ADSORBED WATER DENSITY DISTRIBUTION IN DISPERSE MEDIA

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The results of experimental measurements have been used to obtain relations between the density and the content of bound water and the adsorption characteristics have been calculated for clay minerals substituted with Ca and Na cations. Some of the factors controlling the hydration of exchange cations at adsorbent surfaces have been established.

In [5] the author obtained distribution curves for the density of adsorbed water as a function of the water content and estimated the volumes of the monomolecular layers and the effective specific surfaces of different parts of the crystal lattice for a series of natural monomineral clays of the kaolinite, illite and montmorillonite groups (Glukhovets kaolin, Chasov Yar monothermitic clay, Pyzhev bentonite, Crimean kill).

A similar study has now been made of pure cation-substituted clay minerals.

The samples studied consisted of bentonite clay from the Cherkassy deposit (Ukrainian SSR) (principal rock-forming mineral montmorillonite) and Glukhovets kaolin (rock-forming mineral kaolinite). In order to obtain monomineralic specimens we washed the clays and then selected the most highly disperse fraction, and in order to replace the exchange complex of the natural minerals with Na and Ca ions we converted them to the Na or Ca form by working up the starting specimens 10 times with a 1 N solution of NaCl or $CaCl_2$ at a liquid/solid phase ratio of 8:1 with subsequent repeated extraction of the excess salt with water until a negative chlorine ion reaction was obtained.

In the course of the subsequent experiments with the specimens thus prepared (the apparatus and method were similar to those described in [5]) we found the mean values of the bound water density (denoted by circles in the figures) in the process of desorption from the above-mentioned materials.

For specimens of Glukhovets kaolin substituted with Ca^{+2} and Na^{+} cations we found the following relationship between the mean density and the quantity of adsorbed water:

$$d_{\text{b}} = A\exp(-mP^n) + d''. \tag{1}$$

Curves 3 and 5 in Fig. 1 show this relation together with the experimental data; the scatter of the experimental points does not exceed ±0.5%.

Expressing the volume of adsorbed water as

$$V = \frac{P}{d_{\text{b}}} = \frac{P}{A\exp(-mP^n) + d''} \tag{2}$$

and differentiating both sides of Eq. (2), we obtain

$$\frac{dP}{dV} = d' = \frac{[A + d''\exp(mP^n)]^2}{\exp(mP^n)\,[A + AmnP^n + d''\exp(mP^n)]}. \tag{3}$$

Equation (3) gives the density of strongly bound water (dP/dV = d') in an infinitesimal volume as a function of the amount of adsorbed water P preceding formation of the volume dV (curves 4 and 6 in Fig. 1).

The curves obtained are identical with the curves for the class of hydrophilic disperse systems with a nonexpanding crystal lattice (natural Glukhovets kaolin, Chasov Yar clay, silica gel, and alluvial loam [5]).

It is obvious that all the assumptions and equations for calculating the volumes of the monomolecular layers and the effective specific surfaces made and obtained for materials of this system [5] also remain valid for the adsorbents investigated.

Taking the value $d' = d'' = 1\ \text{g/cm}^3$ in Eq. (3), we obtain the expression

$$A = \exp(mP_{\text{m}}^n)(mnP_{\text{m}}^n - 1), \tag{4}$$

which is the maximum amount of bound water with density higher than that of free water in an infinitesimal volume. This amount of water P_{m} corresponds to the formation of a monomolecular layer on the surface of the adsorbents, which is also confirmed by the values of P_{m} calculated for the test specimens from the heats of wetting (see table).

The equation for calculating the total effective specific surface is written as follows:

$$S = \frac{s'}{v'}\int\limits_0^{P_{\text{m}}} \frac{dP}{d'}. \tag{5}$$

Values of the coefficients in Eqs. (1)–(3), the calculated volumes of the monomolecular layers, and the effective specific surfaces are presented in the table.

