- 9. O. M. Alifanov, E. A. Artyukhin, and B. M. Pankratov, "Solution of the nonlinear inverse problem for the generalized heat-conduction equation in a domain with moving boundaries," Inzh.-Fiz. Zh., 29, No. 1, 151-158 (1975).
- 10. I. M. Taganov, Modeling of Mass and Energy Transport Processes [in Russian], Khimiya, Leningrad (1979).

PROPERTIES OF THE MOTION OF LIQUIDS IN POROUS MATERIALS (REVIEW)

L. L. Vasil'ev and V. A. Maiorov

UDC 532.685

The possibility of precise and predictable control of the flow rate of a liquid in porous materials is one of the most important conditions for reliable operation of various heat- and mass-transfer systems based on the use of fluid flow in these materials. However, experiments on filtration of a fluid in porous materials have shown that an undesirable nonuniform and nonreproducible decrease in time in the flow is observed. In the literature, this phenomenon is known as the "filtration effect" [1] or, in analogy with the flow of a liquid through capillaries, "obliteration" [2] and is observed during motion of different liquids in porous materials [1-14]. A typical example of the decrease in the liquid flow through a porous specimen with a constant pressure differential is presented in Fig. 1.

It is of great interest to generalize and analyze the available experimental data in order to clarify the true reasons for the phenomenon indicated, about which different opinions still exist in the literature.

This problem is discussed most completely in [2, 3]. The following are the main reasons mentioned for the decrease in the liquid flow rate with flow in porous materials:

1) The physical properties (in particular, viscosity) of the liquid in a thin layer near a continuous surface differ from the physical properties in the bulk.

2) Molecular layers that gradually decrease the clear pore openings in the porous structure are adsorbed on the surface of the solid body.

When a liquid makes contact with a solid surface, adsorption films whose properties differ from the properties of the liquid in the bulk are formed. If the liquid is a nonpolar dielectric, whose molecules have a zero dipole moment, then the interaction between the molecules of the material and the liquid stems from molecular force fields. Such liquids include benzene, kerosene, etc. If the liquid is a polar dielectric, then the electric field of the material causes definite orientation of the molecules of the liquid and formation of a polymolecular adsorption layer. Such liquids include water, acetone, etc. If the liquid contains free ions, then due to their adsorption an electrically charged double-layer is formed.

Regardless of the reasons for the formation, changes are observed in the structure of the fluid in surface layers (ordered molecular layers), and therefore, changes in the structurally sensitive physical properties (in particular, viscosity and thermal conductivity). It follows from here that the first of the reasons mentioned above for obliteration is a result of the formation of adsorbed layers.

In order to verify the hypothesis of the considerable influence of an adsorbed layer on the decrease of the liquid flow rate in porous materials, it is necessary to have information concerning the thickness of this layer. Its thickness depends on the thermophysical and thermodynamic properties of the liquid and of the solid body, temperature, and structure of the porous material. By applying shear stresses (external flow), it is possible to decrease the thickness of the adsorbed layers due to detachment of the outer, weakly bound molecules. A gradual weakening of the boundary layers of the fluid with increasing tempera-

A. V. Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Novopolotskii Polytechnic Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 40, No. 4, pp. 1111-1123, June, 1981. Original article submitted June 18, 1980.

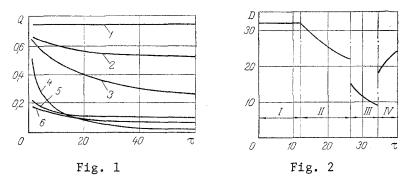


Fig. 1. Change in liquid flow rate during flow through fine-pored metals with a constant pressure differential on the specimen of  $\Delta P = 0.17$  bar [14]: 1) heptane; 2) benzene; 3) isopropyl alcohol; 4) water; 5) 0.5% aqueous solution of a surface active substance; 6) heptane [1-5 are for a specimen consisting of porous titanium with an average pore size of 7.3 µm; 6) fluoroplastic with an average pore size of 3.6 µm]. Q, cm<sup>3</sup>/sec;  $\tau$ , min.

Fig. 2. The change in the flow rate of water through a glass filter with constant pressure differential  $\Delta P = 0.037$  bar and varying inlet temperature [4]: I) vacuum at the inlet 0 mm Hg; II) 93; III) 380; IV) 0 mm Hg. D, cm<sup>3</sup>/bar sec;  $\tau$ , min.

ture should also be expected due to the increase in the intensity of the thermal motion of the molecules.

