

Pressure diffusion and chemical viscosity in the filtration models with state equation in differential form

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Abstract. Some options of coupling filtration models are suggested using irreversible state equations in differential form. State equations include explicitly the coefficient of compressibility, coefficients of concentration expansion and other physical properties affecting rheological properties and composition. To construct the models, the improvement of thermodynamic relations is used. New physical factors are introduced with the help of new thermodynamic variables. The chemical viscosity, pressure diffusion and concentration expansion phenomena are taken into account. The simplest particular problems illustrating the role of new effects are distinguished for stationary filtration regime. The revealed nonlinear effects can be important when considering biology liquid flows in porous biomaterials where deviations from classical laws are possible.

1. Introduction

Many biology objects are the composites with complex structure of porous space. Artificial media synthesized for catalysis and chemical technology should be similar to natural objects [1]. This assumes that simulation of flows in porous natural and man-made biology objects should be based on the filtration laws. However interrelation between various physical effects can lead to the deviation on habitual conceptions.

Classical filtration Darcy's law (1856) connects filtration velocity \mathbf{w} of fluid with pressure field p

$$\mathbf{w} = -\frac{k}{\mu} \nabla p, \quad (1)$$

where k is the permeability, and μ is the friction coefficient of fluid with pore walls or viscosity. There are various generalizations of this law for high rate flows, irreversible conditions, heterogeneous fluids, two-phase flows, media with double porosity, and etc. [2-4]. Thermodynamically based generalization of law (1) for multicomponent and multi-phase flows was made in [5,6]. General form of motion equation includes (1) as particular case:

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \nabla(\mathbf{v}) = \nabla p + \rho(\mathbf{F}_1 + \mathbf{F}_2), \quad (2)$$



where $\mathbf{v} = \mathbf{w}/a$, $a = S_p/S$, and S_p is the area occupied by pores in the section S ; \mathbf{F}_1 is gravity force, and \mathbf{F}_2 is the force of internal friction depending on filtration velocity.

If fluid is multicomponent, the following equations for species are necessary [2,3]

$$\left(\frac{\partial m \rho C_k}{\partial t} + \nabla \cdot \rho \mathbf{w} C_k \right) = -\nabla \cdot \mathbf{J}_k + \sigma_k, \quad (3)$$

where C_k are mass concentrations, \mathbf{J}_k are diffusion fluxes, σ_k are sources of species due to chemical reactions and mass exchange with solid skeleton; m – is porosity. We should add the continuity equation and state equations to the previous one. First of them has usual form

$$\frac{\partial}{\partial t} m \rho = -\nabla \cdot \rho \mathbf{w} + \sigma, \quad (4)$$

where σ is possible mass source from porous skeleton. State equations define the connection between the pressure and other variables, and can be found based on experiment or irreversible thermodynamics.

Naturally, in multicomponent system, the balance of masses and diffusion fluxes take place

This work demonstrates the step-by-step complication of filtration models by taking into account the coupling effects between various physical phenomena, when constitutive equations are based on irreversible thermodynamics, and rheological features are associated with physical effects.

2. Constitutive equations in thermodynamics

Thermodynamics allows ascertaining two groups of constitutive equations [7,8], and assumes that the pressure consists of two parts $p = p^e + p^V$. First term increment depends linearly with the change in volume (strains), concentrations, and other thermodynamical variables. Second term depends on the rates of change of thermodynamical variables. First group of constitutive equations follows from Gibbs equation written in suitable form. These are

$$dp^e = -\rho \beta_T^{-1} d\gamma + \sum_{k=1}^n p_k dC_k; \quad (5)$$

$$dg_k = p_k d\gamma + \sum_{i=1}^n \beta_i^k dC_i, \quad (6)$$

where $p_k = \alpha_k \beta_T^{-1}$, α_k is the concentration expansion coefficient, β_T is isothermal compressibility.

