Engineering of experiment

Alekhin Y.V., Makarova M.A., Kozachenko (Markova) E.A., Shipilova E.S., Nikolaeva I.U., Makarov M.I. Comparison of molecular-mass distribution of particles of colloidal dimensions by data of cascade and continuous filtration of natural waters

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Abstract. The previously developed principles of separation of colloids into size fractions (cascade filtration) have a limitation - the mode of separation of particles of a known size is replaced by gel filtration, when the possibility to control the diameter is lost. To solve the problem in a new approach, we used track membranes with a known diameter of the initial cylindrical pores and the distribution density, for which it is possible to calculate the current values of the hydraulic diameters from the data on the dynamics of the flow rate change as the living section of the pores decreases and the knowledge of the initial flow through distilled water. A consequence of such a continuous separation of colloids, but with a known distribution of their sizes, which are in equilibrium with dissolved forms, is the possibility to analyze the fraction of trace elements that is excreted precisely with particles of known dimensionality, that is, with the fraction of all trace elements that are adsorbed on them.

Keywords: *cascade filtration, continuous filtration, hydraulic diameter, molecular weight distribution of particles, separation of particles of colloidal dimension, microcomponents.*

The principles of separating water samples with a high content of colloids into size fractions (cascade filtration using up to 7-11 filter denominations with a successively decreasing pore diameter) have been developed earlier as well as studies of their migration with trace elements, and the complexation of microelements with DOM of water bodies (Ilina et. Al., 2016; Alekhine, Ilyina, 2015). There are limitations for this method - the separation mode of the known size fraction is replaced by the filtration mode through the colloid gel, and the possibility to control the pores diameter is already lost far from the starting rating of the filter. It is possible to solve the problem without using test protein molecules of a known size if we use track membranes with a known geometric diameter of the approach is the continuous filtration of the initial solution, which is adsorption equilibrium with the truly dissolved forms of the elements, and only partially located on the suspension of the initial cylindrical pores and the density of their distribution in nuclear filters. In this case, it is easy to obtain the values of the effective hydraulic diameter from the data on the dynamics of the flow decrease with the decrease in the live section of the flow and the exact knowledge of the initial volume flow through distilled water (Alekhin et al., 2017). The novelty of our dynamic colloidal particles. The consequence of the process is the permanent withdrawal of various particles of diminishing colloidal dimension on the filter, but always with that fraction of trace elements that is adsorbed on them. The excretion curves (changes in concentration versus time and the total volume of the filtrate) therefore have the form of curves, where for each element the asymptotic limit is its steady-state concentration in a truly dissolved form. For continuous and cascade filtration, large volume samples (up to 35 liters) were used from the lake Ignatkovo and the lake Ereshevik (Vladimir region), as well as the Skazkadon river (North Ossetia), selected in 2015 and 2016. For comparison with the data on cascade filtration, a sample of the lake Ignatkovo 2008 was used (Ilina et al., 2016). Continuous filtration was carried out at a vacuum of 0.16 atm. with the help of Track Frem Membranes 0.2 μm and 0.4 μm, with sampling every 3-4 liters. Later (2017), the data were detailed, sampling every 50 ml. For cascade filtration, both acetyl-cellulose membranes and nuclear (lavsan track) were used. All samples were analyzed for a wide range of trace elements on a high resolution mass spectrometer with inductively coupled plasma Element-2 from ThermoFinnigan; on the content of NPOC on the automatic analyzer TOC-Vcpn of Shimadzu; the optical density was measured on a PortLab 511 spectrophotometer in the range 200-700 nm in 1 nm steps. The study showed that the track membranes are not membranes with a homogeneous pore distribution, since the percentage of cluster pore mergers is large. In the "STIMAN" program using SEM images, planimetric and stereometric analysis data were subjected to statistical processing aimed at obtaining a complex of quantitative information on the microstructure. For a membrane with a declared pore diameter of 0.2 μm, the statistically average hydraulic diameter is 0.38 μm, and for a membrane with 0.4 μm pores, 0.53 μm. Therefore, for each sample with continuous filtration, a preliminary speed control over distilled water is required (output to constant values). At the same time, an additional flushing of the membrane is ensured and the pores of the pinched air are completely displaced. From the volume flow through distilled water, it is easy to switch from filtered volumes to the hydraulic diameter (Alekhin, 1973, Alekhin et al., 2017) using the formula $D^2 / d^2 = V_t / V (H_2O)$ where D is the hydraulic diameter, μm; D is the initial nominal pore size, μm; V_t - volumetric flow at the current time, V (H_2O) is the volume flow through distilled water. When constructing the graphs of the dependence of the hydraulic diameter on the volume (Fig. 1), the data obtained with continuous filtration (time, volume, speed, flow rate for distilled water for each filter rating) were used.