Direct experimental determination of the thickness of very thin boundary layers is very difficult and often leads to contradictory results. The most reliable data, obtained by Deryagin and co-workers, are presented in [15-19], where a complete bibliography concerning this problem is contained. It should be noted that the results obtained by different methods agree completely. Table 1 shows data from [17] on the thickness of boundary layers  $\delta$  for some liquids on the surface of quartz at room temperature. Of interest is the fact that nonpolar liquids ( $\mu = 0$ ) do not form a measurable boundary layer ( $\delta = 0$ ). It is shown in [15, 19] that the average viscosity of the entire boundary layer increases continuously as its thickness decreases, while the assumption of a local exponential decrease in the viscosity of the layer with distance from the solid surface leads to results that agree qualitatively with experiments [19].

The quantitative estimate and experimental check carried out in [19] showed that the electric double-layer and the electroviscous effect (retardation of viscous flow by a reverse electroosmotic flow, caused by the potential of the flow) are not reasons for the noticeable increase in the viscosity of the fluid in the boundary layer. It is also shown in [19, 20] that the difference between the viscosities of water and an aqueous sucrose solution in the layer near the wall and their bulk values decreases with increasing temperature and vanishes completely at temperatures above 70°C.

It follows from the data presented that adsorbed liquid films can have some effect on the decrease in the liquid flow rate, but only in porous materials with average pore size significantly less than 1  $\mu$ m.

Thus, the formation of an adsorbed boundary layer cannot be viewed as a reason for obliteration, since it does not explain a number of the following observed properties of the process of liquid flow in porous materials with various structure and average pore size in the range 1-100  $\mu$ m.

1. Why is there a decrease in the mass flux of the liquid? The presence of boundary layers must only decrease the permeability relative to liquid in comparison to the permeability relative to the gas and make this characteristic reproducible with repeated tests, but not cause a continuous decrease in the liquid flow rate with time with constant filtration conditions.

TABLE 1. Physical Properties of Liquids at a Temperature of  $20^{\circ}C$ 

Liquid	Dipole moment µ, D	Thickness of boundary layers on the surface of quartz δ, μm [17]	Coeff. of surface tension $\sigma \cdot 10^3$ , N/m	Bunsen's absorption coeff. for oxygen
Water	1,84	0,09	72,75	0,031
Acetone	2,85	0,08	23,70	0,216
Benzene	0	0	28,87	0,163
Carbon tetrachloride	0	0	25,68	0,230
Ethyl alcohol	1,68	0,06	22,03	0,143

2. Why does the rate at which the flow rate decreases also increase with increasing liquid flow velocity? In this case, there must be a decrease in the thickness of the adsorbed layers due to removal of the outer, weakly bound rows of liquid molecules, and as a result the time derivative of the mass flux must decrease.

3. Why is a decrease of the flow rate observed for flow of nonpolar liquids (kerosene, benzene, heptane) that do not form a measureable boundary layer?

4. Why, in carefully prepared experiments on the flow of different liquids in porous materials with different structure [4, 6, 8, 21, 22], are a decrease in the permeability relative to the liquid and its unstable change in time generally not deserved?

All these phenomena are explained if the clogging of pore channels by contaminant particles and bubbles of liberated gas is assumed to be the true reason for obliteration.

The most obvious is the first case, if we take into account the extremely wide application of porous materials as filters. All liquids contain a large number of mechanical impurity particles, comparable in size to the diameter of the pore channels. As the liquid flows through the porous material, these particles are retained in the narrowed pore channels and gradually decrease the permeability of the material. The latter is especially noticeable with motion of liquids with a controlled fractional content of impurity particles [23] through openings with fixed sizes (4, 10, 14, and 21  $\mu$ m). For channel diameters less than the maximum particle size, the magnitude of the decrease in the flow rate increases in proportion to the decrease in the channel size. In examining channels, disassembled after the experiment, in direct proximity to the channel inlet, a dark dirty band is visible [23]. When the size of the solid particles is less than the characteristic pore size, coagulation processes, which intensify in a hydrodynamic flow, cause gradual obliteration of the channel [24]. In this connection, it should be noted that in most works in which decreased permeability of the specimens is noted there is no information on how clean the liquid was at the outset.

A valid explanation for the filtration effect due to the gradual clogging of pores by bubbles of dissolved gas liberated from the liquid was first given in [4].

The liquid contains dissolved gases, whose quantity under equilibrium conditions depends on their properties, as well as on the pressure and temperature. The dependence of the equilibrium concentration of the dissolved gas in the liquid on pressure for weakly soluble gases is expressed by Henry's law z = A|t|P, where P is the partial pressure of the gas above the solution; A|t| is a coefficient of proportionality that depends on the properties of the liquid and gas as well as on temperature. For most liquids, A|t| decreases with increasing temperature. Very often, the solubility of the gas in the liquid is characterized with the help of Bunsen's absorption coefficient  $\alpha$ , which equals the volume of the gas, referred to 0°C and 760 mm Hg, absorbed per unit volume of liquid with the partial pressure of the gas equal to 760 mm Hg. Table 1 shows, as an example, data on the absorption coefficient for oxygen.

