LITERATURE CITED

1. K. Lichtenecher, Phys. Z., 10, No. 25, 1005-1008 (1909).
2. V. M. Odelevskii, Zh. Tekh. Fiz., 21, No. 6 (1951).
3. G. N. Dul'nev and Yu. P. Zarichnyak, Thermal Conductivity of Mixtures and Composition Materials [in Russian], Énergiya, Leningrad (1974).
4. N. P. Bogoroditskii, N. V. Kal'mens, et al., Radioceramics [in Russian] GÉI, Moscow–Leningrad (1963).
5. I. S. Semirikov and B. A. Loshkarev, "Achievements and perspectives in development of devices and methods for moisture measurement in solid, liquid, and gaseous materials," in: Reports to the Fifth All-Union Conference [in Russian], Kutaisi (1973), p. 20.

INFLUENCE OF WATER-SOLUBLE POLYMERS AND ELECTROLYTES ON THE PERMEABILITY OF WEAK-FILTERING DISPERSED SYSTEMS

P. P. Olodovskii and M. G. Murashko

UDC 624.433

The mechanisms underlying the moisture-conducting properties of the sodium form of clay minerals after the adsorption of various polymers on their surfaces or during the filtration of electrolytes are studied.

A great deal of research has been carried out in connection with determining the optimum concentrations of water-soluble polymers and estimating the changes taking place in the filtering characteristics of soils under the influence of adsorbed organo-mineral complexes. The subject of the present investigation was the Na form of montmorillonite; the structure-forming agents were polyacrylamide, K-4, and K-6; the electrolyte was an aqueous solution of potassium nitrate with a concentration of 0.05 g-eq/liter.

These systems were subjected to filtration and adsorption analysis and examined under the electron microscope. The filtration technique was analogous to that set out in [1].

The specific surface of the particles in the Na form of montmorillonite was calculated from measurements of the density of the adsorbed water, and in the Na form modified with polymers by reference to the adsorption of a dye (methylene blue).

The specific surfaces and effective linear dimensions of the particles are indicated in Table 1.

In the filtration experiments we established a relationship between certain dimensionless parameters: the porosity coefficient and the product of the permeability coefficient by the square of the specific surface of unit volume of the system. As in the case of the filtration of water, aqueous solutions of inorganic substances, and organic compounds through various clay minerals not modified with polymers, this relationship was linear. Using the method of least squares, we calculated the parameters of the straight lines and (on the basis of the corresponding correlational relationships) the confidence intervals of these parameters as well. The relative error in measuring the permeability coefficients was no greater than 10-15%. Table 2 shows the results of these measurements for the Na form of montmorillonite modified with water-soluble polymers during the filtration of water and aqueous KNO_3 solutions. The relationship between the permeability coefficient and the concentration of the polymers so introduced is shown in Fig. 1; the changes in the relative permeability coefficients of the systems associated with the combined use of polymers and electrolytes appear in Fig. 2.

Central Scientific-Research Institute of the Complex Use of Water Resources Ministry of Water Economy of the USSR. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 30, No. 2, pp. 339-346, February, 1976. Original article submitted April 25, 1975.

TABLE 1. Effective Specific Surfaces and Particle Dimensions of the Na Form of Montmorillonite Modified with Water-Soluble Polymers

Concentration and type of polymer	Specific surfaces of the particles, m²/g		Dimensions of of microaggregates, μ
	method based on measuring density of adsorbed water	method of dye adsorption	
No polymer	547	510	0,43
PAA (0,01)	—	—	0,29
PAA (0,1)	—	—	0,7
PAA (0,05)	—	547	0,1
K-4 (0,1)	—	—	0,19
K-4 (0,025)	—	651	0,13
K-6 (0,025) together with 0.05 N KNO_3	—	552	0,173

TABLE 2. Change in the Filtration Characteristics of the Na Form of Montmorillonite under the Influence of Water-Soluble Polymers and Electrolytes