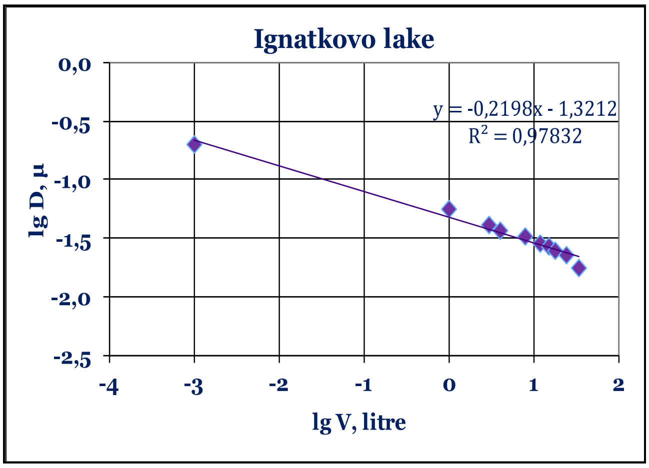

Fig. 1. The dependence of the hydraulic diameter on the filtered volume

By the nature of behavior, elements can be divided into two groups. The first group of elements behaves conservatively (Figure 2). Elements are not adsorbed, do not change their concentrations from the first moment of filtration, are in ionic form.

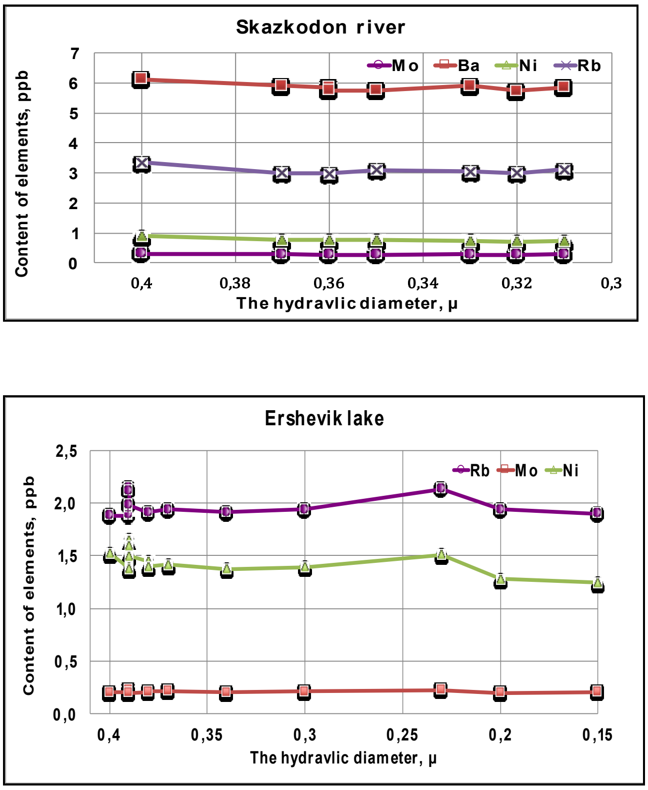

Fig. 2. The change in concentration of microelements in ionic form during continuous filtration