As the liquid moves through the porous material, the pressure in it drops and the dissolved gas can turn out to be in an oversaturated state, in spite of the fact that the liquid was saturated at the point of contact with the gas (e.g., in the compressed gas feeding system). Formation of gas bubbles in the feed line is not likely, since the excess gas pressure in small bubbles must be very high in order to counteract surface tension. The formation and growth of gas bubbles occurs inside the porous structure, where due to the considerable roughness of the surface the conditions for formation of nuclei are more favor-

Porous material	Porosity	diam.,	Permea- bility, Darcy	Form of liquid	Refer- ence
Stainless steel Sintered glass Bronze, fraction A Bronze, fraction B Steel Steel Sintered glass Aleurolite Sandstone	$\begin{array}{c} 0,367\\ 0,346\\ 0,246\\ 0,317\\ 0,34\\ 0,29\\ 0,284\\ 0,250\\ 0,300\\ \end{array}$	24,533,09,933,0529817,11,876,81	$\begin{array}{c} 2,00\\ 2,80\\ 0,24\\ 3,30\\ 5,0\\ 5,9\\ 2,54\\ 0,023\\ 0,416\end{array}$	Water, kerosene Water, kerosene Water, kerosene Diesel fuel Diesel fuel Water Kerosene, benzene Water	[6] [6] [6] [22] [22] [21] [21] [21]

TABLE 2. Characteristics of Some Specimens Studied

able. In addition, residues of air previously filling the porous material can serve as centers for formation of bubbles.

Taking into account a number of assumptions, an approximate equation is derived in [4] for calculating the decrease in the liquid flow rate due to liberation of the dissolved gas with a constant pressure differential on the specimen until the gas bubbles begin to move in the porous structure with the liquid flow:

$$G = G_0 \exp\left(-a \frac{G_0^2 \tau}{P}\right).$$

Here G is the variable magnitude of the flow rate;  $G_o$ , initial flow rate;  $\alpha$ , some constant that depends on the properties of the liquid and of the porous material; P, pressure;  $\tau$ , time.

This equation permits estimating qualitatively the influence of such parameters as Go, P, and  $\tau$ . In particular, it follows from here that as the liquid flow rate increases. the rate at which the clear opening decreases increases. The experimental study completed permitted the author to explain confidently the increase in the resistance of porous materials as the result of clogging of pores by bubbles of dissolved gas liberated from the liquid. The most interesting data [4] are presented in Fig. 2, where the effect of the absolute pressure P on the change in the flow rate of distilled water with time through a glass filter with a constant pressure differential on the filter of  $\Delta P = 0.037$  bar and subsequent steplike increase in the vacuum at the inlet to the filter is shown. In segment I the vacuum constitutes 0 mm Hg, 93 in segment II, 380 in segment III, and 0 mm Hg once again in segment IV. In region I there is no liberation of dissolved air from water saturated at atmospheric pressure, but as the pressure at the filter inlet decreases (region II), the water becomes oversaturated and there is considerable liberation of air bubbles and gradual clogging of the filter. With passage into region III with an even lower absolute pressure, the resistance of the filter increases in a steplike fashion. With a return to atmospheric pressure after the filter in region IV, the flow rate at first is restored in a steplike manner and then gradually.

Liberation of the dissolved gas from the liquid as the liquid moves through a porous material is the reason for the amazing results obtained in the first studies of the filtration effect carried out in [1, 3] and left unexplained: freshly filtered water with repeated use not only did not give the usually observed decrease of the filtration rate, but, what is more, regenerated the filters clogged during earlier experiments. As a result of a special study, the author of [4] established the phenomenon noted above for filtration of oils as well.

Unfortunately, ignorance of the results in [4] for a long time did not permit providing the correct interpretation of the phenomenon and setting up a correct experiment for studying the effect of the degree of presaturation of the liquid by a gas on the magnitude of the increase in the resistance due to clogging of pores by gas bubbles.

Precise experiments taking into account the results of [4] were set up by the authors of [6, 7].

