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The interrelation between structure-sorption characteristics and the water permeability of ion-substituted forms of clay minerals is investigated.

We performed an experimental determination of the permeability coefficients of preparations of ion-substituted (Al, Fe, Ca, Ba, K, Na, Li) and natural forms of Chasov-Yar clay (monothermite) of different porosities, during filtering of water and aqueous solutions.

From the results of the experimental investigations we obtained the relations between the specific permeability, porosity coefficient, effective size of the solvated hulls, and specific surface of particles of the crystal lattice of minerals.

Figure 1 shows a diagram of the filtration instrument by means of which the flow rates of the filtering liquid were measured. The rigid construction of the casing (part 1) allows considerable liquid pressures to

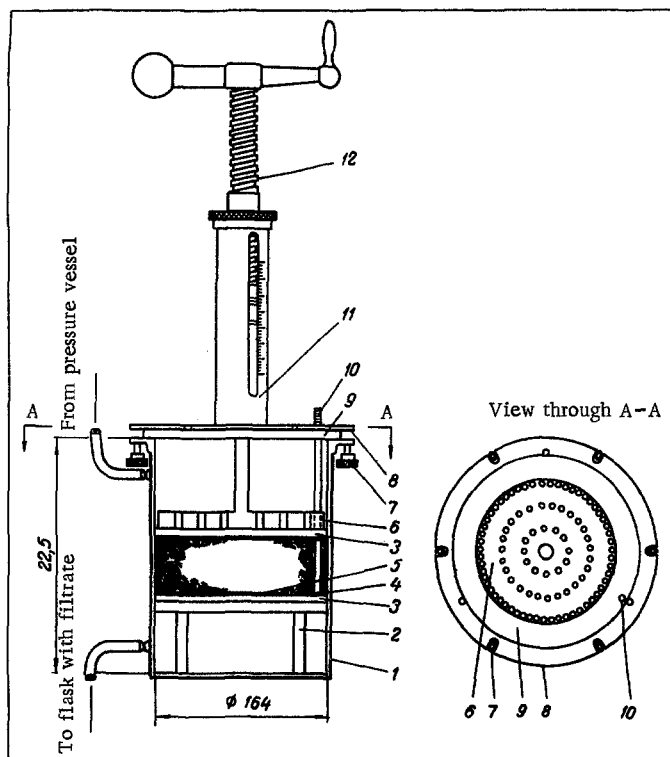


Fig. 1. Diagram of filtration instrument: 1) casing; 2) support; 3) upper and lower strainers; 4) waterproof shield; 5) filter paper; 6) base of press; 7) wing knob; 8) top cover; 9) rubber gasket; 10) air outlet; 11) guide housing of press; 12) press screw.

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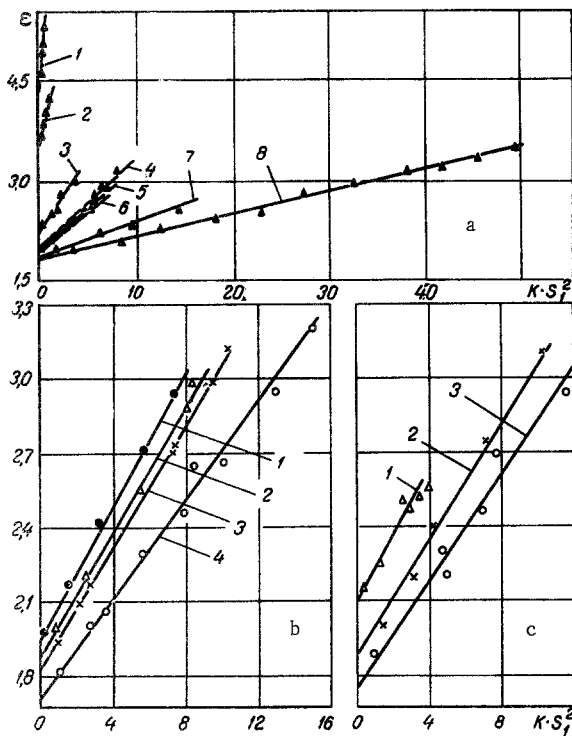


Fig. 2. Relation between the effective specific permeability K , porosity coefficient ϵ , and specific surface S_1 of solid-phase particles per unit volume of the packing. a) For the ion-substituted forms of Chasov-Yar clay: 1) Li form, 2) Na form, 3) K form, 4) natural form, 5) Ba form, 6) Ca form, 7) Fe form, 8) Al form; b, c) for natural forms of Chasov-Yar clay: b) natural semiacid sandy form, filtration of NaCl solutions: 1) 0,00 N, 2) 0,005 N, 3) 0,1 N, 4) 1 N; c) natural plastic form, filtration of CaCl_2 solutions: 1) 0,01 N, 2) 0,2 N, 3) 2 N.