We can call the coefficients p_k as partial pressures. The coefficients β_i^k depend on the mixture under study. Here the coupling or cross effect consists of the interrelation between mechanical and chemical processes. The pressure can change due to the liquid composition variation, and the chemical potentials of the liquid components change when the volume or pressure varies.

Linear Onsager theory gives the second group of constitutive equations. For example, when only one chemical reaction takes place with the rate φ , we can write

$$p^V = -\kappa_V \nabla \cdot \mathbf{v} + \gamma_V A; \quad (7)$$

$$\varphi = -\gamma_V \nabla \cdot \mathbf{v} + k_{ch} A, \quad (8)$$

where κ_V is the volume viscosity, k_{ch} is the reaction rate constant; A is the chemical affinity, $A = (m_R g_R - m_P g_P)$; then $k=R, P$ in (3),(5) and (6); coefficient γ_V describes the viscosity connecting with chemical reaction and the dependence of reaction rate on fluid mobility.

More complex generalizations are possible in modern thermodynamics [9,10] for multi-phase flows in porous media and for the media with double porosity.

3. Examples for stationary filtration regimes

Naturally, all classical filtration models follow from above presented equations. Here we consider only the simplest models to illustrate the influence of “new” factors appearing due to interrelation between phenomena of various physical natures. Note that obtained effects are similar to those which appear when the dependencies of permeability, porosity, viscosity and etc. on pressure are taken into consideration [11,12].

3.1. Imperfect no viscous gas

For imperfect one-component gas, the state equation for “elastic” part of the pressure

$$dp^e = -\frac{\rho}{\beta_T} d\gamma \equiv \frac{1}{\beta_T \rho} d\rho \quad \text{or} \quad \nabla p^e = \frac{1}{\beta_T \rho} \nabla \rho \quad (9)$$

follows from (5). “Viscous” part of the pressure equals to zero, and $p = p^e$. For stationary flow, two equations remain

$$\nabla \cdot \rho \mathbf{v} = 0 \quad \text{and} \quad \mathbf{v} = -\frac{k}{\mu a} \nabla p. \quad (10)$$

If the properties do not change with the pressure, the equation for p takes the form

$$\nabla \cdot \nabla p + \beta_T (\nabla p)^2 = 0. \quad (11)$$

This leads to the simple problem for plane layer

$$\frac{d^2 p}{dx^2} + \beta_T \left(\frac{dp}{dx} \right)^2 = 0; \quad x=0: \quad p = p_A; \quad x=L: \quad p = p_B. \quad (12)$$

It is convenient to write exact analytical solution for this problem in dimensionless variables

$$\bar{p} = p/p_A, \quad u = V/V_*, \quad \xi = x/L; \quad V_* = \frac{k}{\mu a} \frac{p_A}{L}.$$

Consequently we obtain

$$\bar{p} = \frac{1}{\bar{\beta}_T} \ln[(\xi + C_1)C_2], \quad u = \frac{1 - \exp[-\bar{\beta}_T(1-\pi)]}{1 - \xi + \xi \exp[-\bar{\beta}_T(1-\pi)]}. \quad (13)$$

where $\bar{\beta}_T = \beta_T p_A$, $\pi = p_B/p_A$ are parameters, C_1, C_2 are integration constants depending on $\bar{\beta}_T, \pi$ (not presented here). The tendency of the solution change at compressibility decrease is shown from Figure 1. For $\bar{\beta}_T = 0.5$ the result does not distinguish from the solution for incompressible liquid.

More strong effects appear when coupling phenomena are taken into account.