Filtration of water						Filtration of an aqueous KNO_3 solution, 0.05 N, g-eq/liter					
polyacrylamide			K-4			polyacrylamide			K-4		
c, %	ε	$K \cdot 10^{12}$ cm²	c, %	ε	$K \cdot 10^{12}$ cm²	c, %	ε	$K \cdot 10^{12}$ cm²	c, %	ε	$K \cdot 10^{12}$ cm²
0,035	4,93 6 8 10	0,00 0,06 0,27 0,66	0,04	4,98 6,00 8,00 10,00 12,00	0,00 0,04 0,22 0,55 1,07	0,05	4,8 6 8 10	0,00 0,29 1,26 3,06	0,015	4,74 6 8 10	0,00 0,29 1,26 3,03
0,05	3,97 6 8 10	0,00 0,13 0,41 0,92	0,1	6,019 8,00 10 12	0,00 0,11 0,33 0,7	0,1	4,7 6 8 10	0,00 0,18 0,76 1,81	0,025	4,37 6 8 10	0,00 0,34 1,27 2,94
0,1	5,266 6 8 10 12	0,00 0,03 0,18 0,46 0,92								4,37 6 8 10	0,00 0,34 1,26 2,94
	No polymers added					No polymers added					
	5,266 6 8	0,00 0,05 0,27		10 12	0,70 1,4		4,7 6 8	0,00 0,14 0,61		10 12	1,46 2,80

Even an approximate analysis of the results obtained leads to the following conclusions.

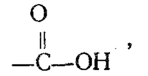
1. The permeability of the Na form of clay minerals increases up to a certain limit with increasing content of polyacrylamide and reaches a maximum (2-3-times increment) for concentrations of 0.05-0.06%.

2. The use of various K-4 additives reduces the permeability of the clays.

3. The combined use of polyacrylamide and an electrolyte (0.05 N KNO_3) increases the permeability of the system (in the region of the optimum polyacrylamide concentration) by a factor of 5-14 times, depending on the porosity.

4. The combined use of K-4 and an electrolyte (0.05 N KNO_3) produces a limiting 5-12-times increment in permeability in the 0.02-0.025% range of polymer contents.

All these phenomena may be explained by considering the mechanism underlying the interaction of the polymer molecules with the active centers on the surfaces of the solid-phase particles. Thus, it is well known that, as a result of the dissociation of polyacryamide and K-4 in water, the amide group is split off and a carboxyl group is formed:



$$-\overset{\displaystyle O}{\overset{\|}{C}}-OH,$$

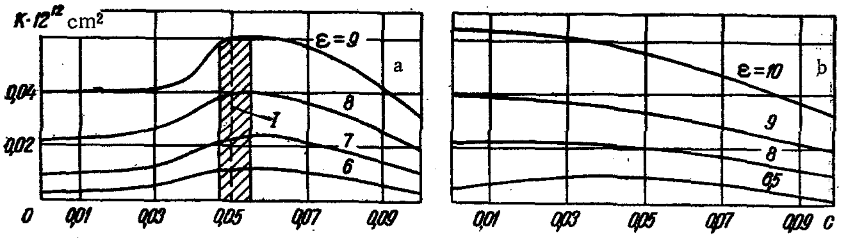
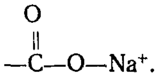


Fig. 1. Permeability coefficient (K) as a function of the polymer concentration during the filtration of water through the Na form of Crimean kill (fuller's earth): a) polyacrylamide; b) K-4; I – optimum concentration, c, %.

while in an alkaline medium incorporating an interstitial solution of the Na form of montmorillonite this group is converted into a mobile link:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-Na^{+}.$$

It has been shown by a number of authors that the adsorption of polymers on the surface of a clay mineral is determined by the development of a hydrogen bond between the carbonyl group C=O of the polyelectrolyte and the hydroxyl of the clay mineral.

Kohl and Taylor [3] studied the adsorption of the polymers VAMA and NPAN on the surface of Wyoming bentonite clay by infrared spectroscopy.

It was found that the infrared absorption band due to the C=O vibration lay in the frequency range 5.8-5.9 μ if the carbonyl group was not subject to the influence of a hydrogen bond, but in the case of an adsorbed polymer molecule there was a displacement of the characteristic frequencies of the C=O group by 0.05 μ in the long-wave direction. This phenomenon may be explained by the development of a strong hydrogen bond between the oxygen of the carboxyl group and the OH group of the mineral.