We measured the permeability at pressure gradients of 320,000 N/m^2 and 150,000, 70,000, 40,000, and 14,000 N/m^2 . Darcy's law (Eq. (1)) was held rigorously in this range.

Figure 2 shows the linear relations between the porosity coefficient of clays and the product of the specific effective permeability and the square of the specific surface of particles of the solid phase (contained in unit volume of the disperse system) obtained from the results of experimental investigations for all ion-substituted and natural forms of Chasov-Yar monothermite clay during filtration of water and aqueous solutions of NaCl and CaCl_2 . Analytically these relations can be represented in the following form:

$$K = \frac{(\epsilon - \epsilon_0)}{bS_1^2}.$$

Setting $S_1 = S\delta$, we obtain

$$K = \frac{(\epsilon - \epsilon_0)(\epsilon + 1)^2}{bd_0^2S^2}.$$

It is quite obvious that any of the "filtration" straight lines obtained can be determined by the values of ϵ_0 and b . Expressing the mass of bound water not participating in filtration as $W = (\epsilon_0 d'')/d_0$ and dividing it by the mass of the monolayer of adsorbed water, we obtain $L = (\epsilon_0 d'')/(d_0 P_M)$ — the effective number of monomolecular layers of liquid not participating in the filtration.

be obtained and measurement of the pressure gradients in a wide range. The soil was placed between two organic glass strainers (part 3) on the inside surfaces of which were glued two layers of filter paper.

A waterproof shield preventing filtration along the wall of the casing was applied along the perimeter of the lower strainer. A uniform distribution of the volume mass in the clay samples placed in the instrument was achieved by squeezing them with a press (parts 6 and 12). Before being placed in the instrument, the soils were soaked above the maximum water content of swelling and held 24 h in a vacuum chamber, where a residual pressure of 15-150 N/m^2 was created. During the experiments, the duration of which varied from 30 to 180 days, periodic measurements (once or twice a day) were made of the flow rate of the filtrate, the temperature of the liquids, and the concentration of salts in it (for electrolytes). The experiment ended when the change in the flow rate of the filtrate during the last 5-7 days did not exceed 5-7% and the concentration of salts in it (for electrolytes) reached the initial concentration contained in the inflowing solution.

The permeability coefficient of the clays was found in the following manner:

$$K = \frac{Q\mu H}{\Delta G F}.$$

We investigated the effect of the pressure gradients on the permeability of soils during filtering of 0,05 N, 0,1 N, and 1 N NaCl solutions and 0,01 N, 0,2 N, and 2 N CaCl_2 solutions.

At the start of the experiment a maximum filtration head was created, and after stabilization of the flow rates and salt concentration in the filtrate smaller heads were substituted.

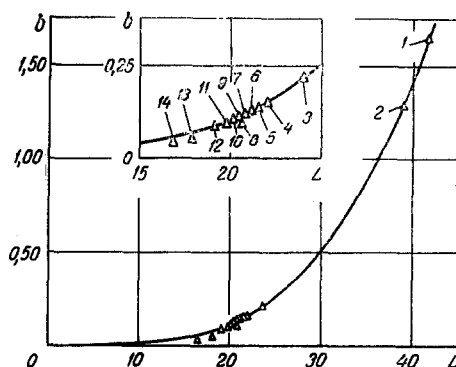


Fig. 3. Relation between the slope of the "filtration" straight lines and the effective number of monolayers of liquid not participating in filtration (an enlargement of 3-14 is shown in the upper part of the figure). The values 1-3, 5, 6, 7, 13, and 14 were obtained for ion-substituted forms of Chasov-Yar monothermite clay during filtration of water: 1) Li form; 2) Na form; 3) K form; 5) natural form; 6) Ba form; 7) Ca form; 13) Fe form; 14) Al form. The values 4, 10, and 11 were obtained for the natural plastic form of Chasov-Yar clay during filtration of CaCl_2 solutions: 4) 0.01 N; 10) 0.2 N; 11) 2 N. The values of 8, 9, and 12 were obtained for natural semiacid sandy form of Chasov-Yar clay during filtration of NaCl solutions: 8) 0.005 N; 9) 0.1 N; 12) 1 N.