Significantly sorbed elements continuously change concentrations in the process, but after the start of filtration, when the content of elements in the filtrate falls sharply, they practically do not change (Fig. 3). The difference between the first and last point in the graphs shows the fraction of the true-dissolved form relative to the gross content. Elements are output with fractions of colloidal dimension, remain - truly-dissolved forms and simple complexes. The percentage of excretion in the form of colloids, this value for all elements is different and characteristic. It is possible to construct series of adsorption for the object of interest. In the world practice it is believed that almost all trace elements are adsorbed by 90-95% on particles of colloidal dimension and only the last 5% refer to the truly dissolved part. Our results on continuous filtration show that the percentage of excretion of trace elements with non-conservative behavior changes with decreasing diameters when pores are blocked with the gel phase and for certain trace elements reaches the limiting values with hydraulic diameters significantly smaller than 0.2 microns or 0.4 microns.

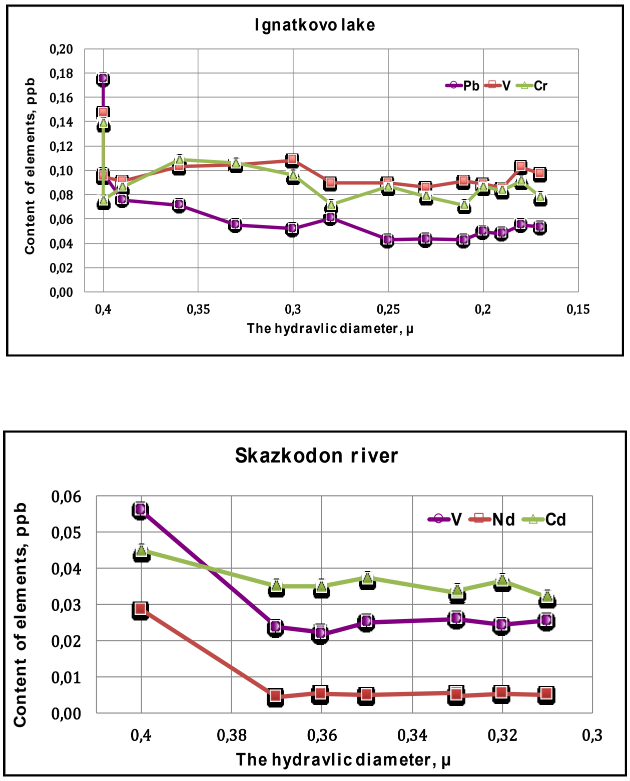

Fig. 3. Regularity of change in concentration of microelements in form of colloids during continuous filtration