Analogous results were obtained by Maslenkova when studying the adsorption of polyacrylamide on kaolinite [4] and by Taimurazova [5] on bentonite, muscovite, and kaolinite containing traces of hydrolyzed polyacrylamide and the sodium salt of hydrolyzed polyacrylonitrile.

It was shown in [6] that the nature of the cation affected the intensity of formation of the hydrogen bond between montmorillonite clay and K-4, and the degree of this interaction was determined by its polarizing capacity. The greatest intensity of the hydrogen bond occurs in H-bentonite and the least in Al-bentonite, other forms occupying an intermediate position. It was concluded in [6] that (for the same concentrations) K-4 interacted more vigorously with dispersed mineral systems giving an acid reaction, while for alkaline systems [Na-bentonite, takyrs, and solonchaks (saline soils)] it was less effective.

The following processes or principles may act as a basis for the physical model (mechanism) underlying the moisture-conduction of the Na form of the clay under the influence of the polymer.

I. The adsorption of PAA and K-4 on free hydroxyl groups of the mineral surface through layers of carbonyl groups results in the binding of the particles into aggregates and hence a rise in permeability.

II. However, the adsorption of K-4 essentially increases the concentration of Na^{+} ions in the interstitial space, and this means the possibility of additional montmorillonite hydration, together with an increment in the swelling capacity of the clay particles and a reduction in the permeability of the system.

III. The number of free hydroxyl groups on unit surface of the mineral is very low, so that under the restricted conditions of interstitial space (as distinct from suspensions) the excess content of the carboxyl ions of the polymer macromolecule determines the incremental content of monotypic charged particles, the repulsion of the particles, the dispersion of the aggregates, and the reduction in the permeability of the system.

IV. The introduction of long chains of macromolecules into the interstitial space leads to an increase in the viscosity of the interstitial solution, which also causes a fall in moisture conduction.

Thus, in the system comprising the Na form of the clay and the polymer, conditions favorable either to the aggregation of the particles or to the disruption of aggregates are created, depending on the concentra-

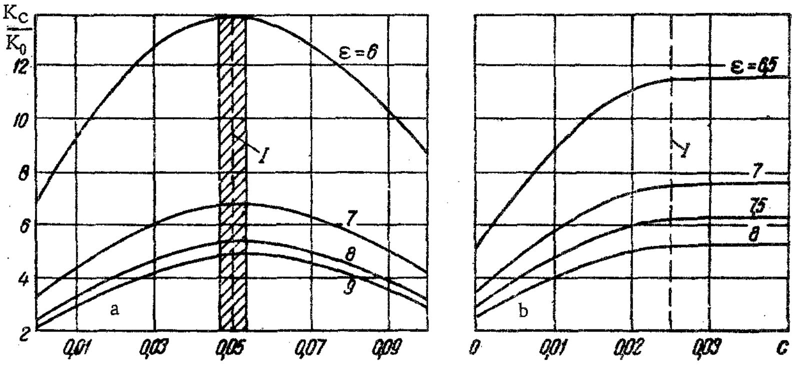


Fig. 2. Dependence of K_c/K_0 on the concentration of polyacrylamide (PAA) (a) and K-4 (b) for various porosities (ϵ). K_c is the permeability of the Na form of Crimean kill treated with PAA or K-4 for the filtration of a 0.05 N KNO_3 solution, while K_0 is the permeability of the polymer-unmodified Na form for the filtration of water. I – optimum concentration.

tion of the structure-forming agents and the constitution of the side chains of the macromolecule.

An analysis of the electron micrographs of particles with added PAA and K-4 indicates the dispersion of the particles (the development of a background).

The specific surfaces of modified clays determined by reference to the adsorption of methylene blue dye are larger than those in polymer-free clays.