Figure 3 shows the relation between L and b ($b = cL^\varphi = 1.53 \cdot 10^{-6} L^{3.73}$) covering all the ion-substituted and natural forms of Chasov-Yar clay that we considered during filtering of water and aqueous solutions of NaCl and CaCl_2 .

Thus it was possible to determine uniquely the slope of the "filtration" straight lines in terms of the effective number of monomolecular layers forming the solvated hulls of particles of the solid phase.

As can be seen from Table 1 and Fig. 3, in terms of the kind of exchange cations the values of the porosity coefficient ϵ_0 , and of L , and b are arranged in the following series: $\text{Li} > \text{Na} > \text{K} > \text{natural form} > \text{Ba} > \text{Ca} > \text{Fe} > \text{Al}$, and the values of the effective permeability coefficients are arranged in the opposite series: $\text{Al} > \text{Fe} > \text{Ca} > \text{Ba} > \text{natural form} > \text{K} > \text{Na} > \text{Li}$.

The water permeability of the Al form of monothermite is approximately four times greater than that of the Ca form and 100 times greater than that of the Na form. Such marked difference in the permeability of ion-substituted forms of clays can be explained by the characteristics of the structure of the chemical bond occurring between the adsorbed cation and anion of the mother surface of the mineral.

We will consider the Al form. The aluminum atom, being adsorbed on the mother surface of monothermite, enters into a covalent or donor-acceptor bond with oxygen atoms or hydroxyl groups of the crystal lattice of the clay mineral, but an analogous covalent bond is possible also between the Al atoms on adjacent particles located close to one another. As a result of such interaction the particles coalesce, i.e., comparatively large aggregates with narrow internal cavities and wide gaps between the aggregates form.

During filtration the water moves along the wide channels, creating within the microaggregates stagnant, stationary zones, the volume of which corresponds to the porosity coefficient ϵ_0 . It is clear that with an increase of the size of the microaggregates their number per unit volume of the disperse system decreases, the channels of the interaggregate voids widen, and consequently the permeability of the system increases and the volume of bound water and the effective number of monomolecular layers of liquid not participating in filtration decrease.

But as a result of adsorption of trivalent Al on the surface of the mineral a maximum concentration of active centers is created (of all the systems studied, adsorbed Al has the minimum ionic radius $r_1 = 0.5 \text{ \AA}$

TABLE 1. Value of the Effective Specific Permeability K for Porosity Coefficients and Ion-Substituted Forms of Chasov-Yar Monothermite Clay

ε	Al form		Fe form		Ca form		Ba form		Natural form		K form		Na form		Li form	
	ε ₀	$K \cdot 10^{-12} \text{ cm}^2$	ε ₀	$K \cdot 10^{-12} \text{ cm}^2$	ε ₀	$K \cdot 10^{-12} \text{ cm}^2$	ε ₀	$K \cdot 10^{-12} \text{ cm}^2$	ε ₀	$S \cdot \text{m}^2/\text{g}$	ε ₀	$K \cdot 10^{-12} \text{ cm}^2$	ε ₀	$S \cdot \text{m}^2/\text{g}$	ε ₀	$K \cdot 10^{-12} \text{ cm}^2$
2,000	1,78	1,17	1,80	1,01	202,0	0,186	1,923	202,0	1,94	202,0	2,2	224,6	3,7	221,3	4,8	252,0
2,200	1,78	2,66	1,80	2,30	202,0	0,740	1,923	202,0	1,94	202,0	2,2	224,6	3,8	221,3	4,9	252,0
2,500	1,78	5,203	1,80	4,89	202,0	1,830	1,923	202,0	1,94	202,0	2,2	224,6	3,9	221,3	5,00	252,0
2,800	1,78	8,684	1,80	8,13	202,0	3,28	1,923	202,0	1,94	202,0	2,2	224,6	4,1	221,3	5,20	252,0
3,500	1,78	20,57	1,80	19,37	202,0	8,26	1,923	202,0	1,94	202,0	2,2	224,6	4,1	221,3	5,20	252,0

and the maximum valence) and conditions arise for intense cohesion of the elementary particles with the formation of large microaggregates.