Many studies have been made of the effect of the nature of the exchange cations on the adsorption properties of clays and adsorbents in general. Thus, F. D. Ovcharenko [3] has arranged cations in the following order according to their effect on the heat of wetting for Glukhovets kaolin:

$$Ca^{+2} > Mg^{+2} > H^{+} > Na^{+} > K^{+}.$$

For kaolin Siefert [9] obtained the series $Ca^{+2} > H^{+} > Na^{+} > K^{+}$. At the same time he established the following order of decreasing sorption of water vapor by kaolinite at a relative humidity of 10%: $Ca^{+2} > H^{+} = Na^{+} > K^{+}$. The authors of [7] obtained the cation series $Mg^{+2} > Ca^{+2} > Na^{+} > K^{+}$ with respect to characteristic dehydration temperature on clay minerals.

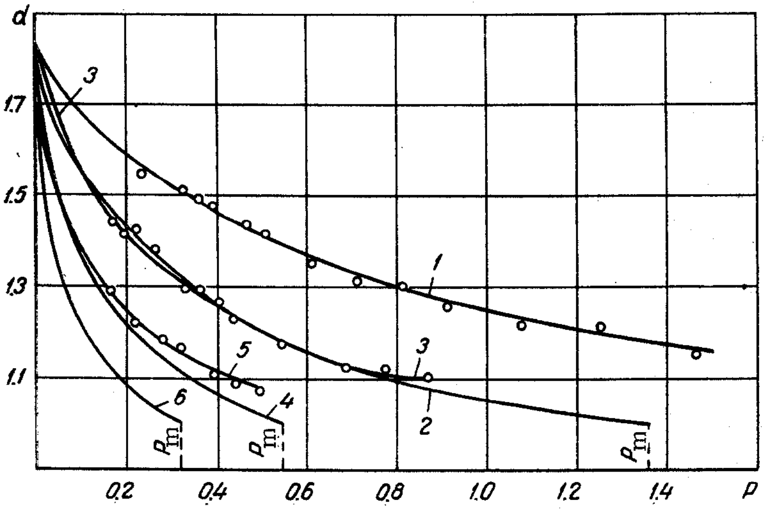

Fig. 1. Density of bound water d, g/cm^3, as a function of the bound water content P, %, for Glukhovets kaolin and its cation-substituted forms: 1, 3, and 5) values of the mean density of the adsorbed water d = d_b for natural Glukhovets kaolin, and for Glukhovets kaolin substituted with Ca and Na cations; 2, 4, and 6) values of the density of adsorbed water in an infinitesimal volume d = d' for Glukhovets kaolin: natural, Ca cation-substituted, and Na cation-substituted.

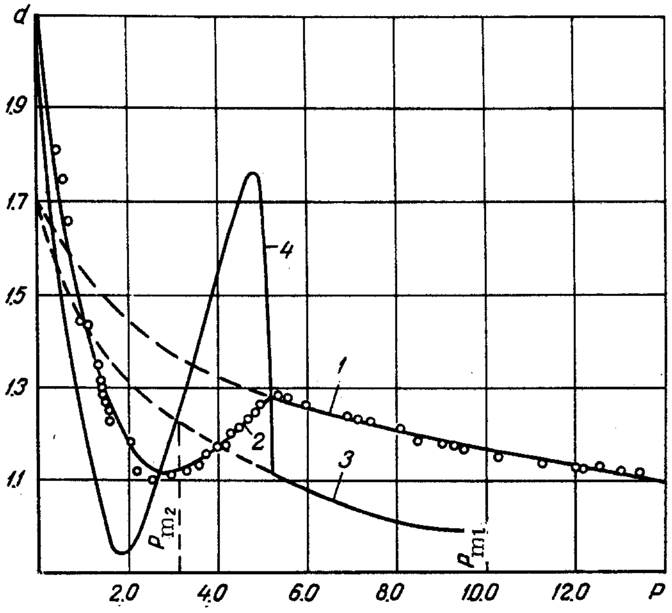

Fig. 2. Bound water density d, g/cm^3, as a function of the bound water content P, %, for Ca cation-substituted Cherkassy bentonite: 1, 2) values of mean density of adsorbed water d = d_b; 3, 4) values of density of adsorbed water in an infinitesimal volume d = d'.

This cation sequence, based on the effect on the adsorption capacity of disperse systems, is attributable to the ion-dipole interaction between the molecules of adsorbed substance and the cations, in which an important part is played by the ion radius, the charge and nature of the cation, and its deformability and position in the anionic skeleton [4, 6].