The investigations in [6] were carried out with porous specimens with a thickness of 12.5 mm, whose characteristics are presented in Table 2. The permeability of the specimens in the course of the studies (relative permeability) is expressed as fractions of the perme-

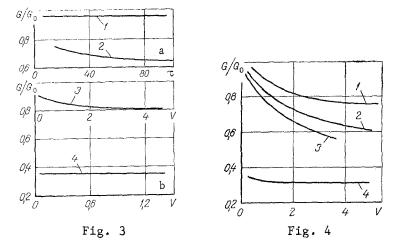


Fig. 3. Change in the flow rate of water saturated with air flowing through a porous glass specimen [6] (a) and kerosene saturated with air flowing through a porous bronze, fraction A, specimen [6] (b): 1) saturation of porous material by water at first is complete and finally 86.5%; 2) at first partial and finally 86.5%; 3) saturation of porous material by kerosene at first is complete and finally 93.6%; 4) first partial and finally 80.7%. V, liters;  $\tau$ , sec.

Fig. 4. Change in permeability with flow of kerosene oversaturated with air and containing air bubbles through different porous materials [6]: 1) glass,  $\tau = 8.5$  min; 2) bronze fraction B,  $\tau = 12.5$  min; 3) bronze fraction A,  $\tau = 64$  min; 4) stainless steel,  $\tau = 38$  min. V, liters.

ability with motion of deaerated liquid. The experiments were carried out with water and kerosene with a constant pressure differential on the specimen.

The state of the liquid in the porous body at the inlet and outlet was determined carefully in the experiments. It was established that if the liquid reaches a state of saturation with the gas only at the outlet from the specimen, then the permeability does not depend on the amount of gas contained in the porous body prior to the experiment. Even for a specimen that was originally dry, the absolute (100%) permeability is attained rapidly, since air is pushed out by the liquid and its residues dissolve in the flow of saturated liquid. The absolute permeability is attained almost immediately with the use of kerosene and after 30-40 sec in experiments with water.

If the liquid at the outlet from the specimen is significantly oversaturated, then a decrease of permeability of the specimens is always observed due to liberation and accumulation of gas bubbles inside the porous material. As the liquid flows through the specimen, gas is liberated in proportion to its degree of oversaturation at local pressures and temperature. The change in permeability is quantitatively not reproducible, since the gas content of the pores depends mainly on the degree of wetting of the surface and on the presence of bubble formation, and these characteristics cannot be controlled. If the fluid brought up to the specimen does not contain gas bubbles, then a decreased but stationary liquid flow rate is attained. For porous structures, which are initially completely saturated with liquid, such a stationary state is established very rapidly, but for structures that initially contain some quantity of gas, the time for establishing the stationary state increases considerably.

Figure 3 shows the change in the liquid flow rate (relative permeability) under such conditions. The initial and final values of the saturation of the porous structure by the liquid are indicated in each case. The decrease in permeability is significantly greater for porous structures initially not completely saturated by the liquid, due to the presence of a large number of centers for liberation of gas. In all cases, the stationary state is reached and the pores are not completely clogged for liquid flow, which is explained by the

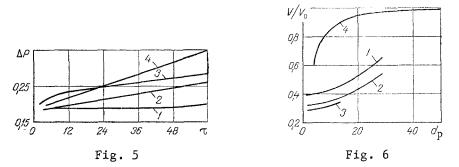


Fig. 5. Effect of the liquid properties on the intensity of the increase in the pressure differential on a specimen with constant flow rate [7].  $\Delta P$ , bar;  $\tau$ , min.

Fig. 6. Dependence of the decrease in the liquid flow rate as a function of the average pore size in the material and properties of the liquid.  $d_p$ ,  $\mu m$ .

onset of equilibrium in the number of centers for gas liberation and removal of bubbles. At the same time, the reduced value of the permeability established is not a fixed quantity for each specimen and depends on the conditions of the process, i.e. it is not reproducible.

If the liquid brought up to the specimen contains gas bubbles, then the decrease in permeability is significant and the stationary state is approached very slowly, which is illustrated in Fig. 4.

The results, confirming the conclusion as to the influence of the liberated dissolved gas, were obtained in [7] for flow through commercial filter paper, contaminated with diesel fuel, at a constant rate.

In the first case, the experiment was performed with partial preliminary removal of dissolved air. For this, diesel fuel was heated and held for some time at a temperature of 40°C. Prior to entry into the specimen, the temperature of the fuel was lowered with the help of a heat exchanger to 20°C. In the second case, at this temperature a fuel was studied that, due to preliminary cooling and holding at a temperature of 10°C, turned out to be oversaturated by air. The results are presented in Fig. 5 (curves 1 and 2, respectively). Curve 3 shows the results of the flow of fuel through specimen, partially saturated by air. Under these conditions, the resistance increases at first considerably more rapidly. It should be noted that the conditions for this experiment are similar to the conditions of the experiments in [6], whose results are presented in Fig. 3. It is observed that the results agree qualitatively. Next, the influence of the volatility of the liquid on the intensity of the filtration effect was estimated. For this, 1.5% by weight of ethyl ether was introduced into the fuel. This addition noticeably changed only the saturated vapor pressure; all other properties of the mixture were practically identical with the properties of the pure fuel. The results (curve 4) confirm the effect of volatility of the liquid on the intensity of vapor-gas bubble formation and the increase in the resistance of the porous material that the bubbles cause.

