A chemical reaction model in a porous medium

L I Kuzmina1 and Yu V Osipov2*

1 National Research University Higher School of Economics, 20 Myasnitskaya str., Moscow, 101000, Russia
2 Moscow State University of Civil Engineering, 26 Yaroslavskoe highway, Moscow, 129337, Russia

E-mail: yuri-osipov@mail.ru

Abstract. Chemical reactions in a porous medium are found in many natural phenomena and technological processes. Reactive substances dissolved in groundwater can significantly change the soil strength. The precipitate formed as a result of the reaction changes the porous medium structure and affects the porosity and permeability. A one-dimensional model of the reaction of two reagents in a homogeneous porous medium with a linear reaction function is considered. The model includes the mass balance equations of each reagent and precipitate, and the kinetic equation of precipitate growth. It is assumed that the precipitate is stationary and the growth rate of the precipitate is proportional to the reagents’ concentration. A carrier fluid with constant concentration reagents is injected at the empty porous medium entrance. The reaction front moves in a porous medium at a constant speed. The exact solution to the problem is constructed by eliminating the unknown functions and lowering the equations’ order. A Riemann invariant that relates the concentration of sediment and reagents to the system’s characteristics was found. The reaction’s numerical simulation is performed. It is shown that, for a long time, the reagents’ concentrations and the precipitate tend to final limit values. Sediment profiles always decrease monotonously, and the type of the profiles’ convexity changes.

Introduction

Chemical reactions in porous media are found in natural phenomena and in industrial technologies. The sediment formation during the chemicals’ interaction reduces the oil wells’ productivity on the offshore [1]. Chemical reactions in a porous environment contribute to the groundwater pollution, affect the radioactive substances’ mobility in underground storage. [2].

Chemically active substances in the form of tiny particles are transported through the channels of the porous medium by a carrier fluid or air stream. Reagents enter into a chemical reaction with the stationary precipitate formation, which affects the reaction intensity.

The classical model of suspension filtration in a porous medium includes the equation of mass balance of suspended and precipitated particles and the kinetic equation of sediment growth [3]. At a low C of the suspended particles concentration, the sediment growth rate is proportional to the first-degree C linear filtering function. The proportionality coefficient depends on the sediment concentration S and is called the filtration coefficient. The most commonly used linear blocking filtering function, called the Langmuir coefficient [4] is:

\[ \Lambda(S) = \lambda(S_{\text{max}} - S) \, . \]  

(1)
Various models of chemical reactions in a porous medium are based on theories of random walks, substances’ mixing, as well as various hybrid models [5-7]. In [8], the basic equations of chemical reactions based on mixing theory are considered. Sludge growth is proportional to the reagents’ concentration product. However, the model assumes that the coefficient of proportionality (reaction coefficient) is constant.

In a number of practical problems, the accumulated sediment slows down the chemical reaction. By analogy with the classical filtration model, the article considers a model with a variable reaction coefficient (1). Function (1) describes a decelerating chemical reaction: the rate of sedimentation decreases with increasing concentration $S$. With a long time, the sediment concentration tends to a final limit value $S_{\text{max}}$ [9].

For complex mathematical models, as a rule, numerical solutions are constructed [10, 11]. In some cases, it is possible to find the exact solution [12, 13]. Exact solutions make it possible to determine the dependence of the solution on the model parameters and solve the inverse problem [14, 15].

An exact solution of a one-dimensional model of the two reagents chemical reaction in a homogeneous porous medium is constructed. The reaction is accompanied by the formation of a precipitate that slows down the reaction rate. It is assumed that reagents of constant concentration are supplied to the entrance of the porous medium; at the initial moment, the porous medium does not contain reagents and sediment. An exact solution to the problem is constructed in implicit algebraic form.

1. The mathematical model

In the area of $\Omega = \{0 < x < 1, t > 0\}$ the first-order hyperbolic system is considered

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_1}{\partial x} + \Lambda(S)C_1C_2 = 0;$$

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_2}{\partial x} + \alpha \Lambda(S)C_1C_2 = 0, \quad 0 < \alpha < 1;$$

$$\frac{\partial S}{\partial \tau} - \Lambda(S)C_1C_2 = 0.$$  (4)

with a linear reaction coefficient (1).