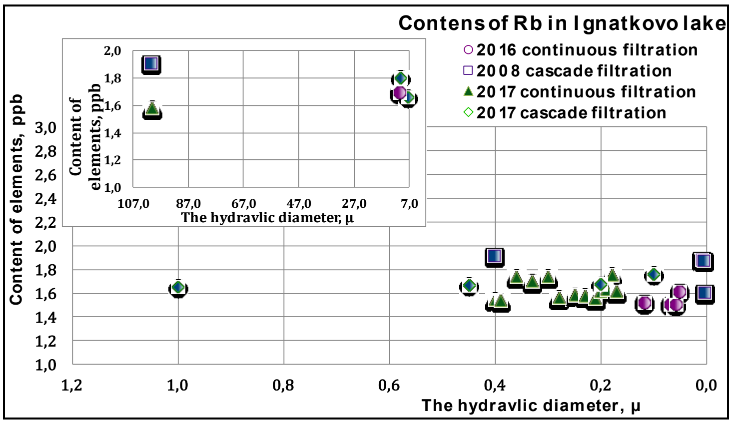

Fig. 4. The comparison of the results of the cascade and continuous filtration

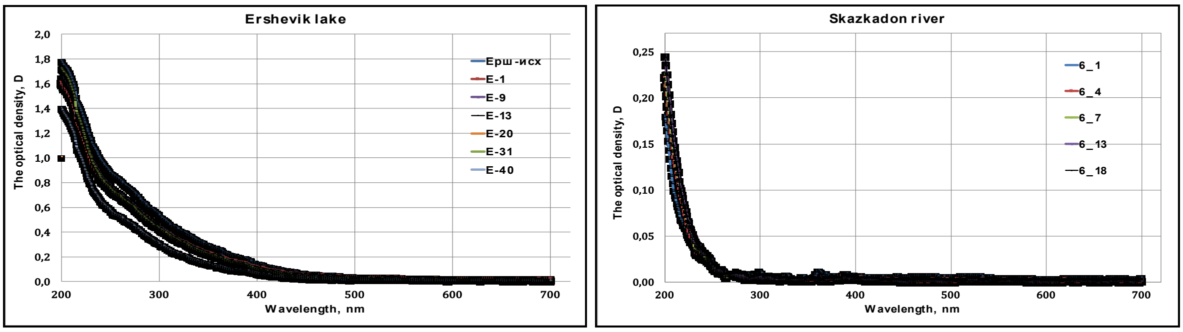

Fig. 5. Distribution of absorption spectrum of dissolved organic matter during continuous filtration for the sequential filtrate

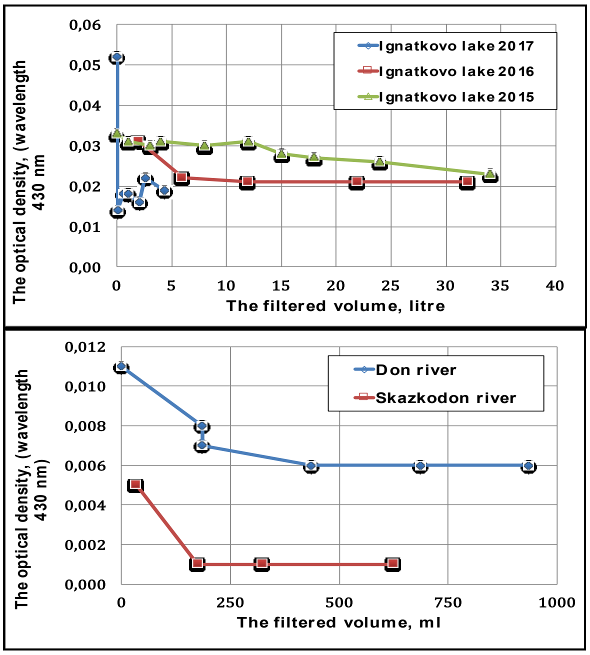

Fig. 6. Distribution of absorption spectra of dissolved organic matter at 430 nm with respect to expenditure.

The removal of fractions of colloidal dimension on the membranes of FitreM 0.2 µm, 0.4 µm covers the interval of volumes 1-3, not more than 5 liters, and then we pass to the gel filtration regime, which is reflected in the ratios of the concentrations of microelements. In the process of micro- and gel filtration, the concentration ratio for each element shows the ratio of the fractions of colloid fractions of different dispersity at each time point (in each sample of the sequential filtrate) and dissolved. This allows us to detail information on the distribution of trace elements in size fractions during continuous filtration, and to study their molecular mass distribution. A comparison was made of the cascade and continuous filtration data (Fig. 4). When moving from volumetric flow to hydraulic diameter, it is clearly seen that a change in the filtration regime occurs with the transition to gel filtration with small pore diameters. Data for continuous and cascade filtration are consistent across many elements (Cd, Sb, Re, U, Co, Cr, Ni, etc.).

There is a decrease in the optical density from the initial sample to the last filtrate (Figure 5), which makes it possible to use spectrophotometry as one of the ways to control the reliability of data on organic matter namely of the humic nature. With the starting high contents of dissolved and suspended OM in the filtrates, instability is observed in the NPOC-excretion curves associated with coagulation.