The change in the permeability with flow of an oversaturated liquid through a porous material, to a large extent, depends on the average pore size in the structure. As the average and especially the minimum pore diameter  $d_p$  decrease, the magnitude of the capillary pressure  $\Delta P_c = 4\sigma \cos \Theta/d_p$ , resisting the forcing of gas bubbles through the narrow channels, increases. As a result, as  $d_p$  decreases, a larger quantity of gas is retained in the specimen. In addition, as the pore sizes decrease, the conditions for nucleation of gas bubbles become more favorable. In order to check this behavior, experiments must be conducted on the porosity of specimens made of the same material. Figure 6 (curves 1-3) shows data [11] on the flow of water, ethanol, and acetone, respectively, through porous glass filters. Here V is the volume of the filtrate over a definite period of time; V<sub>0</sub> is the volume of the degassed filtrate (theoretical volume). The decrease in permeability begins to be noticeable at a pore diameter of  $\simeq 50 \ \mu m$  and rapidly increases as it decreases. Curves 1-3 show the effect of the solubility of air in the liquid on the decrease in permeability. As the solubility increases (sequentially: water, ethanol, and acetone (see Table 1)), the intensity of this process must increase. This is mainly confirmed by the results obtained.

for water, the decrease in permeability is too large compared to the decrease in the solubility of air. This is explained in [11] by the considerably larger magnitude of the coefficient of surface tension for water (in comparison to the other fluids) (see Table 1). Figure 6 (curve 4) also shows data from [10] for 50KhG steel for flow of water. All data are observed to agree qualitatively. On the other hand, it is difficult to compare the numerical magnitudes, since they depend on the amount of liquid that has passed, the properties of the porous material, the saturation of the liquid with gas, etc. Here, we note also that for a specimen made of powdered nickel with average pore size exceeding 70  $\mu$ m, the increase in resistance was 18% with very prolonged (over the course of 53 h) flow of aerated water with a specific mass flow rate of 9.75 kg/m<sup>2</sup>·sec [8].

In estimating the effect of the average pore size of the specimens on the decrease in the liquid flow rate, the dependence of the results not so much on the magnitude of the capillary pressure  $\Delta P_c$  as on the ratio between the capillary pressure and the pressure differential on the specimen  $\Delta P$  becomes obvious: the decrease in flow rate becomes noticeable and considerable if the ratio  $\Delta P_c/\Delta P$  is greater than or comparable to unity. For  $\Delta P_c/\Delta P > 1$ , the gas bubbles formed cannot be pressed out of the porous structure by the liquid flow. In addition, it is in this particular case that the increase in the pressure differential leads to a more intense increase in the resistance due to the increase in the amount of gas liberated with an increase in the liquid flow rate. For  $\Delta P_c/\Delta P \ll 1$ , bubbles are not retained in the porous structure and the resistance increases due to formation of a two-phase gas—liquid flow. An estimate of this ratio for the results of a few works that contain information on the magnitudes of d<sub>p</sub> and  $\Delta P$  confirms its validity. Thus, for water at 20°C [14] (see Fig. 1),  $\Delta P_c/\Delta P \approx 2.3$ ; for the experimental results of [9]  $\Delta P_c/\Delta P \approx 0.5$ ; for the results of the investigations described in [11],  $\Delta P_c/\Delta P \approx 1$ -10.

Since the solubility of the gas depends on the temperature of the liquid, an increase in the liquid temperature has a considerable effect on the intensity of the process of increasing the resistance of porous materials. As the saturation temperature is approached, the vapor pressure of the liquid becomes so large that the effect of the solubility of the gas on the growth of vapor-gas bubbles may already be neglected [11] (Fig. 7). As the saturation temperature of acetone  $t_s = 56^{\circ}$ C is approached, the resistance of the specimen increases sharply. This stems from the fact that an intense growth of vapor-gas bubbles begins and there is a transition into the two-phase flow regime. However, the main reason for this process is still the initial creation of gas bubbles; vapor bubbles cannot appear for t  $\ll t_s$ .