The observed increment in the moisture-conduction coefficients of the clay–polyacrylamide complex for optimum concentrations of the structure-forming agent (0.05-0.06%) is determined by the predominant influence of the first process, while the reduction in permeability for low PAA concentrations arises from processes III and IV. The reduction in the water permeability coefficients of the Na-clay–K-4 complex in any range of polymer concentrations is determined by processes II, III, and IV.

A different situation arises in the filtration of electrolytes. For any dispersed systems the presence of soluble salts is accompanied by the compression of the immobile hydrate layers around the solid-phase particles and an increase in moisture conduction. We presented these results earlier [7] when studying monothermite.

For minerals with an expanding crystal lattice, the introduction of hydrated ions into the interpacket space is accompanied by a compression or expansion (swelling) of the particles, and this process (influencing the rate of transfer of the liquids [7]) depends on the dimensions of the hydrated ions and their number in the absorbing complex. The radius of the hydrated Na^+ cation is 2.7 Å, that of the K^+ being 2.32 Å, and hence the presence of an aqueous solution of potassium nitrate increases the moisture conduction of the system, quite apart from any dependence on the polymer content.

On introducing electrolytes and, in particular, aqueous solutions of 0.05 N KNO_3 into the interstitial space, ion-exchange takes place between the sodium and the potassium, both that adsorbed on the surface of the mineral and that encountered in an absorbed complex close to the carboxyl ions of the polymer macromolecule.

The hydration capacity of potassium cations is lower than that of sodium, so that as a result of such an exchange the compression of the immobile solvate shells arising around the solid-phase particles and the active centers of the polymer macromolecule is partially reversed, and this process promotes an increase in the moisture conduction of the system.

We see from Fig. 2 that, depending on the exact value of the porosity, there may be a 5-14-times increment in the permeability coefficients of the Na form of polymer-modified montmorillonite for the filtration of electrolytes (relative to that of water); the increment attributable to the use of structure-forming agents amounts to 200%.

Thus, in determining and regulating the moisture-conducting properties of finely dispersed systems, water-soluble polymer macromolecules constitute not only particle coagulators, but also accumulators of active exchange ions, and this qualitatively determines their capacity to increase the rate of transfer of

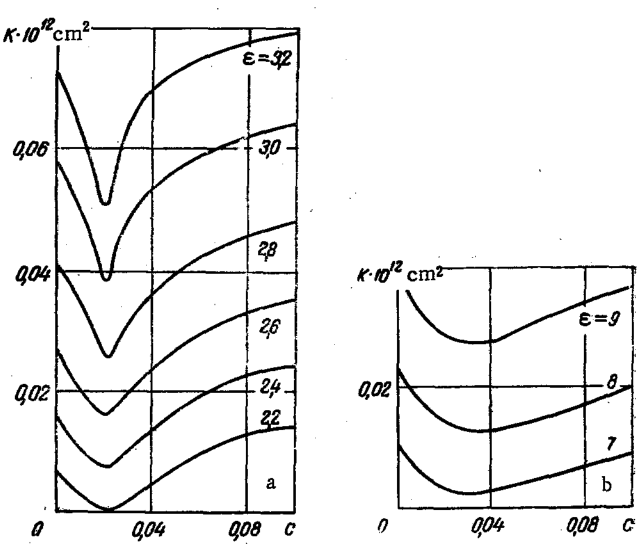


Fig. 3. Permeability coefficient (K) as a function of the porosity coefficient (ϵ) and the concentration of the solutions (c, g-mole/liter); a) K form of Crimean kill, KCl solutions; b) Na form of Crimean kill, NaCl solutions.

aqueous solutions of mineral salts, or to augment the degree and intensity of the desalinization of soils in leaching processes.

According to the nonosmotic theory (or the Donann theory of membrane equilibrium), the distribution of the mobile components of the system (i.e., the ions) between the solid and liquid phases obeys a strict stoichiometric law. A condition for this equilibrium is equality between the concentration products of the active ions in the surface layer and in the external equilibrium solution.