Most of the organic matter in a number of samples is represented by humic and fulvic acids, which are the most important complexing agents, and organometallic complexes are present both in the composition of water-soluble compounds and in the form of adsorbed forms on aggregates and organic matter suspensions; they persist for a long time in a wide range of conditions of water flow. Measured by the method of catalytic combustion, OM gives the content of total organic carbon, but the main contribution to the change in the composition of filtrates, with continuous filtration, is provided by the OM content of humic nature, and when solving problems associated with retention of organic matter on filters, we propose to use the spectrophotometry method. In order to estimate the delay on the filter dominating in natural waters, OM of humic nature, plots of the optical density at 430 wavelengths from the filtered volume were plotted (Fig. 6).

Thus, as a result of the study, the following results were obtained. The Traper membranes are not membranes with a uniform pore distribution, since the percentage of cluster pore mergers is large. Therefore, for each sample with continuous filtration, preliminary speed control over distilled water is necessary. It is necessary to detail the data on the initial dynamics of changes in costs and concentrations, since the main processes of clogging (decreasing) pore space occur precisely at this stage.

In the waters of North Ossetia (the Skazsky Glacier area) with a low organic matter content, colloids of the order of 0.4 µm are characteristic of V, Nd, Cd, the other elements are characterized by ion migration forms. For the river Don colloidal forms are defined for Cd, Te, Nd, U, for other elements - ionic. In waters with a high OM content (Vladimirskaya Meshchera, Lake Ignatkovo and Lake Ershevik), colloids are incorporated into Pb, V, Cr, and for the lake. Yershevik also has Zr, Y, Ba, Ce, Pr, Nd, Co, U, the remaining elements dominate ionic forms.

When measurements of spectrophotometric characteristics (wavelengths of 200-700 nm with a step of 1 nm), a decrease in the optical density from the initial sample to the last filtrate is observed, which makes it possible to use spectrophotometry as one of the methods for monitoring the reliability of data on OM of the humic nature and its molecular mass distribution .

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Zharikov A.V[1]., Malkovsky V.I.[1,2] New method of experimetal study of rock sample permeability UDC552.08:556.332.4

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Abstract. New technique of permeability anisotropy determination in rock sample during the single test run is presented.

Keywords: rock, sample, permeability, anisotropy, fluid

Parameters of fluid flows in rock massifs depend in many cases on massif rocks anisotropy. Laboratory determination of anisotropic permeability of deep-seated rocks calls for reconstruction of a loaded state of the rocks in the experiment because their permeability can depend to a substantial extent on mechanical stress [Shmonov et al., 2002]. Different components of anisotropic permeability tensor are usually measured in separate experiments. After each experiment, the rock sample is unloaded and rearranged in measuring cell for measurement of another component of permeability tensor. Then the sample is loaded again, the measurement of the new component of permeability tensor is carried out and so on. This approach seems to be worthwhile only in a case when transport properties of the sample return to their initial state after loading and unloading. However, it follows from experiments that this condition is satisfied not always [Morrow et al., 1986], moreover, a difference between the initial and final state of the permeability after loading and unloading can be very significant [Darot & Reuschle, 2000].

Occurrence depth conditions are determined by both mechanical load and temperature. Hence, it is necessary in many cases to measure sample permeability at considerably elevated temperatures. Conventional procedure of anisotropic permeability measurements at elevated temperatures is similar to the described above technique of permeability measurement at elevated pressure. At first temperature of the measuring cell is increased and one of permeability components is measured, then the sample is rearranged in the cell, the temperature is increased again and the next component of the permeability is measured, and so on. Initial and final permeability in each cycle of such temperature changes can differ [Moore et al., 1986].

As it follows from foregoing, determination of anisotropic permeability of rocks, characteristic feature of which are substantial residual effects of cyclic changes of temperature and mechanical load, calls for development of a method which permits to measure all components of permeability tensor during a single experiment (i.e. without cyclic changes of temperature and mechanical load).As a first step in development of the method we propose an experimental technique for determination of permeability tensor components in a case if two main components of the tensor are equal. This type of anisotropy is typical of e.g. for schistose rocks and gneisses.