3.2. Compressible viscous liquid

For imperfect single component compressible liquid, the state equation stays the same. However the pressure consists of two parts and Darcy law turns to

$$\mathbf{v} = -\frac{k}{\mu a} \nabla p = \frac{k}{\mu a} [\nabla p^e + \nabla p^V]. \quad (14)$$

Using (9) for first part of the pressure (“elastic”) and relation

$$p^V = -\kappa_V \nabla \cdot \mathbf{v} \tag{15}$$

for “viscous” part, we find the equation for the velocity

$$\beta_T \mathbf{v} \nabla (\kappa_V \nabla \cdot \mathbf{v}) + \nabla \cdot \mathbf{v} - \mu a \beta_T k^{-1} \mathbf{v} \mathbf{v} = 0. \tag{16}$$

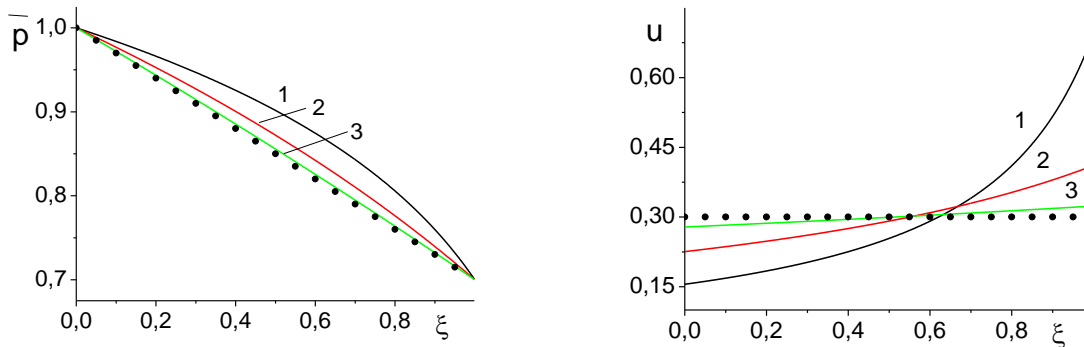


Figure 1. Pressure and velocity in plane layer for the case of filtration of imperfect gas; $\beta_T = 1. - 5$; 2. $- 2$; 3. $- 0,5$, points correspond to incompressible liquid

For example, for plane layer, this equation is reduced to

$$\beta_T \kappa_V V \frac{d^2 V}{dx^2} + \frac{dV}{dx} - \frac{\mu a}{k} \beta_T V^2 = 0. \tag{17}$$

It is not difficult using (14) to obtain the equation for total pressure for this case

$$\beta_T \kappa_V \frac{k}{\mu a} \left(\frac{dp}{dx} \right) \frac{d^3 p}{dx^3} - \frac{d^2 p}{dx^2} - \beta_T \left(\frac{dp}{dx} \right)^2 = 0. \tag{18}$$

Additionally we have the relation $\rho V = const$ from continuity equation.

3.3. Binary non-viscous imperfect mixture

For imperfect two-component compressible mixture without viscosity ($p = p^e$) and without chemical reaction, the state equation will contain new parameter, namely – concentration expansion coefficient α_C :

$$dp = \frac{1}{\beta_T} \left(\frac{d\rho}{\rho} + \alpha_C dC \right). \tag{19}$$

This parameter α_C has thermodynamical definition: $\alpha_C = \alpha_2 - \alpha_1, \alpha_k = (\partial \gamma / \partial C)_T / \gamma$; the coefficients α_2, α_1 can be calculated based on atomic volumes. Neglecting the pressure diffusion, we come for stationary filtration regime to the coupling equation system including (10) and

$$\nabla p = \frac{1}{\beta_T} \left(\frac{\nabla \rho}{\rho} + \alpha_C \nabla C \right), \tag{20}$$

$$a \mathbf{v} \nabla C = D \nabla \cdot \nabla C. \tag{21}$$

Here usual Fick law and condition $D\rho = const$ are assumed correct.

From these equations one can find the equation for the pressure

$$\nabla \cdot \nabla p + (\beta_T \nabla p - \alpha_C \nabla C) \nabla p = 0, \quad (22)$$

coupled with the concentration.