Visual confirmation of the presence of gas bubbles in transparent gas filters or in filters placed between glass plates is presented in photographs in [4, 6, 7]. It is interesting to note also that the liberation of air in the form of a chain of bubbles in the bulk of the liquid above the specimen surface was observed in [14] for flow of water through a titanium filter with an average pore size of 7.3  $\mu$ m under the action of a pressure differential of only 0.52 bar.

In almost all the works, with the exception of [6-8, 21-22], the saturation of the liquid with dissolved air prior to passage into the porous specimen was not controlled. At the same time, the system used in [10, 12, 13] for delivering liquid with the help of pressurization by compressed air at high pressure justifies the assumption of a quite high concentration of dissolved air. In this respect, the data in [13], where porous materials were periodically purged (the influence of purging on the decrease in permeability was indicated previously: curve 3 in Fig. 5), are especially characteristic.

The mechanism for increasing resistance with liberation of gas bubbles inside a porous structure is as follows. The gas bubbles formed gradually grow and occupy the center of a pore, which leads to a greater decrease in the liquid flow rate compared to the change in the volume occupied by the fluid. Quantitative relations between the change in the liquid volume in the pores (saturation s) and change in permeability for flow of water determine the dependence of the relative phase permeability for liquid  $f_e$  and gas  $f_g$  phases as a function of the saturation s of a porous structure with the liquid phase. These dependences are found experimentally and, in particular, for flow of a gas-water mixture in soils, are described by the following formulas [25]:

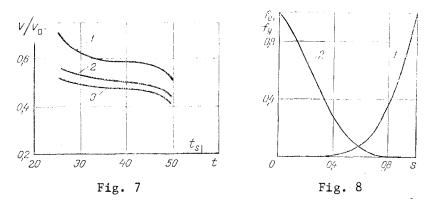


Fig. 7. Temperature dependence of the decrease in the flow rate of acetone flowing through a glass filter [11]: 1)  $\Delta P = 0.026$  bar; 2) 0.053; 3) 0.106.

Fig. 8. Relative phase permeability of liquid (1) and gas (2) as a function of saturation s of a porous medium by a liquid phase during gas-water flow in soils [25].

$$f_{e} = \left(\frac{s - 0.2}{0.8}\right)^{3.5}, \ 0.2 \leqslant s < 1; \ f_{e} = 0, \ 0 < s < 0.2;$$
$$f_{g} = \left(\frac{0.9 - s}{0.9}\right)^{3.5} \cdot (1 + 3s), \ 0 < s < 0.9; \ f_{g} = 0, \ 0.9 < s < 1.5$$

They are illustrated graphically in Fig. 8.

Therefore, until the gas bubbles occupy  $\approx 0.1$  of the pore volume, they do not move in the porous medium (f<sub>g</sub> = 0), but in this case the permeability for the liquid decreases from f<sub>e</sub> = 1 at s = 1 to f<sub>e</sub> = 0.626 at s = 0.90, i.e., by 37.4%. The dependences presented above for phase permeability were obtained for the flow of a gas-water mixture prepared prior to introduction into the specimen. It is shown in [26] that for values of the saturation close to unity the relative phase permeability for liquid f<sub>e</sub> does not depend on the method for creating the two-phase mixture inside the porous structure, while the gas permeability f<sub>g</sub> can change by factors of 10, and in addition, the smallest magnitude of the gas permeability occurs precisely with liberation of gas in the form of bubbles from the liquid. This is explained by the fact that for motion of a prepared gas—liquid mixture the components move separately, and in addition, the gas moves along the largest pores, while the liberated gas bubbles are pushed through all pore channels, including the narrow ones. Thus, it may be expected that the liberated gas bubbles leave the porous structure with values of the saturation less than s = 0.9 (in contrast to the dependences presented in Fig. 8), for which the relative permeability to liquid is less than f<sub>e</sub> = 0.626.

When air bubbles occupy a significant part of the pores (s  $\leq 0.9$ ), the liquid flow begins to push bubbles through the narrowed pore channels. The resistance of the specimen no longer increases and it is stabilized, while at the same time the pressure differential on the specimen is much greater than the capillary pressure:  $\Delta P > \Delta P_c$ . For  $\Delta P_c > \Delta P$ , gas bubbles gradually accumulate inside the porous structure and cause further decrease in the permeability for the liquid.

The considerable dependence of the intensity of the decrease of the flow rate on the form of the liquid, noted in [1, 9, 11, 13, 14], is explained by the different (and in addition uncontrollable) saturation of these liquids by dissolved air, different surface tension, and wettability. The influence of the first two causes was demonstrated earlier. The wettability, determined not only by the properties of the liquid but by the porous material as well, has a significant effect on the intensity of formation of gas bubble nuclei inside the porous structure.

