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MECHANISM OF MASS TRANSFER OF THE LIQUID PHASE IN THE DISPLACEMENT
OF GAS BY LIQUID IN NONUNIFORM POROUS MEDIA

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An analysis is made of the possible mechanism of mass transfer in the motion of gas-liquid systems in low-permeability porous media. The mechanism is based on the phenomenon of capillary recondensation.

A considerable part of the gas reserves in the world are confined in low-permeability resevoirs (permeability less than 10^{-3} μm^2). The mechanism of mass transfer determines the motion of gas-liquid systems in media with a low permeability, the conditions for removal of gas and condensate from the bed, the interaction of the drilling-fluid filtrate with the rocks of the bed as it is being opened up by drilling, and other factors. In the case of isothermal two-phase motion, the dominant process of mass transfer is determined by value of the diffusional Peclet number (Pe_d). This number characterizes the ratio of the hydrodynamic and diffusion flows of a substance:

$$Pe_d = \frac{vL}{D} .$$

(1)

In the penetration of a fluid into a gas-saturated porous medium, consideration should be given to diffusion in the length direction of the pores. The characteristic rate can be determined in accordance with the Poiseuille law for laminar motion in a cylindrical capillary

$$v = \frac{r^2}{8\mu} \frac{\Delta P}{L} .$$

In this case, Eq. (1) takes the form

$$Pe_d = \frac{r^2 \Delta p}{8\mu D} .$$

(2)

For low-permeability rock with pores having a radius on the order of 10^{-6}-10^{-8} m in the case of realistic values of the diffusion coefficient 10^{-6}-10^{-8} m^2/sec and viscosity 10^{-3}-10^{-2} Pa·sec and pressure gradients due either to capillary forces or the gradient of the external pressure field at distances commensurate with the size of a block (10^3-10^5 Pa), the number Pe_d will take values on the order of unity or several orders less, i.e., under these conditions the diffusion mechanism of mass transfer is either comparable to the hydrodynamic mechanism or is dominant. This conclusion is backed up by a well-known analysis of moisture exchange processes in low-permeability clayey rocks [1, 2].

The diffusional mechanism of mass transfer may either by diffusion itself or osmotic phenomena considered as a group [1]. We will not concern ourselves here with the latter, since they can take place in the presence of a bound liquid phase either initially present
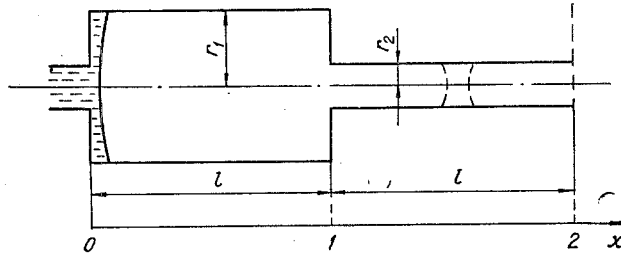
Fig. 1. Capillary model for studying recondensation.

in the porous medium or formed early in the process by a different mass transfer mechanism such as capillary seepage. In tests conducted by S. N. Zakirov and L. G. Gerov [3] to study gas removal from cracked-porous rock when the gas was displaced by water, the investigators observed penetration of the liquid phase into samples of a resevoir from the Chirin deposit (characteristic pore size 10^{-8} m) in the absence of an external pressure gradient. The authors linked this effect with capillary impregnation. However, in accordance with the value of the number $Pe_d = 10^{-3}$-10^{-5}, the propagation of the substance in the rock should have been of a diffusional nature. It is nonetheless true that, in the case, the mass transfer mechanism should have provided for the formation of the liquid phase in the porous medium.

Thus, it is possible to hypothesize the existence of a special diffusional mass transfer mechanism. In the case of the displacement of gas by liquid in nonuniform beds with low-permeability inclusions, this mechanism can in conjunction with capillary impregnation cause the liquid phase to penetrate the inclusions. Below we describe and analyze this process, which has been termed "capillary recondensation."

The wetting liquid moves in the porous medium under the influence of capillary forces, displacing the gas. As the size of the region occupied by the liquid phase increases, there is a reduction both in the capillary pressure gradient per unit length and the rate of advance of the displacement front. In the presence of factors which oppose motion (gravity, external hydrodynamic gradient, static shear stress in the liquid), the displacing phase may come to a complete stop. Here, the miniscus will be located in the broadest part of the pore channel and will have a relatively small curvature — resulting in minimal capillary pressure. Due to the continuous evaporation of liquid from the surface of the meniscus, vapor diffuses into the narrow part of the capillary. After a certain period of time, the concentration of this vapor and the corresponding partial pressure reach values critical for the given pore radius (the partial pressure here being lower than that at the meniscus in the broad part of the channel). At these values, the polymolecular film on the wall of the pore collapses and the pore is spontaneously filled with liquid. The condensed phase cannot penetrate into the capillary farther than the wide section — where the vapor pressure cannot reach the local critical value — while the meniscus cannot advance due to the low capillary pressure. Consequently, the combination of diffusion and capillary condensation lead to the successive flooding of a chain of sections of pore channels with relatively small radii, thus helping the liquid to penetrate the porous medium.

