adsorptive capacity and porosity of the structure of the samples, it is possible to change the transfer coefficients in the required direction and so create optimal conditions for the drying process.

NOTATION

S, specific surface, m^2/g; m, porosity; ρ, density of solid phase, g/cm^3; r, pore radius, cm; D_S, surface-diffusion coefficient, cm^2/sec; D, vapor-diffusion coefficient, cm^{-2}/sec; a, mass of adsorbed material per unit volume of porous body, g/cm^3; γ_0, mass of solid phase per unit volume of porous body; R, universal gas constant, erg/mole; T, absolute temperature, °K; M, mass of a mole of evaporating material, g/mole; U, mass content, g/g of solid phase; $\beta = da/dc$, adsorption-isotherm parameter; c, mass of vapor in pore space per unit volume of porous body, g/cm^3; D_i, effective internal-diffusion coefficient, cm^2/sec; a_m, coefficient of liquid diffusion, cm^2/sec; K, mass-conduction coefficient, $sec \cdot (mole/cm^3)$; C_m, specific mass capacity, mole/erg; p, vapor pressure above adsorbate; p_S, saturated vapor pressure; j, mass flow, $g/(cm^2 \cdot sec)$; θ, number of statistical monolayers of adsorbate; μ, chemical potential, erg/mole; τ, time, sec.

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METHOD OF ESTIMATING CHANGE IN FILTRATIONAL CHARACTERISTICS OF DISPERSE SYSTEMS CAUSED BY WATER-SOLUBLE POLYMERS

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UDC 532.546

It is shown that the filtration coefficients of polymer-modified disperse systems can be determined directly from calculations of their specific surface.

The influence of water-soluble polymers and electrolytes on the permeability of weakly filtering disperse systems (Na forms of montmorillonite) was studied in [1], where the data of filtrational, adsorption, and electron-microscopic investigations were used to construct a mechanism (a physical model) of the interaction of polymer macromolecules with the active centers of clay minerals and the concentrations of these polymers corresponding to maximum permeability were determined.

The main aim of the present work is to generalize the results of investigations of various rock-forming clay minerals, formulating a method of calculating the change in the filtration coefficients of soils on adding organomineral complexes.

In the investigations, natural forms of kaolinite and montmorillonite and the Na form of kaolinite were taken as the clay minerals, and polyacrylamide, K-4, and K-9 were chosen as the polymer additives.

Filtrational, adsorption, and electron-microscopic investigations of the system were carried out.

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TABLE 1. Specific Surface and Dimensions of Clay Mineral Microaggregates

Mineral	Specific surface of particles, m^2/g	Polymer additive, % of dry-soil weight	Microaggregate dimensions, μ
Glukhov kaolin (natural)	55	0,00	0,791
		PAA (0,025)	0,663
		PAA (0,05)	0,330
		K-4 (0,025)	0,570
		K-4 (0,05)	0,417
Glukhov kaolin (Na form)	27,2	0,00	0,633
		PAA (0,05)	0,515
		PAA (0,1)	0,430
Natural form of Crimean Kill earth (montmorillonite)	Interlayer surface 566 External surface 311 Total surface 877	0,00	0,368
		K-9 (0,05)	0,340
		K-4 (0,05)	0,271
		K-4 (0,1)	0,363

The procedure adopted for the filtrational investigations was similar to that outlined in [2]. The specific surface of the particles was calculated on the basis of measurements of the density of the adsorbed water. Values of the specific surface and effective linear dimensions of the particles are given in Table 1.

In the filtration experiments, a relation was found between two dimensionless parameters — the porosity ε and the product of the permeability and the square of the specific surface of unit volume of the system, KS_1^2. As also in the filtration of water, aqueous solutions of inorganic material, and organic compounds through various clay minerals unmodified by polymers, this relation was found to be linear.

By the method of least squares, the parameters of the straight lines were calculated and, on the basis of correlational relationships, the confidence limits of these parameters were calculated; also, the accuracy of the determination of the permeability was estimated in the regions of KS_1^2. For all the systems investigated, this accuracy was 6.3% on the average and did not exceed 12%.

On the basis of a physical model (mechanism) of the formation of the moisture-conducting properties of clays under the influence of a polymer, the following processes or principles were formulated.

I. The adsorption of K-9, polyacrylamide (PAA), and K-4 on free hydroxyl groups of the mineral surface through their carboxyl groups is due to the binding of particles in aggregates and hence the increase in permeability. This increase is determined by the number of adsorption centers (active ionogenic groups) C per unit length of spiral (chain), which varies in the series

$$C_{K\text{-}9} > C_{PAA} > C_{K\text{-}4}.$$

II. However, the adsorption of K-4 and K-9 in fact increases the concentration of Na^+ ions in the pore space, and this means that there is an increased possibility of hydration of the montmorillonite or kaolinite, increase in swelling of the clay particles, and decrease in permeability of the system.