A very important characteristic of the process of creation of gas bubbles in the porous structure is the adhesion tension  $\tau = \sigma \cos \theta$ , which determines the work of formation of the bubble surface on a boundary with a solid surface. The adhesion tension is a complex property, including both the surface tension of the liquid as well as its wettability, the contact angle  $\theta$ .

A qualitative understanding of the effect of adhesion tension on the change in the liquid flow rate can be obtained by analyzing curves 1 and 6 in Fig. 1. Curve 1 characterizes the change in the flow rate of heptane through a titanium specimen with a thickness of 0.37 mm with an average pore size of 7.3 um, while curve 6 characterizes the change in the flow rate of heptane through a porous fluoroplastic with thickness of 1.25 mm with an average pore size of 3.62  $\mu$ m. Heptane wets the metal ideally ( $\Theta = 0^{\circ}$ ) and the fluoroplastic much less efficiently ( $0 = 24^{\circ}$ ). From here it follows that the decrease in the adhesion tension with flow of heptane through fluoroplastic improves the conditions for the creation of bubbles, which leads to a gradual decrease in the flow rate. In order to check the possibility of eliminating the liberation of air dissolved in water due to the improvement of the wettability, a 0.5% solution of a surface active substance in water was used in [14] (curve 5). In comparison to pure water (curve 4), the flow rate of the solution with the surface active substance at first decreases much less sharply, and then remains practically constant. In contrast to pure water, from the very beginning of the flow of the solution of the surface-active substance, liberation of a large quantity of air bubbles with greatly varying sizes (from millimeter to a bubble mist) was observed on the outer surface of the specimen, which indicates the establishment of the two-phase regime for motion of the gasliquid flow through a porous material. Thus, in contrast to what was expected, the addition of the surface-active substance improved the conditions for formation of bubbles due to a more significant decrease in surface tension. In addition, a decrease in surface tension with the addition of the surface active substance also decreases the resistance for motion of a two-phase flow in a porous material due to the decrease in capillary pressure with forcing of bubbles even through the smallest pore channels, which is indicated by the appearance of a bubble mist.

It is not possible to separate the effect of adhesive tension (wettability) from the effect of the quantity of dissolved gas and the magnitude of the surface tension on the increase in resistance in the other cases [1, 9, 11, 13, 14] of flow of liquids with different physical properties, since the magnitudes of the surface tension of liquids are close to one another, porous materials have different structures, there is no information on the concentration of gas dissolved in the liquid, etc.

It follows from what was presented above that the liberation of dissolved gas is the basic reason that the increase in resistance with flow of a liquid through porous materials is not reproducible. The internal resistance of a porous structure, as shown in [8, 21, 22], can be stabilized by degassing the liquid in a vacuum. The characteristics of these specimens are presented in Table 2. The results obtained indicate the fact that the permeabilities of the specimens to liquid and gas are the same, are constant in time, and do not depend on the form of the liquid and on the pore size. The results of [21] should be especially noted: It is shown therein that even in porous materials with average pore sizes of about 1 µm no decrease was observed in the permeability with very prolonged (up to 200 h) filtration.

An experimental setup with which the absolute (100%) permeability of a porous material was obtained for flow of a liquid through initially dry specimens with much less strict conditions for degassing (the liquid at the outlet was saturated with gas) is described in [6].

Thus, the main reasons for the nonreproducible increase in resistance for flow of liquids through porous materials with average pore size greater than 1 µm are: clogging of pores by liberated bubbles of gas dissolved in the liquid; contamination of the porous material by mechanical impurities, contained in the liquid that has not been sufficiently carefully cleaned. The sharply contradictory results of earlier investigations on the motion of liquids in porous materials, presented in [1-3], are explained by the inadequate care in setting up the experiment. In order to exclude the unreproducible increase in resistance with flow of a liquid, it is necessary to eliminate the possibility of reaching a state of equilibrium in the saturation of the liquid by dissolved gas at the outlet from the specimen by using liquids that are degassed beforehand and to carefully clean the fluid of mechanical impurities with the help of filters having an average pore size not less than 1.5-2 times less than the average pore size of the porous specimen.