It should be noted that the mechanism of recondensation can similarly explain the propagation of a nonwetting liquid into a porous medium. In this case, the saturated vapor has a higher partial pressure in the narrow part of the pore, and condensation takes place in the broad part. The arguments presented below can also be generalized in corresponding fashion.

To make a more detailed analysis of capillary recondensation, we conducted a theoretical study of the process at the level of a single pore. Just as the porous medium is characterized by the mean radius of a pore channel, we can introduce effective parameters of a more complex, corrugated capillary with alternating broad and narrow sections. These additional parameters — the ratio of the mean radii of the sections and the frequency of their alternation (or mean section length) — are determined by the micro-nonuniformity of the porous medium. Figure 1 shows a unit of such a corrugated pore. To evaluate the duration of the transitional process on the given characteristic segment, we formulated the following model problem:

$$\frac{\partial^2 c_i}{\partial x^2} = \frac{\partial c_i}{\partial t}, \quad i = 1, 2;$$

(3)

1057

$$c_1|_{x=0} = 1; \quad c_2|_{x \to \infty} = 0; \quad c_1|_{x=1} = c_2|_{x=1}; \quad a\frac{\partial c_1}{\partial x}\bigg|_{x=1} = \frac{\partial c_2}{\partial x}\bigg|_{x=1};$$

$$c_1|_{t=0} = c_2|_{t=0} = 0; \quad t = \frac{\tau D}{l^2}, \quad a = \frac{r_1^2}{r_2^2}. \tag{4}$$

Equations (3) and (4) describe the diffusion of vapor in a channel of variable cross section. It should be noted that the use of the equations of hydrodynamics to describe molecular diffusion in microscopic pores is valid for the transverse scales we are considering — on the order of 10^{-6}-10^{-8} m — since they are considerably greater than the molecular diameter [4]. The formulation of the problem does not consider: a) the finiteness of the length of the narrow capillary (in the formulation of the second boundary condition); b) the thickness of the polymolecular film; c) the presence of vapor in the capillary at the initial moment of time. However, these assumptions are not of fundamental importance for an approximate analysis.

We sought the solution of the problem in the form

$$c_i = c^0(\eta) + (a-1) f_i(x, t), \tag{5}$$

where $\eta = x/2\sqrt{t}$; $c^0(\eta) = \mathrm{erfc}(\eta)$ is the similarity solution of the problem for a semi-infinite capillary of constant cross section.

The functions $f_i(x, t)$ were found by the method of operational calculus using asymptotic theorems with inverse transformation. With a high degree of accuracy

$$f_1 = \frac{x}{a+1}\exp\left[\left(\frac{a}{a+1}\right)^2 t\right]\mathrm{erfc}\left(\frac{a}{a+1}\sqrt{t}\right); \tag{6}$$

$$f_2 = \frac{1}{a+1}\left\{\left(1 + \frac{ax}{a+1}\right)\exp\left[\left(\frac{a}{a+1}\right)^2 t\right] \times \right.$$

$$\left. \times \mathrm{erfc}\left(\frac{a}{a+1}\sqrt{t}\right) - \frac{x}{\sqrt{\pi t}}\right\}. \tag{7}$$

Since the vapor concentration is distributed over the narrow pore nonuniformly, it is impossible to unambiguously prescribe the condition of collapse of the polymolecular film. Thus, we used two approaches to calculate the time of condensation. It can be assumed that the moment of condensation coincides with the time of attainment of the critical value c_2^*: a) the minimum relative concentration in the narrow pore, i.e., the concentration in the extreme right section $x = 2$; b) the mean integral concentration on the segment $1 \le x \le 2$. It is evident that the time of collapse according to the first criterion T_c' will always be greater than the time calculated by the second method T_c''.

Figure 2 shows the time dependence of the quantity $c_2|_{x=2}$ for $a = 10$ (wetting liquid) and $a = 0.1$ (nonwetting liquid). It is apparent that concentration increases relatively rapidly in the initial period of the diffusion process. The curves then flatten out substantially even in semi-logarithmic coordinates. Thus, the critical values of relative concentration c_2^* — which are close to unity in practice — may be attained over a period of time several orders greater than the characteristic time of diffusion l^2/D.