From our bound water density distribution curves and the adsorption characteristics for Glukhovets kaolin, both natural and substituted with Ca^{+2} and Na^{+} cations, we can derive the following order of decrease in bound water density for the same content and mineral adsorption properties: natural Glukhovets kaolin > > Glukhovets kaolin substituted with Ca^{+2} cations > > Glukhovets kaolin substituted with Na cations. This result can be attributed to partial compensation of the charges on the parent surface of the mineral, especially on shear areas, i. e., the occurrence of more thinly distributed concentrated positive charges of various magnitude depending on the valence of the cation. The appearance of active centers thinly distributed as compared with the parent surface is accompanied by an orientation of the water molecules favorable for the formation of hydrogen bonds, which also leads to looser packing of the adsorbate.

For a disperse system with an expanding crystal lattice (Cherkassy bentonite substituted with Ca^{+2} cations) we obtained two types of relations between the mean density, the density in an infinitesimal volume of adsorbed water and the quantity P in the form

$$d_{b_1} = A\exp(-mP^n) + d'' = 0.715\exp(-0.26P^{0.75}) + 1, \tag{6}$$

$$\frac{dP}{dV} = d' = \frac{[A + d''\exp(mP^n)]^2}{\exp(mP^n)[A + AmnP^n + d''\exp(mP^n)]} = \frac{[0.715 + \exp(0.26P^{0.75})]^2}{\exp(0.26P^{0.75})[0.715 + 1.43P^{0.75} + \exp(0.26P^{0.75})]} \tag{7}$$

in the moisture content range 5.4–13.6% and

$$d_{b_2} = A\exp(-mP^n)[1 - (P-b)^c(B-P^D)^k] + d'' = 0.715\exp(-0.26P^{0.75}) \times [1 - (P-1.0)^{0.75}(1.96 - P^{0.4})^{1.1}] + 1, \tag{8}$$

$$\frac{dP}{dV} = d' = \left(d_{b_2}^2\right) \times \left(d_{b_2} + mnP^n[d_{b_2} - 1] + [d_{b_1} - d_{b_2}]\left[\frac{cP}{P-b} - \frac{kDP^n}{B-P^D}\right]\right)^{-1} \tag{9}$$

in the range 0.0–5.4%.

We also obtained equations for calculating the effective specific surfaces of different parts of the crystal lattice:

$$S_{\text{eff. in}} = 2\frac{s'}{v'}\int_0^{P_{m2}} \frac{dP}{d'} = 244.6\ \text{m}^2/\text{g}, \tag{10}$$

$$S_{\text{eff. ex}} = \frac{s'}{v'}\int_{P_{m2}}^{P_m} \frac{dP}{d'} = 443.6\ \text{m}^2/\text{g}, \tag{11}$$

$$S_{\text{eff. total}} = S_{\text{eff. in}} + S_{\text{eff. ex}} = 688.2\ \text{m}^2/\text{g}. \tag{11a}$$

Relations (6–9) are presented in Fig. 2. They are similar to those obtained for natural Crimean kill and Pyzhev bentonite [5].

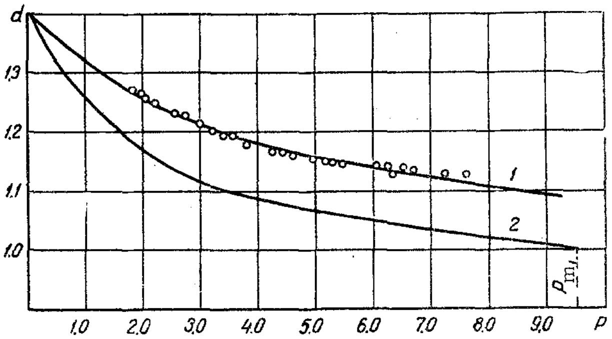

Fig. 3. Bound water density d, g/cm^3, as a function of the bound water content P, %, for Na cation-substituted Cherkassy bentonite: 1) values of mean bound water density $d = d_b$; 2) values of density of adsorbed water in an infinitesimal volume $d = d'$.