The initial and boundary conditions determine the only solution to the problem:

$$C_i(x,t)|_{t=0} = p_i, \quad C_i(x,t)|_{x=0} = p_2, \quad p_1 > 0, \quad p_2 > 0;$$

$$C_i(x,t)|_{x=0} = 0, \quad C_i(x,t)|_{x=0} = 0, \quad S(x,t)|_{t=0} = 0.$$  (6)

The solution to problem (2) - (6) has the form [16]:

$$C_i(x,t) \begin{cases} = 0, & t < x, \quad i = 1, 2; \\ > 0, & t > x. \end{cases} \quad S(x,t) \begin{cases} = 0, & t < x, \\ > 0, & t > x. \end{cases}$$  (7)

At the front of the reaction - the $t = x$ characteristic, the function $C(x,t)$ has a gap; function $S(x,t)$ has no gap in the area of $\Omega$.

We replace the conditions (5), (6) with one condition on the characteristic

$$S|_{t=x} = 0.$$  (8)

In the area of $\Omega = \{0 < x < 1, t > x\}$ the solution to the problem (2) - (5), (8) is unique and coincides with the solution to problem (2) - (6) [17].
We introduce the characteristic variables (Riemann variables) \( \tau = t - x, \quad x = x \). In the new variables in the field \( \Omega_1^0 = \{0 < x < 1, \quad \tau > 0\} \) the problem (2) – (5), (8) with the filter function (1) takes the form:

\[
\frac{\partial C_1}{\partial x} + \lambda (S_{\text{max}} - S)C_1C_2 = 0; \\
\frac{\partial C_2}{\partial x} + \alpha \lambda (S_{\text{max}} - S)C_1C_2 = 0; \\
\frac{\partial S}{\partial \tau} - \lambda (S_{\text{max}} - S)C_1C_2 = 0; \\
C_1(x, \tau)|_{\tau=0} = p_1, \quad C_2(x, \tau)|_{\tau=0} = p_2; \\
S(x, \tau)|_{\tau=0} = 0. 
\]

Let us subtract the equation (10) from the equation (9) multiplied to \( \alpha \):

\[
\alpha \frac{\partial C_1}{\partial x} - \frac{\partial C_2}{\partial x} = 0 \Rightarrow \frac{\partial}{\partial x} (\alpha C_1 - C_2) = 0. 
\]

We integrate the equation (14) with respect to \( x \)

\[
\alpha C_1 - C_2 = K(\tau). 
\]

Let us find the constant \( K(\tau) \) from the boundary conditions (12)

\[
K(\tau) = \alpha p_1 - p_2. 
\]

We substitute the constant (16) into the equation (15)

\[
C_2 = \alpha C_1 - \alpha p_1 + p_2. 
\]

Substituting the relation (17) into the equations (9), (11), we obtain a closed system of two equations with two unknowns

\[
\frac{\partial C_1}{\partial x} + \lambda (S_{\text{max}} - S)C_1(\alpha C_1 - \alpha p_1 + p_2) = 0; \\
\frac{\partial S}{\partial \tau} - \lambda (S_{\text{max}} - S)C_1(\alpha C_1 - \alpha p_1 + p_2) = 0. 
\]

2. The analytical solution

We denote \( C_1(x, \tau)|_{\tau=0} = C_{1,0}(x) \). According to the condition (13), at the reaction front \( \tau = 0 \) the equation (18) has the form:

\[
\frac{dC_{1,0}}{dx} + \lambda S_{\text{max}} C_{1,0}(\alpha C_{1,0} + p_2 - \alpha p_1) = 0. 
\]

We transform the equation (20)

\[
\frac{dC_{1,0}}{dx} = -\frac{\lambda C_{1,0}(\alpha C_{1,0} + p_2 - \alpha p_1)}{S_{\text{max}}}. 
\]

