechanism of the impurity propagation is convective transport. It can be seen in Figure 2 that at the initial stage the behavior of the concentration front is extremely complex, since at the first step the competition of all mechanisms, such as adsorption, desorption, and convective transfer, takes place. However, at large times, when the desorption is turned off, an identical view of the solution is observed for the full system of equations (4) – (7) and one-wave equation (13), Figure 2 (dashed line). One can conclude that the difference between these solutions increases with the diminution of critical velocity parameter.

6. Conclusion

The effect of desorption crisis during the impregnation of a porous material by a nanosuspension is analyzed theoretically. It is shown that the specific material constant, i.e., the critical velocity parameter plays an essential role at the initial stage of filtration process in the course of saturation of the porous medium. This parameter is responsible for the inverse effect of the porous flow on the sorptive properties of the medium. It determines the moment of the desorption stoppage with the subsequent decrease of porous velocity. For characteristic thickness of the workpiece, the calculation results show that the concentration front of the immobile impurity moves faster with the diminution of this parameter, that gives more short time of the sample saturation. In the limiting case of large times, the solution of the linearized problem is compared with the calculation results gotten in the complete formulation. In the upshot the good conformity is obtained for analytical and numerical data.

References

1. Salles J, Thovert J F and Adler P M 1993 Chem. Eng. Sci., 48(16) 2839–2858
2. Demin V A, Maryshev B S and Menshikov A I 2020 Comput. Contin. Mech. 13 83–97
3. Gruesbeck C and Collins R E 1982 Soc. Pet. Eng. J. 22 847–856
4. Nield D A and Bejan A 2006 Convection in porous media (Springer and Business Media, New York)
5. Roache P J 1976 Computational Fluid Dynamics (Hermosa Publishers, Albuquerque)
6. Klimenko L S, Maryshev B S 2020 Chem. Eng. J. 381 122644