A comparative analysis was made of the effect of the parameters of the capillary model in condensation time with identical values of the effective radius of the corrugated pore:

$$r_{ef} = 2r_1\left(\frac{1}{1 + a^{1/2} + 2a^{-3/2}} + \frac{1}{1 + a^{1/2} + 2a^2}\right). \tag{8}$$

The effective radius of a corrugated pore r_{ef} will be assumed to be the radius of a capillary of length $2l$ and constant cross section in which the period of capillary impregnation coincides with the time of impregnation of a single unit. Meanwhile, since the rate of impregnation of a unit depends on the direction of motion, in deriving (8) we examined the mean value between the effective radii for forward and reverse impregnation.
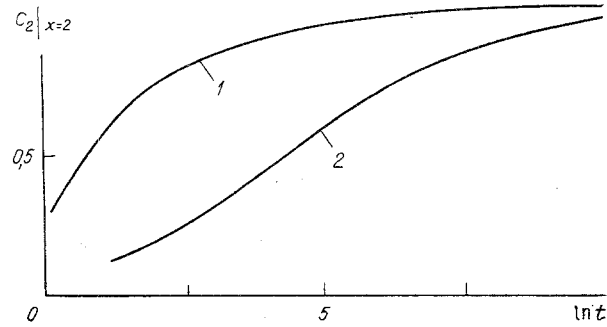
Fig. 2. Time change in vapor concentration on the right boundary of the capillary model: 1) a = 10; 2) a = 0.1.

It was found that the critical value c_2^* can be determined from the formula

$$c_2^* = \chi_{ef}^{\nu},$$ (9)

where

$$\gamma = 2 (a^{1/2} - 1) \left(\frac{1}{1 + a^{1/2} + 2a^{-3/2}} + \frac{1}{1 + a^{1/2} + 2a^2} \right).$$

It can be shown that

$$\gamma (a) = - \gamma \left(\frac{1}{a} \right).$$ (10)

The last conclusion is consistent with representations on the existence of a definite symmetry to phenomena for wetting and nonwetting liquids, and it confirms the validity of the expression chosen for effective radius.

Figure 3 shows results of calculation of the dependence of the dimensionless time of condensation (according to the two criteria) on the micro-nonuniformity parameter a. We took χ_{ef} = 0.95 for a wetting liquid. For the fluids known to wet rock, this value corresponds to pores of the radius 10^{-6}-10^{-8} m. For nonwetting liquids, accordingly, we used χ_{ef} = 1/0.95 = 1.05.

We see that with recondensation of the wetting liquid (a > 1), an increase in the parameter a leads to a decrease in the time T_c. For a nonwetting liquid (a < 1), the relation $T_c(a)$ is nonmonotonic. For a porous medium with a high degree of micro-nonuniformity (in the present case, a < 0.3-0.4), a reduction in the parameter a leads to an increase in T_c. This is connected with the fact that the vapor pressure (concentration) must be brought up to the critical value in a relatively large volume before condensation begins. This factor dominates over the reduction in the critical value that takes place in this case. At large a, however, the last factor is dominant and the relation $T_c(a)$ moves in the opposite direction.

The time T_c must be considered the lower estimate of the period of the recondensation wave T_{pc} (by the period of the recondensation wave, we mean the time interval during which the above-described mass-transfer process is completed at the level of one unit), since it is by no means mandatory that a drop of the liquid condensate occupy a position such that its right boundary turns out to be in the adjacent broad section of the pore. Thus, the formation of the primary volume of the liquid phase may signal only the end of the initial period of the process in a unit volume. It is assumed that mass transfer subsequently proceeds by the same scheme.

Due to continuing diffusion from the section x = 0, with a relatively high saturation vapor pressure, toward the left boundary of the drop — the vapor pressure of which corresponds to the radius of the narrow capillary — the size of the liquid volume will increase. Liquid will be continuously evaporated into the gas from the other meniscus of the drop. Drops will
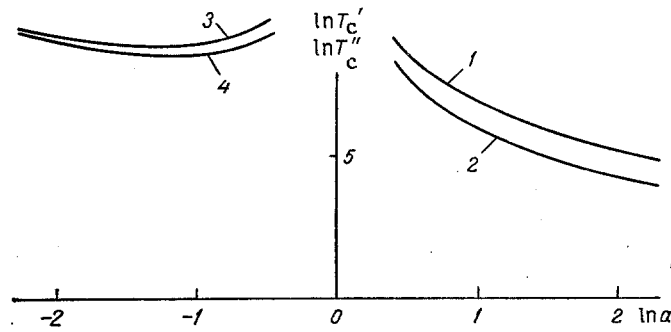
Fig. 3. Dependence of the time of recondensation T_c on the micro-nonuniformity parameter a:
1,3) T_c'; 2, 4) T_c''

move into the adjacent pore only when they completely fill the narrow channel, a meniscus of smaller curvature appears in the wide pore on the left, and a capillary pressure gradient is therefore created on the right.