We integrate the equality (21) with respect to \( dx \) from 0 to \( x \):
\[
\int_0^{c_{1,0}} \frac{dC_{1,0}}{dx} \frac{1}{\lambda C_{1,0}(\alpha C_{1,0} + p_2 - \alpha p_1)} \, dx = -S_{\text{max}}. \tag{22}
\]

Using the condition (12), we transform the integral (22):
\[
\int_p^{c_{1,0}} \frac{dC}{\lambda C(\alpha C + p_2 - \alpha p_1)} = -S_{\text{max}}. \tag{23}
\]

We denote
\[
\Phi(C_{1,0}) = \int_p^{c_{1,0}} \frac{dC}{\lambda C(\alpha C + p_2 - \alpha p_1)}. \tag{24}
\]

Then
\[
C_{1,0}(x) = \Phi^{-1}(-S_{\text{max}}), \tag{25}
\]

where \( \Phi^{-1} \) is the function inverse to \( \Phi(C_{1,0}) \).

If \( p_2 - \alpha p_1 \neq 0 \), then:
\[
\int_p^{c_{1,0}} \frac{dC}{\lambda C(\alpha C + p_2 - \alpha p_1)} = \frac{1}{\lambda(p_2 - \alpha p_1)} \left( \ln \frac{C_{1,0}}{C_{1,0} + \frac{p_2 - \alpha p_1}{\alpha}} - \ln \frac{p_1}{p_2} \right). \tag{26}
\]

The solution (25) takes the form:
\[
C_{1,0}(x) = \frac{(p_2 - \alpha p_1)p_1}{p_2 e^{\lambda(p_2 - \alpha p_1)S_{\text{max}} - \alpha p_1}}. \tag{27}
\]

Note that the function \( C_{1,0}(x) \) decreases at the reaction front \( \tau = 0 \) as with \( p_2 - \alpha p_1 > 0 \), so with \( p_2 - \alpha p_1 < 0 \).

In the area of \( \Omega_i \) the solution is similar to [18]. We express the function \( S \) from the equation (18)
\[
S = \frac{\partial C_1/\partial x}{\lambda C_1(\alpha C_1 - \alpha p_1 + p_2)} + S_{\text{max}}. \tag{28}
\]

We differentiate the relation (28) with respect to \( \tau \) and use the function (24)
\[
\frac{\partial S}{\partial \tau} = \frac{\partial}{\partial \tau} \left( \frac{\partial}{\partial x} \Phi(C_1) \right). \quad \tag{29}
\]

From the equations (18), (19) the relation follows:
\[
\frac{\partial S}{\partial \tau} = -\frac{\partial C_1}{\partial x}. \tag{30}
\]

We substitute the equality (30) into the equation (29) and change the differentiation order
\[
\frac{\partial}{\partial x} \left( \frac{\partial}{\partial \tau} \Phi(C_1) \right) + \frac{\partial C_1}{\partial x} = 0. \tag{31}
\]

We integrate (31) at \( x \):
\[
C_i + \frac{\partial \Phi(C_i)}{\partial \tau} = g(\tau),
\]
(32)

or
\[
C_i + \frac{\partial C_i}{\partial \tau} \frac{1}{\lambda C_i(\alpha C_i - \alpha p_1 + p_2)} = g(\tau).
\]
(33)

Let us define the integration constant \( g(\tau) \) and consider the equation (33) at the entrance of the porous medium \( x = 0 \). From the condition (12) \( g(\tau) = p \) the equation (33) takes the form
\[
C_i + \frac{\partial C_i}{\partial \tau} \frac{1}{\lambda C_i(\alpha C_i - \alpha p_1 + p_2)} = p.
\]
(34)

According to the condition (12), the equation with separable variables (34) has a solution
\[
\int_{C_i(x, \tau)}^{C_i(x, \tau)} \frac{dC}{(p_1 - C)\lambda C(\alpha C + p_2 - \alpha p_1)} = \tau.
\]
(35)

Calculating the integral (35), we find the \( C_i(x, \tau) \) solution’s implicitly:
\[
-\frac{1}{p_1 p_2} \ln \left| \frac{p_1 - C_1}{p_1 - C_{1,0}} \right| + \frac{1}{p_1 (p_2 - \alpha p_1)} \ln \left| \frac{C_1}{C_{1,0}} \right| - \frac{\alpha}{p_2 (p_2 - \alpha p_1)} \ln \left| \frac{\alpha C_1 + p_2 - \alpha p_1}{\alpha C_{1,0} + p_2 - \alpha p_1} \right| = \lambda \tau,
\]
(36)

where the function \( C_{1,0}(x) \) is given by the formula (25).