## LITERATURE CITED

- 1. V. Zigel', Filtration [in Russian], GINTI, Moscow (1939).
- 2. S. V. Belov, Porous Metals in Machine Building [in Russian], Mashinostroenie, Moscow (1976).
- 3. A. S. Berkman and I. G. Mel'nikova, Porous Permeable Ceramic [in Russian], Stroiizdat, Leningrad (1969).
- W. Mehner, "Gassausscheidung als Ursache des Filtereffektes," Dei Chemische Fabrik, 4. 10, No. 1/2, 2-9 (1937).
- 5. P. Duwez and H. E. Martens, "The powder metallurgy of porous metals and alloys having a controlled porosity," Met. Technol., 15, No. 4, 1-27 (1948).
- 6. P. Eisenklam, "Porous masses," Chem. Eng. Practice, 2, 342-463 (1956).
- 7. L. A. Emel'yanov, Filtration of Diesel Fuel [in Russian], Mashgiz, Leningrad (1962).
- 8. H. R. Kunz, L. S. Langston, B. H. Hilton, S. S. Wyde, and G. H. Nashick, "Vapor chamber fin studies," NASA Report CR-812 (1967).
- N. P. Potapova, "Investigation of the action of ultrasound on the flow of a pure liquid 9. through porous barriers," in: Acoustics and Ultrasound [in Russian], No. 2, Tekhnika, Kiev (1966), pp. 70-76.
- S. V. Belov and G. P. Pavlikhin, "Certain properties of the filtration of liquids 10. through porous metals," Izv. Vyssh. Uchebn. Zaved., Mashinostr., No. 6, 70-76 (1972).
- R. Hennig, "Beitrag zur Untersuchung der Filterverstropfung durch Gasausscheidung und 11.
- Flussigkeits-verdampfung," Chem. Tech., 27, No. 8, 446-448 (1975). A. G. Kostornov and M. S. Shevchuk, "Hydraulic characteristics and structure of porous 12. metals made of metallic fibers. III. Investigation of the behavior of the permeability of materials to liquids," Poroshk. Metall., No. 9, 50-56 (1977).
- 13. A. G. Kostornov, "Phenomenon of obliteration in permeable fiberlike materials," Poroshk. Metall., No. 6, 35-38 (1978).
- A. F. Kudryashov, "Emanation of liquid and gas flow in fine-pored materials in applica-14. tion to filtration and ultrafiltration processes," Author's Abstract of Candidate's Dissertation, Technical Sciences, MIKhM, Moscow (1975).
- B. V. Deryagin and M. M. Samygin, "Measurements of the viscosity of thin polymolecular 15. liquid layers," in: Conference on the Viscosity of Liquids and Colloidal Solutions [in Russian], Vol. 1, Izd. Akad. Nauk SSSR, Moscow (1941), pp. 59-66.
- B. V. Deryagin and N. A. Krylov, "Anomalous phenomena in fluid flow through rigid 16. narrow-pored filters," in: ibid., Vol. 2 (1944), pp. 52-53.
- U. B. Bazaron, B. V. Deryagin, and A. V. Bulgadaev, "Investigation of shear elasticity of liquids in the bulk and in boundary layers," in: Studies of Surface Forces [in 17. Russian], Nauka, Moscow (1967), pp. 43-52.
- Z. M. Zorin, V. D. Sobolev, and N. V. Churaev, "Change of capillary pressure, surface 18. tension, and viscosity of liquids in quartz microcapillaries," in: Surface Forces in Thin Films and Dispersed Systems [in Russian], Nauka, Moscow (1972), pp. 214-221.
- B. V. Deryagin, B. V. Zheleznyi, Z. M. Zorin, V. D. Sobolev, and N. V. Churaev, 19. "Properties of liquids in thin quartz capillaries," in: Surface Forces in Thin Films and Stability of Colloids [in Russian], Nauka, Moscow (1974), pp. 90-94.
- Z. M. Tovbina, "Viscosity of aqueous solutions in silica gel capillaries," in: Studies 20. of Surface Forces [in Russian], Nauka, Moscow (1967), pp. 24-30.
- G. F. Trebin, Filtration of Liquids and Gases in Porous Media [in Russian], Gostop-21. tekhizdat, Moscow (1959).
- Ya. A. Kaminskii, "Motion of gases and liquids in porous metalloceramic material," 22. Poroshk. Metall., No. 8, 53-61 (1965).
- 23. G. A. Nikitin and S. V. Chirkov, Effect of Impurities in Liquids on the Operational Reliability of Hydrosystems in Aircraft [in Russian], Transport, Moscow (1969).
- N. N. Krasikov, "Obliteration of capillary openings during flow of mineral oils," Inzh.-Fiz. Zh., <u>20</u>, No. 2, 210-214 (1971). 24.
- 25. I. A. Charnyi, Undergound Hydro- and Gasdynamics [in Russian], Gostoptekhizdat, Moscow (1963).
- D. A. Éfros, Investigation of Filtration of Nonuniform Systems [in Russian], 26. Gostoptekhizdat, Leningrad (1963).