The mathematical modeling of the process is based on the following premises. It is assumed that the distribution of vapor concentration is quasisteady on the interval between the two menisci and can be described by a piecewise-linear law. To determine the mass flow of gas which evaporates from the right meniscus of the drop and subsequently diffuses into the pore channel, we used a similarity relation which is analogous to the above-examined function $c^0(\eta)$. If the first position is nearly exact, then use of the similarity solution does not provide for expansion in the channel beyond the right meniscus (this leads to understatement of the mass flow) and does not take into account the initial distribution of concentration in the diffusion region. From this viewpoint, the resulting estimate of flow is substantially understated.

We ultimately obtained an approximate expression which describes the filling of a narrow pore by liquid condensate and which makes it possible to determine the duration of this process T_f:

$$\left[\frac{1 - c_2^*}{c_2^*} \; \frac{a}{(1 + 0.5a)} \, T_f - \frac{2}{\sqrt{\pi}} \, \sqrt{T_f} \right] = \beta.$$ (11)

This quantity may change approximately within the range 10^2-10^4, depending on the saturation vapor pressure and the molecular weight of the liquid.

The character of the relation $T_f(a)$ is similar to that of $T_c(a)$. However, with relatively large β, the value of T_f may be one or two orders of magnitude greater than T_c. Accordingly, there is nearly the same difference between the lower (T_c) and upper $(T_c + T_f)$ estimates of the period of the recondensation wave T_{pc}.

Let us find the ratio of the time of capillary impregnation of a block of length L to the time during which a recondensation wave travels the same distance. We define the period of impregation T_{pL} as the time during which a wetting liquid fills a capillary of radius r_{ef} (as above, the time has been made dimensionless with respect to ℓ^2/D):

$$T_{pL} = \frac{4\mu L^2 D}{P_{c\,ef} r_{ef}^2 \, \ell^2}.$$ (12)

The total recondensation time T_{pcL} is proportional to the number of these units $L/2\ell$:

$$T_{pcL} = T_{pc} \; \frac{L}{2l}.$$ (13)

Thus:

$$\frac{T_{pL}}{T_{pcL}} = \frac{8\mu D L}{P_c r_{ef}^2 / T_{pc}}.$$ (14)

Since we lack a priori information on the values of averaged parameters characterizing the micrononuniformity of the porous medium a and ℓ, even the calculations with Eq. (14) are very approximate. Nevertheless, by varying the parameters of the model within the broadest possible range for actual conditions, we come to the conclusion that for low-permeability inclusions with the above-indicated characteristics, the time of propagation of a recondensation wave may be considerably shorter than the duration of capillary impregnation.

The present investigation is the first stage of a larger study of the mechanism of mass transfer in a porous medium. Several questions pertinent to the study went unanswered. For example, it is still unclear how the period of recondensation in a single unit T_{cp} relates to the duration of the condensation process. These and other unanswered questions will be the subject of a future investigation.

NOTATION

v, rate of convective motion; L, characteristic size of zone in which the main change in the potential of the motive force for mass flow takes place; r, pore radius; μ, dynamic viscosity; Δp, characteristic pressure gradient; c, vapor concentration based on the concentration at the stationary meniscus; τ, time; ℓ, length of the constant-radius section of a capillary of variable cross section; D, coefficient of molecular diffusion; t, dimensionless time; x, linear coordinate made dimensionless with respect to the length ℓ; T, dimensionless characteristic time of mass-transfer processes; χ, relative partial pressure of saturated vapor; β, ratio of the density of the liquid condensate to the partial density of the vapor at its critical concentration in the narrow pore.

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EFFECT OF TEMPERATURE ON RHEOLOGICAL CHARACTERISTICS

OF WATER SOLUBLE POLYMER COMPLEXES

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Results are presented from a study of the effect of temperature on rheological characteristics of aqueous solutions of polymers and polycomplexes based thereon.

The rheological characteristics of water-soluble polymer materials depend significantly on temperature, which to a great extent controls the effectiveness of their use in various technological processes [1, 2]. This is related to change in the molecular characteristics of individual polymers [3]. Still more complex and practically unstudied is the behavior of polyelectrolyte complexes (PEC's), despite their primary significance in living nature and their ever wider employment in technology.

The dimensions of macromolecular complexes in a solution are determined not only by entropy factors, but also by polymer–solvent and polymer–polymer energy interactions [4]. Supramolecular formations in dilute polymer solutions have various densities and degrees of organization dependent on their chemical nature. Change in temperature and the changes pro-