With this method, two main components of the permeability tensor are determined in a single experiment without rearranging of the sample in the measuring cell and without changes in experiment conditions (temperature and mechanical loading). The experiment is carried out at constant conditions in two steps. The sample of cylindrical shape is fixed between two pistons so that two equal main components of the permeability tensor correspond to coordinate axes which are parallel to the cylinder bases, and the third component corresponds to the cylinder axis. As applied to the mentioned rock examples with the considered type of the anisotropy, this implies that the axis of the cylindrical sample is normal to schistosity or foliation. The main component of the permeability tensor corresponding to the sample axis is denoted as axial component. Other two components are denoted radial components. During the first operation mode (first step), fluid flows into the sample and flows out through a small orifice in the inlet pistons on the axis of the sample. Outflow through the outlet piston is open. Stream lines in this case are clearly curvilinear. Presence of a radial component of the flow in the inlet part of the sample causes a substantial influence of the radial component of permeability on flow parameters. During the second operation mode, fluid flows into the sample through both orifice on the sample axis and an annular groove at the periphery of the inlet section of the sample (Fig. 1). Presence of the additional annular inflow leads to a decrease in curvature of the stream lines. A comparison of flow characteristics obtained in two operation modes permits to differentiate influence of axial and radial components of permeability.

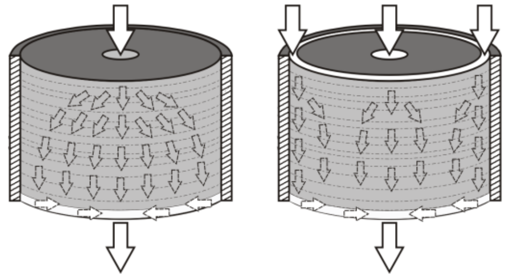
Operation mode 1 Operation mode 2

Fig. 1. Schematic diagram of anisotropic permeability experimental determination.

1. Problem formulation

We consider the following model for determination of flow characteristic in the first and second operation modes. We consider the case when a gas is used as the fluid. Let us introduce cylindrical coordinates r, z, where the z-axis is directed along the axis of the sample from its inlet section to the outlet section, r is distance from the sample axis.
Let us assume that porosity of the sample is little, so that an influence of fluid compressibility in pore voids of the sample can be neglected. As it follows from experience of gas flow samples, the assumption is valid with a satisfactory accuracy in the pressure range 0.1–2 MPa at porosity up to 10%. Taking into account this assumption, we can write equations of Darcy's law and continuity equation for the velocity field components v_z and v_r even at transient flow as

$$v_z = -\frac{k_z}{\mu}\frac{\partial p}{\partial z}, \quad v_r = -\frac{k_r}{\mu}\frac{\partial p}{\partial r}; \qquad \frac{\partial \rho v_z}{\partial z} + \frac{1}{r}\frac{\partial (r\rho v_r)}{\partial r} = 0,$$

where k_z, k_r are axial and radial components of permeability, μ is dynamic viscosity, p is pressure.

Substitution of the expressions of the flow velocity field components into the continuity equation gives

$$\frac{\partial}{\partial z}\left(k_z \rho \frac{\partial p}{\partial z}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(k_r r \rho \frac{\partial p}{\partial r}\right) = 0 \qquad (1)$$

Dependence of permeability components on gas pressure can be approximated by Klinkenberg formula (1941).

$$k_z = k_z^0(1 + b/p), \quad k_r = k_z^0(1 + b/p),$$

where b, k_z^0, k_r^0 are constants.

Since the temperature in the sample is constant, the equation of gas state can be written as $\rho = ap$, where a is constant.

Then Eq.(1) takes the form

$$k_z^0 \frac{\partial}{\partial z}\left[(p+b)\frac{\partial p}{\partial z}\right] + \frac{k_r^0}{r}\frac{\partial}{\partial r}\left[r(p+b)\frac{\partial p}{\partial r}\right] = 0 \qquad (2)$$

Eq. (2) governs the fluid flow in the sample at the both operation modes of the experiment.