III. The number of free hydroxyl groups per unit surface of the mineral is negligible, and hence, under natural conditions of the pore space (in contrast to a suspension), the excess content of carboxyl ions of the polymer macromolecule determines the additional content of similarly charged particles, the repulsion between them, dispersion of the aggregates, and decrease in the permeability of the system.

IV. The introduction in the pore space of long macromolecular chains leads to increase in viscosity of the pore solution, which also leads to decrease in permeability.

Thus in clay—polymer systems, conditions for the aggregation or disruption of the particles may arise, depending on the polymer concentration, the structure of the side chains of the molecule, and the properties of the solid-phase surface.

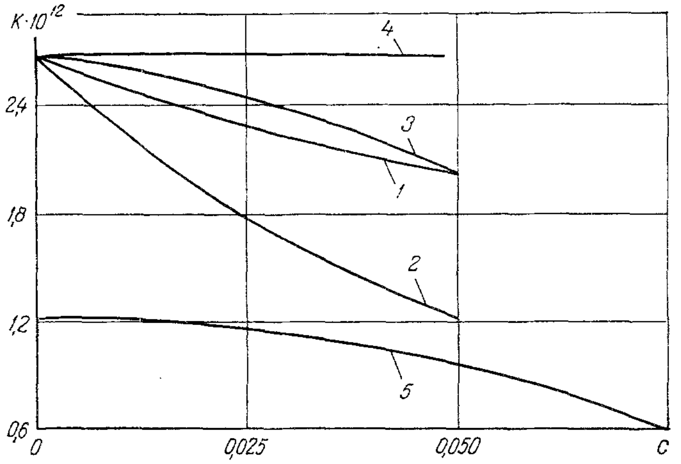

Fig. 1. Dependence of permeability K on concentration of polymers in the filtration of water and aqueous solutions of KNO_3 through Glukhov kaolin and the Na form with porosity $\varepsilon = 1.1$. Additions to the natural form: 1) PAA; 2) K-9; 3) PAA together with 0.01 N KNO_3; 4) K-4 in the filtration of water and 0.01 N aqueous KNO_3 solutions. Addition to the Na form: 5) PAA. $K \cdot 10^{12}$, cm^2; C,%.

In Fig. 1 the dependence of the permeability of natural Glukhov kaolin and the Na form on the polymer concentration in the filtration of water is shown. As is evident from Fig. 1, permeability decreases with increase in the concentration of ionogenic groups in the series: $K_{K-9} > K_{PAA} > K_{K-4}$. The specific surface of the particles of solid phase is comparatively small: 55 m^2/g for the natural form of kaolinite and 27 m^2/g for the Na form. In fact, the introduction of long chains of polymer macromolecules in the pore space, even in inconsiderable amounts, leads to an additional content of similarly charged particles, i.e., dispersion of the aggregates, which is also seen on microphotographs of kaolinite with additions of PAA and K-4.

In Fig. 2, the porosity ε is plotted against KS_1^2, the product of the permeability and the square of the specific surface in unit volume of the disperse system, for the natural form of Crimean kill earth (montmorillonite). As is evident from Fig. 2, in contrast to the systems studied previously, the curves of $\varepsilon = f(KS_1^2)$ show the existence of two regions (the presence of a discontinuity), the porosity ε being a linear function of the dimensionless quantity KS_1^2 in each of the two regions.

In Fig. 3, the permeability is plotted against the concentration of polymer additive. A fairly rough analysis of the results obtained leads to the following conclusions.

1. The optimum concentration of K-9 is in the range 0.025-0.05% and the maximum increase in permeability is more than 300%.
2. The optimum concentration of K-4 is 0.1% and the maximum increase in permeability is 280%.
3. The greatest increase in permeability is observed at high porosities, after the discontinuity on the curves of $\varepsilon = f(KS_1^2)$.

All these results may be explained on the basis of the principles (mechanism) of swelling of natural bentonite and the interaction of polymer macromolecules with active centers of its surface.

It is known that montmorillonites are characterized by interlayer (intracrystalline) and interparticle swelling.

Thus it was noted in [3, 4] that crystalline swelling of montmorillonites is not accompanied by macroswelling, while agreement between adsorption and x-ray data is obtained if these two processes are distinguished, and it was shown that the swelling of montmorillonite is more the result of increase in distance between the particles than of hydration of the interaggregate space.