It is known that an absorbing complex of natural bentonites contains about 20% Ca cations; therefore total substitution with these cations cannot sharply change the adsorption properties of the mineral. However, it is possible to observe a certain decrease in the bound water density (peaks in the 5–5.5% zone on curves 1, 4, Fig. 2) around the edges of alumosilicon units of the crystal lattice as compared with natural clays. This effect is evidently associated with partial compensation of the charges on shear areas of the parent surface by adsorbed cations.

For Na cation-substituted Cherkassy bentonite we obtained relations (Fig. 3) between the mean density, the density in an infinitesimal volume of adsorbed water, and the quantity P in the following form:

$$d_b = A\exp(-mP^n) + d'' = 0.4\exp(-0.25P^{0.75}) + 1, \tag{12}$$

$$\frac{dP}{dV} = d' = \frac{[A + d''\exp(mP^n)]^2}{\exp(mP^n)[A + AmnP^n + d''\exp(mP^n)]} = \frac{[0.4 + \exp(0.25P^{0.75})]^2}{\exp(0.25P^{0.75})[0.4 + 0.075P^{0.75} + \exp(0.25P^{0.75})]}. \tag{13}$$

The solution of Eq. (13) for $d' = d'' = 1\ g/cm^3$ gives $P_m = 9.62\%$ of the moisture content.

Curves 2 and 4 in Fig. 2, which are characteristic of natural and Ca cation-substituted bentonite clays and describe the bound water density distribution on the internal surfaces of the structural elements of the crystal lattice [5], are missing in Fig. 3.

Adsorption Characteristics of Glukhovets Kaolin and Its Cation-Substituted Forms

Adsorbent	Coefficient			P_m,%		S, m^2/g	
	A, g/cm^3	m $(1/g)^n$	n	From density distribution curves	From heat of wetting [3]	From density distribution curves	From heat of wetting [3]
Natural Glukhovets kaolin	0.843	1.242	0.75	1.364	1.1	80.24	76.0
Ca cation-substituted Glukhovets kaolin	0.878	2.447	0.75	0.556	0.680	21.7	38.0
Na cation-substituted Glukhovets kaolin	0.698	3.593	0.75	0.320	0.314	19.0	21.7

Hendricks, Nelson, and Alexander [8], investigating the adsorption of water by montmorillonite saturated with various cations, obtained for Na-montmorillonite prepared at 5 and 10% relative humidity an interplanar spacing along the perpendicular to the cleavage equal to 9.8 Å, the amount of water adsorbed by this mineral corresponding to 2.5–4% of the moisture content. It is clear that in this case all the adsorbate was distributed exclusively over the external basal surface of the montmorillonite. According to [8], the beginning of formation of a layer of bound water on the internal surfaces of the structural elements is observed at a relative humidity of about 40% when 10.5% of the water is bound. Therefore, our curves 1 and 2 in Fig. 3 indicate the distribution of adsorbed water density only on the external basal surfaces of the mineral. As in the case of disperse systems with a nonexpanding crystal lattice, the equation for calculating the external effective specific surface for the Na form of Cherkassy bentonite will be

$$S_{\text{eff. total}} = \frac{s'}{v'} \int\limits_0^{P_m} \frac{dP}{d'} = 615 \ \text{m}^2/\text{g}. \qquad (14)$$

NOTATION

d_b is the mean density of bound water; P is the weight of bound water; d" is the density of free water; d' is the density of adsorbed water in an infinitesimal volume; A, m, n, B, c, b, D, k are the coefficients determined by the physicochemical properties of the adsorbent surface; $S_{\text{eff. total}}$ is the total effective specific surface; $S_{\text{eff. ex}}$ is the effective specific surface of shear areas and external basal areas; $S_{\text{eff. in}}$ is the effective specific surface of internal areas of structural elements of crystal lattice; P_m, P_{m1} are the amounts of bound water corresponding to the formation of a monomolecular layer on the external basal areas and shear areas of the mineral; P_{m2} is the same on the internal basal surfaces of the expanding crystal lattice of the mineral; s' is the area occupied by a single water molecule on the surface of the adsorbent (in our calculations $s' = \delta^2$, δ is the diameter of the water molecule); v' is the volume of a single water molecule.

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