Boundary conditions for the first operation mode are written in the form

$$r=0,\quad \partial p/\partial r=0;\qquad r=r_0,\quad \partial p/\partial r=0;$$
$$z=0,\quad \begin{matrix} r<r_{in}, & p=p_{in}; \\ r>r_{in}, & \partial p/\partial z=0; \end{matrix} \qquad (3),$$
$$z=l,\quad p=p_{out}$$

where r_{in} is diameter of the orifice in obturator of the inlet section of the sample, l is sample length.

Boundary conditions for the second operation mode are written as

$$r=0,\quad \partial p/\partial r=0;\qquad r=r_0,\quad \partial p/\partial r=0;$$
$$z=0,\quad \begin{cases} r<r_{in}\ \text{или}\ r_0-\delta_b<r<r_0, & p=p_{in}; \\ r_{in}<r<r_0-\delta_b, & \partial p/\partial z=0; \end{cases} \qquad (4),$$
$$z=l,\quad p=p_{out}$$

where δ_b is width of the annular grooves at the periphery of the inlet obturator, p_{in} and p_{out} are pressures at inlet and outlet of the measurement cell.

Let us introduce a variable $\psi=\dfrac{p^2}{2}+bp$.

It is natural to name the variable dynamic potential of fluid flow. Its values at inlet and outlet of the measurement cell are

$$\psi_{in}=\frac{p_{in}^2}{2}+bp_{in},\quad \psi_{out}=\frac{p_{out}^2}{2}+bp_{out}.$$

Let us introduce dimensionless variables

$$Z=\frac{z}{l},\quad R=\frac{k_z^0 r}{k_r^0 l},\quad \Psi=\frac{\psi-\psi_{out}}{\psi_{in}-\psi_{out}},\quad R_{in}=\frac{k_z^0 r_{in}}{k_r^0 l},\quad R_0=\frac{k_z^0 r_0}{k_r^0 l},\quad \Delta_b=\frac{k_z^0\delta_b}{k_r^0 l}.$$

Eq. (2) in the dimensionless variables takes the form

$$\frac{\partial^2\Psi}{\partial Z^2}+\frac{1}{R}\frac{\partial}{\partial R}\left(R\frac{\partial\Psi}{\partial R}\right)=0. \qquad (5)$$

The boundary conditions (3) are written in the form

$$Z=0,\quad \begin{matrix} R<R_{in}, & \Psi=1; \\ R_{in}<R<R_0, & \partial\Psi/\partial Z=0; \end{matrix}$$
$$Z=1,\quad \Psi=0; \qquad (6)$$
$$R=0,\quad \partial\Psi/\partial R=0;$$
$$R=R_0,\quad \partial\Psi/\partial R=0.$$

The boundary conditions (4) take the form

$$Z=0,\quad \begin{matrix} R<R_{in}\ \text{или}\ R_0-\Delta_b<R<R_0, & \Psi=1; \\ R_{in}<R<R_0-\Delta_b, & \partial\Psi/\partial Z=0; \end{matrix}$$
$$Z=1,\quad \Psi=0; \qquad (7)$$
$$R=0,\quad \partial\Psi/\partial R=0;$$
$$R=R_0,\quad \partial\Psi/\partial R=0.$$

Mass of the fluid which flows through the section $z=l/2$ per unit time is

$$q=2\pi\int_0^{r_0}k_z v_z\rho r\,dr=-2\pi k_z^0 a\int_0^{r_0}r\frac{\partial\psi}{\partial r}dr=-2\pi k_z^0 a\left(\frac{k_z^0}{k_r^0}\right)^2(\psi_{in}-\psi_{out})\int_0^{R_0}\frac{\partial\Psi}{\partial R}R\,dR$$

Let us designate

$$Q=-\int_0^{R_0}\frac{\partial\Psi}{\partial R}R\,dR.$$

Then

$$q_i=2\pi k_z^0 a\left(\frac{k_z^0}{k_r^0}\right)^2(\psi_{in}-\psi_{out})Q_i,\quad i=1,2$$

, where i is operation mode number.