In the interaction of the solid phase of the system with a binary monovalent electrolyte (for example, of the NaCl and KNO_3 type), according to the law of mass action the distribution of the active ions is described by the following equation:

$$(a_K + a_A)\cdot a_A = a_V^2 . \qquad (1)$$

According to the theory of membrane equilibrium [8] the existence of an active concentration of surface ions (a_K) leads to the "negative sorption" of the electrolyte, i.e., there is a deficit of ions in unit volume of the pores of the substance in question ($a_A < a_V$).

Our filtration experiments with the Na and K forms of montmorillonite during the flow of NaCl and KCl solutions of various concentrations showed (Fig. 3) that the minimum values of the permeability of the systems and the maximum swelling humidities occurred, not for zero concentration of the solutions, as had always been observed in soils consisting of minerals with a nonexpanding crystal lattice, but for a certain "critical" concentration of the solutions. For the Na form of the solution this concentration was 0.03 N NaCl and for the K form 0.02 N KCl.

Analogous phenomena (changes in maximum swelling humidity in relation to the concentration of contiguous solutions) were observed in [9].

Thus, for clay soils possessing a well-developed specific surface and a large exchange capacity, desalinization by the ordinary leaching method will not be complete.

After the adsorption of water-soluble polymers some of the exchange active cations are concentrated, not at the solid—liquid interface, but in the interior of the interstitial space, and an absorbing complex less stable with respect to external actions is formed. The degree and intensity of the desalinization of this kind of system should exhibit an increase.

Thus, L. B. Smolin indicated a rise in the water permeability and erosion-loss of salts from solonchak meadow sierozem (gray desert) soil in the presence of K-4 [10]. According to the results of the tests carried out in this investigation, it was concluded that in order to create favorable properties in typical gray desert soils, small (0.02%) doses of K-4 should be used.

In our own investigations the optimum K-4 concentration in its combined use with electrolytes (mineral fertilizers) for weakly filtering clays equalled 0.025% of the weight of the solid phase, while the rate of transfer of aqueous solutions of mineral salts in the region of optimum concentration was 5-15 times greater than the rate of water filtration through unmodified Na-form clay minerals (the exact figure depending on the porosity).

A technical-economic analysis shows that the use of organo-mineral additives to improve the filtration properties of heavy saline clay soils with an initial filtration coefficient of under 0.05 m/day is in fact viable.

NOTATION

K, permeability coefficient of dispersed systems for liquid filtration; ε, porosity coefficient; c, concentration of polymers introduced into the clay; a_K, effective concentration of the active surface ions (exchange cations); a_A, active concentration of the electrolyte transferred to the surface layer; a_V, active concentration of the equilibrium solution.

LITERATURE CITED

1. M. G. Murashko, P. P. Olodovskii, and G. A. Ivkovskaya, Inzh.-Fiz. Zh., 19, No. 2 (1970).
2. P. P. Olodovskii, Inzh.-Fiz. Zh., 17, No. 4 (1974).
3. R. A. Kohl and B. A. Taylor, Soil Science, 91, No. 4 (1961).
4. G. A. Maslenkova, "Physicochemical foundations of artificial structure formation," in: Agrophysical Papers [in Russian], No. 10, FAN, Tashkent (1962).
5. L. Kh. Taimurazova, and A. A. Ignat'eva, Vestn. Mosk. Gos. Univ. Biol. Pochvoved., No. 2 (1955).
6. K. S. Akhmedov et al., Water-Soluble Polymers and Their Interaction with Dispersed Systems [in Russian], FAN, Tashkent (1969).
7. P. P. Olodovskii, M. G. Murashko, G. A. Ivkovskaya, and Z. V. Kopets, in: Geological Engineering Properties of Clay Soils and Processes in these Soils [in Russian], Izd. MGU (1972).
8. O. N. Grigorov et al., Electrokinetic Properties of Capillary Systems [in Russian], Izd. Akad. Nauk SSSR, Moscow (1956).
9. E. M. Sergeev et al., in Geological Engineering Properties of Clay Soils and Processes in these Soils [in Russian], 1st ed., Izd. MGU (1972).
10. L. B. Smolina, in: Structure Formation in Dispersed Systems in the Presence of Polyelectrolytes [in Russian], FAN, Tashkent (1970).