The mechanism of formation of microaggregates is analogous for Fe, Ca, and the Ba forms of monothermite, but since the concentration of active centers occurring on the surface of the mineral as a result of adsorption of Fe, Ca, and Ba is lower than in the case of adsorption of Al and decreases in the series Al > Fe > Ca > Ba, then the probability of the formation of three-dimensional structures from elementary particles of the clay mineral corresponds to such series (the number of bonds between particles per unit volume of the disperse system decreases). This phenomenon causes an increase of the number of microaggregates and a decrease in their effective size.

A different situation is observed in ion-substituted minerals formed by univalent cations.

In the case of adsorption of K, Na, and Li a strong ionic bond occurs between the atoms and anions of the mineral, and positive charges are created on the external faces of the crystals, the concentration of which is inversely proportional to the size of the cation. Electrostatic repulsive forces and Van der Waals attractive forces act between the clay particles carrying such like charges.

The total effect is determined by the concentration of active centers and mainly causes dispersion of the solid phase. Considerable resistances to the movement of the liquid occur in such a finely disperse system, and consequently sufficiently developed immobile solvated hulls form.

This is why in terms of the kind of exchange cation the permeability coefficients of monothermite are arranged in the series Al > Fe > Ca > Ba > K > Na > Li, and the values of the porosity coefficients of the systems corresponding to the volumes of the immobile solvated hulls are arranged in the opposite series Li > Na > K > Ba > Ca > Fe > Al, and the unique relation between L and b becomes understandable.

Thus the structure of the chemical bond of the exchange cation with anions of the mother surface of the lattice determines the permeability of the ion-substituted forms of clay minerals and their capacity for swelling in an aqueous medium.

As is seen from Fig. 2, in terms of the concentration of the filtering NaCl solution the values of the permeability coefficients of the natural form of Chasov-Yar clay are arranged in the following decreasing series: 1 N, 0.1 N, 0.005 N, 0.00 N; for CaCl₂ solutions: 2 N, 0.2 N, 0.01 N; and the values of ε₀, b, and L in the opposite series: 0.00 N, 0.005 N, 0.1 N, 1 N for NaCl and 0.01 N, 0.2 N, 2N for CaCl₂. A slight increase in the rates of filtration is observed on marked increase of the salt content in solution. These phenomena find explanation in the physical theory of coagulation by electrolytes developed by B. V. Deryagin [1]. According to the theory, an increase of the concentration of electrolytes added to a colloid system causes compression of the diffusion layers around the solid-phase particles, which leads to convergence of particles, i.e., to the formation of larger microaggregates and thus to an increase of permeability and a decrease of the capacity for swelling of the system.

The results of the investigations permit an outline of the basic premises for compiling diagrams for the calculation of the permeability of soils with a different mineralogical composition. These diagrams can be based on a series of "filtration" straight lines (analogous to those shown in Fig. 2) obtained during flow of water and aqueous and nonaqueous solutions in a wide

range of pressure gradients through the principal rock-forming clay minerals, loams, and sandy loams in their natural and ion-substituted forms.

Such diagrams will permit a calculation of the permeability coefficients of any finely disperse system for different values of its porosity from a knowledge of the specific surface of the solid-phase particles and maximum water content of swelling of the crystal lattice of the mineral.

NOTATION

K	is the permeability coefficient;
H	is the height of soil layer in instrument;
Q	is the average flow rate of liquids that passed through layer H;
μ	is the dynamic viscosity of filtering liquid;
ΔG	is the pressure over upper edge of soil;
F	is the cross-sectional area of investigated specimen;
ε	is the porosity coefficient of clays;
ε_0	is the porosity coefficient for $K = 0$ corresponding to mass of water not participating in filtration;
S_1	is the specific surface of solid-phase particles contained in a unit volume of the disperse system;
δ	is the unit weight of dry clay;
S	is the specific surface of a unit mass of dry clay;
b	is the slope of "filtration" straight lines;
P_m	is the mass of monolayer of adsorbed water;
L	is the effective number of monomolecular layers of liquid not participating in filtration;
d_0	is the density of dry soil;
d^n	is the density of filtering liquid.

LITERATURE CITED

1. B. V. Deryagin, Transactions of the Third All-Union Conference on Colloid Chemistry [in Russian], Izd. AN SSSR (1956).