With a known function \( C_i(x, \tau) \) the decision \( C_2(x, \tau) \) is defined by formula (17).

We differentiate the equality (35) with respect to the variable \( x \):
\[
\frac{\partial C_i}{\partial x} \frac{1}{(p_1 - C)\lambda C(\alpha C - \alpha p_1 + p_2)} - \frac{\partial C_{1,0}}{\partial x} \frac{1}{(p_1 - C_{1,0})\lambda C_{1,0}(\alpha C_{1,0} - \alpha p_1 + p_2)} = 0,
\]
(37)

Using the equations (18), (20), we obtain:
\[
\frac{S - S_{\text{max}}}{p_1 - C_1} + \frac{1}{p_1 - C_{1,0}} = 0 \quad \text{from the relation (37)}.
\]
(38)

We express the solution \( S \) from the equation (38)
\[
S = S_{\text{max}} - \frac{p_1 - C_1}{p_1 - C_{1,0}}.
\]
(39)

The relation (39), linking solutions on the characteristics, is called the Riemann invariant [19].

3. Numerical modeling

Below are the reagents and sediment’s graphs constructed according to the formulas (17), (36), (39) for \( p_1 = p_2 = 1, \alpha = 0.5, \lambda = 1, S_{\text{max}} = 1 \).

Figure 1 shows the graphs of the reagents’ concentration:

a) dynamics at the exit of the porous medium;

b) profile at the moment \( t = 1 \).
Figure 1. The reagents concentrations:

a) \( C_1(l,t), C_2(l,t). \)

b) \( C_1(x,1), C_2(x,1). \)

The graphs showing the change in concentration in a sample of a porous medium at a fixed point in time are called profiles. Figure 2 shows the sediment graphs: a) the dynamics at the porous medium outlet; b) profile at \( t=1. \)

Figure 2. The sediment concentration:

a) \( S(l,t). \)

b) \( S(x,1). \)

Figure 3 shows the sediment profiles a) at \( t=3; \) b) at \( t=10. \)

Figure 3. The sludge profiles:

a) \( S(x,3). \)

b) \( S(x,10). \)

Figures 1 a), 2 a) show that the reagents and sediment concentrations tend to finite the limits for a long time: \( C_1(l,t) \to p_1, \ C_2(l,t) \to p_2, \ S(l,t) \to S_{\text{max}}. \)
4. Discussion
The chemical reaction front moves at a constant speed. Similar to the suspensions and colloids filtration in a porous medium in the front, the porous medium is empty, and there are reagents and sediment behind the front.

The comparison of the found chemical reaction model’s solutions with the suspension filtration problem’s solutions in a porous medium shows that the proposed model is comparable to filtration in the case of a nonlinear concentration function [20]. The linear dependence of the reaction rate on each reagent’s concentration leads to a quadratic concentration function.

The sediment profile always decreases monotonously. With increasing time, the profile’s convexity changes. When filtering a bi-dispersed suspension, the profiles are not monotonic [21]. The study of the profiles’ monotonicity if two types of precipitate are formed during a chemical reaction is of great interest. This task will be considered separately.

Summary
A model of a chemical reaction in a porous medium, taking into account the reagents’ interaction and the sediment formation is constructed.

The exact solution to the problem is found in implicit algebraic form.

The relationship between the reactants’ concentrations and the precipitate is determined by the Riemann invariant.

A numerical simulation of the chemical reaction is performed.

The exact solutions allow the experiments’ fine-tuning [22].