With the pulse decay method developed by Brace (1968) and modified, as it is described in [Malkovsky et al., 2009), sample permeability is determined on the basis of measurements of the pressure in the inlet reservoir which is connected with the inlet section of the sample. According to an operation mode, the reservoir can be connected with the cross section only through the axial orifice (operation mode 1) or simultaneously through the orifice and the annular groove at the periphery of the sample (operation mode 2). The gas flows out from the outlet section of the atmosphere.

The equation of gas balance in the inlet reservoir takes the form

$$Va\frac{dp_{in}}{dt}=-q_i \qquad (8),$$

where V is reservoir volume.

Substitution of the expressions for q_i and dynamic potential ψ into Eq. (8) gives

$$\frac{dp_{in}}{dt}=-\left(\frac{p_{in}^2}{2}+bp_{in}-\frac{p_{out}^2}{2}-bp_{out}\right)2\pi l k_z^0\left(\frac{k_r^0}{k_z^0}\right)^2 Q_i. \qquad (9)$$

Let us denote

$$C_i=2\pi l k_z^0\left(\frac{k_r^0}{k_z^0}\right)^2 Q_i,\quad E_i=C_i\left(\frac{p_{out}^2}{2}+bp_{out}^2\right),$$

where i is experiment number.

Then Eq. (9) takes the form

$$\frac{dp_{in}}{dt}=-C_i\left(\frac{p_{in}^2}{2}+bp_{in}\right)+E_i.$$

This is a special case of Riccati equation with separating variables. General solution of the equation takes the form

$$\frac{p_{in}-p_{out}}{p_{in}+p_{out}+2b}=\tau$$

,where

$$\tau=\left.\left(\frac{p_{in}-p_{out}}{p_{in}+p_{out}+2b}\right)\right|_{t=0}\times\exp\{-C_i(p_{out}+b)t\}.$$

It follows here from

$$p_{in}=\frac{(p_{out}+2b)\tau+p_{out}}{1-\tau}. \qquad (10)$$

On the basis of measurements in the both operation modes, values of k_z^0, k_r^0, b are determined from a condition of minimum of the function

$$\Phi(k_z^0,k_r^0,b)=\sum_{i=1}^{2}\sum_{j=1}^{J_i}\left[\left(p_{in}^{\text{calc}}(t_j)-p_{in}^{\exp}(t_j)\right)^2\right]_i\to\min$$

where p_{in}^{calc} is value of p_{in} calculated with use of the formula (10); $p_{in}^{\exp}$ is measured value of p_{in}; J_i is a number of p_{in} measurements during the experiment in the i-th operation mode.

The described procedure is a base of a technique for measurement of axial and radial permeability components and parameter b for rocks with an explicit layered structure.

An example of technique application for determination of anisotropic permeability of rocks from the ore deposit Streltsovskoye. We determined values of the permeability in vertical (normal to layering) and horizontal (parallel to layering) directions: $k_{vertical}$ = 0.1517·19^{-18}m^{2}and $k_{horizontal}$ = 0.6583·19^{-17}m^2.

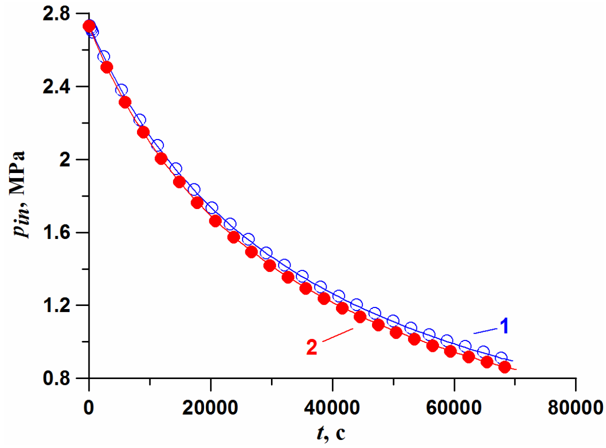

Fig. 2. The data of anisotropic permeability determination in dacite sample. Circles denote measured values of pressure in the inlet reservoir; solid lines correspond to calculated values. 1, 2 – operation modes.

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