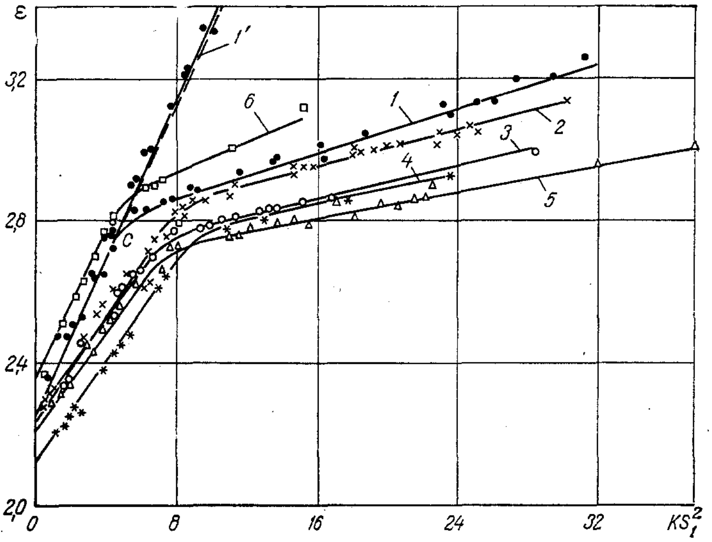

Fig. 2. Curves of porosity ε against KS_1^2, the product of the permeability and the square of the specific surface of unit volume of the system in the filtration of water through natural Crimean kill earth (montmorillonite) with additions of K-4 and K-9: 1) without polymers; 2) 0.05% K-4; 3) 0.1% K-9; 4) 0.1% K-4; 5) 0.05% K-9; 6) 0.15% K-4.

It is known that the concentration of exchange cations is a factor that has a great effect on the swelling of montmorillonite clays and also on their hydrophilic properties.

In a study of the change in interplane distances in the course of hydration [3], it was shown that the following groups of cations may be distinguished in terms of the different forms of swelling of monoionic montmorillonite:

1) Na^+, Li^+: samples give extension of the lattice in steps up to 22 Å, and then smooth extension proportional to the degree of hydration;
2) K^+, Cs^+: samples do not swell by more than 15 Å;
3) Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}: samples swell in steps, but not more than 19 Å. Up to 22 Å swelling is discontinuous, depends on the exchange cation, and is almost unaccompanied by macroscopic swelling. This region is called the region of crystalline swelling; there follows the osmotic region and, at still higher moisture contents, the montmorillonite is transformed into a thixotropic suspension.

Thus, the experimentally observed discontinuity on the curves of $\varepsilon = f(KS_1^2)$ is due to the existence of two regions of swelling. The first region, from 77 to 100% moisture content, is associated with both intracrystalline and interparticle (osmotic) swelling, and the second region, from 100 to 118%, with interparticle swelling only.

It would be expected that, in the filtration of water through samples of natural bentonite with a pore volume corresponding to the first region of swelling, the whole of the particle surface is involved, but that with increase in the total moisture content in the sample only the surface of the external basal planes is involved.

In Fig. 2, the continuous curve 1 and the dashed curve 1' show the rectification of the two regions obtained for water, which is achieved by substituting into the dimensionless parameter KS_1^2 the specific surface of the external basal planes for the value of ε at the point of discontinuity C. For the other cases, this verification was impossible because of the lack of reliable data on the change in the various surfaces of the bentonite under the influence of polymers.

It is clear that the enormous K-4 and K-9 macromolecules cannot completely penetrate into the interaggregate space and are absorbed mainly through their carboxyl groups on the external basal planes of the crystalline lattice and therefore their role as particle coagulator and hence as accelerator of moisture transfer appears more strongly in the second stage

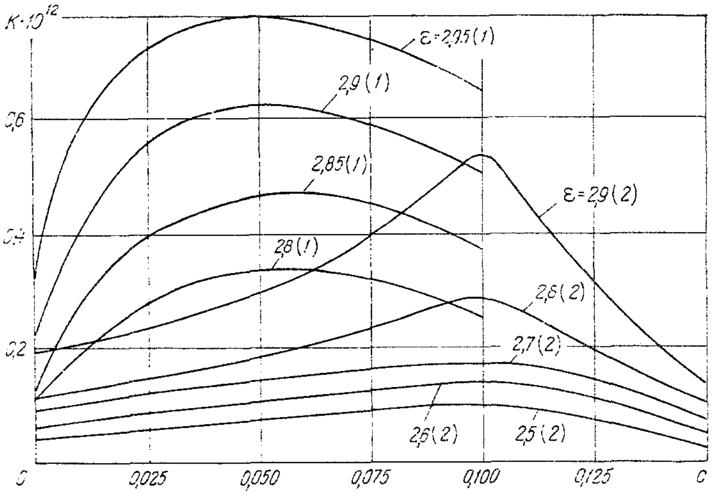

Fig. 3. Dependence of the permeability K on the concentration of K-9 — curves marked (1) — and K-4 — curves marked (2) — in the filtration of water through natural Crimean kill earth (montmorillonite). $K \cdot 10^{12}$, cm^2.