References
[1] Bedrikovetsky P G et. al. 2009 Produced water re-injection with seawater treated by sulphate reduction plant: injectivity decline, analytical model Journal of Petroleum Science and Engineering 68 (1-2) 19-28
[2] Appelo C A J and Postma D 2005 Geochemistry, Groundwater and Pollution (CRC Press) 683.
[3] Herzig J P, Leclerc D M and Legoff P 1970 Flow of suspensions through porous media - application to deep filtration Industrial and Engineering Chemistry 62(5) 8-35.
[4] Bedrikovetsky P G et. al. 2006 Correction of basic equations for deep bed filtration with dispersion Journal of Petroleum Science and Engineering 51 68-84.
[5] Paster A, Aquino T and Bolster D 2015 Incomplete mixing and reactions in laminar shear flow Physical Review E 92(1) 012922.
[6] Dentz M, Le Borgne T, Lester D R and de Barros F P J 2017 Mixing in groundwater The Handbook of Groundwater Engineering (CRC Press, Boca Raton) 13 383–412
[7] Siuliukina N and Tartakovsky D M 2018 A hybrid multiscale model of miscible reactive fronts Water Resources Research 54 61–71.
[8] Valocchi A J, Bolster D and Werth C J 2019 Mixing-Limited Reactions in Porous Media Transport in Porous Media 130(1) 157-182.
[9] Vyazmina E A, Bedrikovetskii P G and Polyanin A D 2007 New classes of exact solutions to nonlinear sets of equations in the theory of filtration and convective mass transfer Theoretical Foundations of Chemical Engineering 41(5) 556-564.
[10] Galaguz Yu P and Safina G L 2016 Modeling of Particle Filtration in a Porous Medium with Changing Flow Direction Procedia Engineering 153 157-161.
[11] Safina G L 2019 Numerical solution of filtration in porous rock E3S Web of Conferences 97 05016.
[12] Zhang H, Malgaresi G V C and Bedrikovetsky P 2018 Exact solutions for suspension-colloidal transport with multiple capture mechanisms International Journal of Non-Linear Mechanics 105 27-42.
[13] Borazjani S and Bedrikovetsky P 2017 Exact solutions for two-phase colloidal-suspension transport in porous media Applied Mathematical Modelling 44 296–320.
[14] Vaz A, Maffra D, Carageorgos T and Bedrikovetsky P 2016 Characterization of formation damage during reactive flows in porous media *Journal of Natural Gas Science and Engineering* **34** 1422-1433.

[15] Alvarez A C, Hime G, Silva J D and Marchesin D 2013 Analytic regularization of an inverse filtration problem in porous media *Inverse Problems* **29** 025006.

[16] Galaguz Yu P, Kuzmina L I and Osipov Yu V 2019 Problem of deep bed filtration in a porous medium with the initial deposit *Fluid Dynamics* **54** (1) 85–97.

[17] Kuzmina L I, Nazaitkinskii V E and Osipov Y V 2019 On a deep bed filtration problem with finite blocking time *Russian Journal of Mathematical Physics* **26** (1) 130-134.

[18] Kuzmina L and Osipov Y 2017 Filtration model of the unsteady suspension flow in a porous medium *MATEC Web of Conferences* **117** 00097.

[19] Osipov Yu V, Safina G L and Galaguz Yu P 2020 Filtration model with multiple particle capture *IOP Conf. Series: Journal of Physics* **1425** 012110.

[20] Kuzmina L I, Osipov Yu V and Zheglova Yu G 2018 Analytical model for deep bed filtration with multiple mechanisms of particle capture *International Journal. of Non-Linear Mechanics* **105** 242–248.

[21] Malgaresi G, Collins B, Alvaro P and Bedrikovetsky P 2019 Explaining non-monotonic retention profiles during flow of size-distributed colloids *Chemical Engineering Journal* **375** 121984.

[22] Yang S, Russell T, Badalyan A, Schacht U, Woolley M and Bedrikovetsky P 2019 Characterisation of fines migration system using laboratory pressure measurements *Journal of Natural Gas Science and Engineering* **65** 108-124.