Then the problem for plane layer with given pressure drop will include the coupled equations:

$$\frac{d^2 p}{dx^2} + \left(\beta_T \frac{dp}{dx} - \alpha_C \frac{dC}{dx} \right) \frac{dp}{dx} = 0; \quad (23)$$

$$-\frac{k}{\mu} \frac{dp}{dx} \frac{dC}{dx} = D \frac{d^2 C}{dx^2}. \quad (24)$$

The boundary conditions for pressure are similar to (12), and for concentration are

$$x=0: C=C_1; p=p_A \text{ and } x=L: C=C_2; p=p_B. \quad (25)$$

The problem will be a more complex, if diffusion coefficient depends on the pressure and concentration.

3.4. Filtration together with the pressure diffusion

Here we use the state equation (6) for chemical potentials and take into account that diffusion fluxes for species are proportional to gradient of their chemical potentials. For binary imperfect mixture and $T=const$, one can write the relations

$$\mathbf{J}_k = -\sum_i L_{ki} \nabla \left(\frac{g_i}{T} \right) \quad (26)$$

for mass fluxes of species, where chemical potentials follow from (6) or similar equation is written based on Gibbs equation for Gibbs energy $g = \sum_k g_k C_k$. Usual diffusion theory gives

$$\mathbf{J} = -D\rho f(C) \nabla C - \frac{DCm}{RT} \alpha_C \nabla p^e. \quad (27)$$

where m is the molar mass of diffused species, R – is universal gas constant. The equations for parts of the pressure and for velocity stay the same. The diffusion equation gains additional term:

$$\alpha \nabla \rho \nabla C = \nabla \cdot [\rho D f(C) \nabla C] + \nabla \cdot [B C \nabla p^e], \quad (28)$$

where $B = \frac{Dm\alpha_C}{RT}$ is pressure diffusion coefficient. This is not independent value and is calculated from other properties.

3.5. Filtration together with chemical reactions

The most complex model appears when chemical reaction can accompany the flows in porous body. Different situation are possible here. Firstly, when part of fluid is absorbed by solid skeleton, in (3) $\sigma_k = \sigma C_k < 0$. In this case, diffusion equations (21), (28) do not change.

Secondly, when reactions happen in volume of pores, $\sigma = 0$, and

$$\sigma_k = m_k \sum_i \nu_{ki} \Phi_i, \quad (29)$$

where φ_i is the rate of reaction i . For one reaction with the rate (8), it is necessary to calculate chemical affinity. By definition, the chemical affinity equals to the sum of chemical potentials of species multiplied by corresponding molar mass and stoichiometric coefficients. So, for reaction $\nu_1 R_1 + \nu_2 R_2 \rightarrow \nu_3 Product$, we can write

$$A = -(\nu_1 m_1 g_1 + \nu_2 m_2 g_2 + \nu_3 m_3 g_3). \quad (30)$$

Hence, $A = A(p^e, C_1, C_2, C_3)$, it is not difficult, using the Gibbs-Duhem equation and differential relations of type (6), to obtain

$$dA = -f_p(C_k) dp^e - f_1(C_k) dC_1 - f_3(C_k) dC_3$$

with functions f_p, f_1, f_3 depending on composition and physical properties. This speaks that “viscous” pressure (7) and “elastic” pressure (5) will be interrelated with each other. Hence, chemical viscosity will include primary (connected with composition change) and secondary (connected with viscosity change in chemically reacted mixture) effects. Note the both effects can appear in incompressible liquid, when

$$\nabla p^V = -[f_1 + f_p(p_1 - p_2)] \nabla C_1 - [f_3 + f_p(p_3 - p_2)] \nabla C_3$$

These effects demand a special investigation.

4. Conclusion

So, the resources of irreversible thermodynamics are demonstrated to reveal the features of filtration flows leading to the deviation from Darcy law. Some limiting situations are studied to show the nonlinearities associated with coupling effects between various phenomena. Pressure diffusion and chemical viscosity can be important for biological applications where mass transfer is insured by diffusion together with filtration.

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