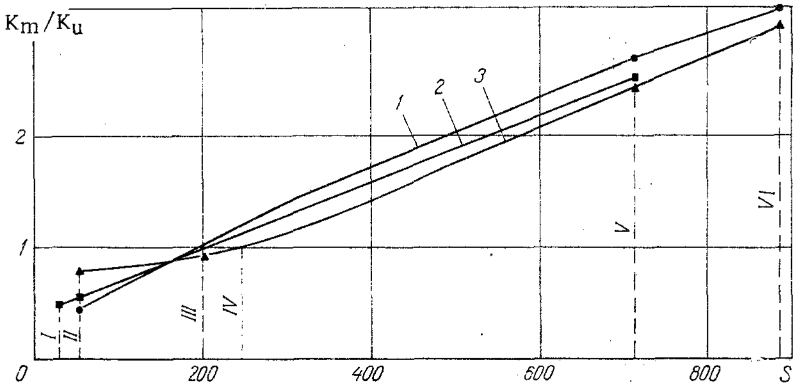

Fig. 4. Relative changes in the filtration coefficient of clay soils modified by polymers in the region of optimum concentration for mean values of the porosity; K_m is the filtration coefficient of modified soil for water or aqueous solutions of mineral fertilizers; K_u is the filtration coefficient of unmodified soil. Polymer additives: 1) K-9; 2) PAA; 3) K-4. Soil: I) Na form of bentonite; II) natural kaolinite; III) middle-gypsum clay of Golodna steppe; IV) takyr-like clay of Karshinsk steppe; V) Na form of montmorillonite; VI) natural montmorillonite. S, m^2/g.

of swelling. This growth (as for the systems considered earlier) is determined by the number of adsorption centers (active ionogenic groups) C in unit length of spiral (chain), which forms a series

$$C_{K\text{-}9} > C_{PAA} > C_{K\text{-}4}.$$

Filtrational and adsorption experiments on a number of systems — kaolinite and montmorillonite in both natural and Na forms, takyr-like clays of the Karshinsk steppe, middle-gypsum clays of the Golodna steppe — allowed all the results obtained to be generalized and to be represented in the form of curves relating the relative changes in the filtration coefficients of clay soils modified by polymers and the specific surface of the particles for the water-soluble polymers K-9, PAA, and K-4 (Fig. 4). In constructing these curves, the filtration coefficients of modified soils in the region of optimum polymer concentration, calculated for mean values of the porosity $\bar{\varepsilon} = (\varepsilon_0 + \varepsilon_{max})/2$, were compared with the filtration coefficients of unmodified soils corresponding to the same porosities.

As is evident from Fig. 4, the curves are strictly monotonic functions and hence (on further refinement of the curves) it is possible to calculate the change in filtration coefficients under the influence of water-soluble polymers, given only the specific surface of the soil particles. This means that it is possible, without lengthy and difficult experimental work, to make relatively rapid estimates of the likely change in the filtrational properties of soils when a particular organomineral fertilizer is used. Simply on the basis of the water-soluble polymers K-9, PAA, and K-4 investigated, the following conclusions can be drawn:

1) for clay soils with specific surface of the particles less than 200 m^2/g, the use of water-soluble polymers impairs their filtrational properties;

2) the use of these polymers in clays with a highly developed specific surface (up to 900 m^2/g) allows their filtrational coefficients to be increased by more than 300%.

It must be noted that all these results have been obtained from a comparison of the permeability of modified and unmodified soils for the filtration either of water or of aqueous solutions of mineral salts.

If the permeabilities of weakly filtering systems of the Na form of clay soils, i.e., pure alkaline soils, for water are compared with the permeabilities of these systems for aqueous solutions of potassium nitrate, then [1] the transfer coefficients in the latter case are found to be greater by a factor of 10-30. For land in this state (as confirmed by technicoeconomic calculations using valuable agricultural crops) the use of organomineral complexes is an effective measure.

NOTATION

K, permeability of disperse systems in liquid filtration; ε, porosity; C, concentration of polymer additive in system; S_1, specific surface of unit volume of solid phase; S, specific surface of unit mass of solid phase.

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THERMOPHYSICAL CHARACTERISTICS OF LIGHTWEIGHT AGGREGATE CONCRETE IN THE COURSE OF HARDENING DURING HEAT TREATMENT IN CHAMBERS HAVING THERMALLY INSULATING SURFACES

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The dynamic characteristics of the changes taking place in the internal transfer coefficients and criteria of lightweight aggregate concrete during heat treatment in a "dry" ambient are presented.

In order to predict and calculate the modes of heat treatment to be applied to concrete and reinforced concrete objects it is essential to be aware of the mechanisms underlying heat and mass transfer in these materials, as well as the values assumed by thermophysical parameters

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