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Fig. 1

Figure 1: Fig. 1

Abstract

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A Comprehensive Study of the Structure of Certain Natural Disperse Systems with an "Elastic" Skeleton

(Presented by Academician M. M. Dubinin, February 26, 1965)

A comprehensive study of the structure of highly disperse and porous bodies makes it possible to reveal most fully the structural features of the specimens under investigation and, consequently, to indicate more precisely the ways in which they may be used. A critical comparison of the data obtained in this way makes it possible to establish the limits of applicability and the accuracy of various independent methods.

Similar studies have been carried out by M. M. Dubinin and T. G. Plachenov with collaborators for coals ([1,2]), by A. V. Kiselev, V. M. Lukyanovich, I. E. Neimark, and E. A. Porai-Koshits with collaborators for silica gels ([3,4]), by V. T. Bykov with collaborators for natural sorbents of the Far East ([5]), and by other authors.

Fig. 1. Isotherms of sorption of water vapor *(a)* and benzene *(b)* by Trepel clays at 20 ± 0.1°.
1 —adsorption, 2 —desorption

We have carried out a comprehensive study of the structure of montmorillonite-containing trepel clays from a number of deposits in the Volga region ([6]). In doing so, we used adsorption-structural ([7]), mercury-porosimetric ([8,9]), and, for the general characterization, electron-microscopic and X-ray methods.

The breadth and diffuseness of the lines of the diffraction rings in the X-ray patterns and the presence of a large number of fine particles of various sizes in the electron-microscopic photographs indicate the polydispersity of the specimens under consideration ([6]). The particles possess a branched network of transition pores.

The presence of a branched network of transition pores is also well confirmed by the data of adsorption-structural analysis, which was carried out from isotherms of sorption of water and benzene vapors. The investigations were performed on a vacuum sorption apparatus with spring balances ([10]). The vapor sorption isotherms for the clays (Fig. 1) have an S-shaped form, characteristic of sorbents in which sorption is accompanied by capillary condensation. For all specimens, a loop of large irreversible hysteresis is characteristic, reflecting the noncoincidence of the adsorption and desorption branches of the isotherms over the entire range of relative pressures. Irreversible hysteresis indicates irreversible sorption of part of the adsorbate, which is associated with swelling of the clay minerals and partial chemisorption of the adsorbate in the interpacket layers of montmorillonite. Swelling of the specimens in benzene vapor is small (the displacement of the desorption branch of the isotherm relative to the adsorption branch is ~ 0.1—0.2 mmol/g), whereas in

in water vapor reaches a considerable value (swelling ~ 2.3 mmole/g). This indicates that the investigated samples of trepel-like clays have an "elastic" skeleton, which agrees well with their mineralogical composition ([6]).

However, despite swelling, from the desorption branches of the isotherms one can calculate, by the Thomson equation, the distribution of pore volume according to the values of their effective radii. The samples are characterized by a gradual decline of the curve of pore-volume distribution by radius, which makes it possible to classify them as sorbents with a heteroporous structure.

Table 1

Comparative characterization of the sorption capacity of trepel-like clays

Sample No.	Deposit	$S^{*}_{H_2O}$	$S^{*}_{C_6H_6}$	$S^{**}_{H_2O}$	$S^{**}_{C_6H_6}$	S^{***}	V_{Σ}, cm^3/g	V_S by benzene, cm^3/g	V_S by water, cm^3/g
7	village of Razboishchino, Saratov Region	210	60	285	50	15	0.100	0.104	0.234
10	Udarnik state farm, Saratov Region	270	164	280	100	22	0.202	0.244	0.360

Sample No.	Deposit	$S^{*}_{H_2O}$	$S^{*}_{C_6H_6}$	$S^{**}_{H_2O}$	$S^{**}_{C_6H_6}$	S^{***}	V_{Σ}, cm^3/g	V_S by benzene, cm^3/g	V_S by water, cm^3/g
13	city of Saratov, Altynnaya Hill	225	75	320	70	30	0.130	0.115	0.220
16	city of Saratov, Lopatina Hill	165	75	305	70	20	0.095	0.077	0.133
26	city of Saratov, Lopatina Hill	220	115	290	80	35	0.166	0.196	0.277
36	city of Saratov, Lopatina Hill	170	105	295	65	35	0.157	0.214	–

* Values of specific surface areas by BET.
** The same, by heats of wetting.
*** The same, according to mercury porosimetry data.

The values of the volumes of water and benzene adsorbed at $P/P_S = 1$ do not coincide (Table 1). This is connected with the nature of the vapor and the structure of the principal pore-forming mineral, montmorillonite, since in this case, in the sorption of vapors, in addition to the surface of the sorbent skeleton, the interlayer spaces of the crystalline structure of the mineral also participate.

The influence of the elastic skeleton was also reflected in the values of the specific surface area. The values of the specific surface area of the skeleton of the clay samples studied were determined by the BET method (^{11}). The use of the

Fig. 2. Differential structural curve of pore-volume distribution by radii for specimen No. 7. 1 –according to mercury porosimetry data, 2 –according to capillary condensation of benzene vapor data

Figure 2: Fig. 2. Differential structural curve of pore-volume distribution by radii for specimen No. 7. 1 –according to mercury porosimetry data, 2 –according to capillary condensation of benzene vapor data

BET method for determining the specific surface area in this case is of a formal character because of the change in interlayer distances of the crystal lattice in the process of vapor sorption, especially water vapor. Nevertheless, this method makes it possible to estimate, in a first approximation, the value of the specific surface area of the clay skeleton (Table 1). The values of specific surface area by water considerably exceed the specific surface areas by benzene (Table 1), which is connected with the nature of the adsorbate and adsorbent, as well as with the nature of their interaction with one another.

The specific surface areas of clays determined from the heats of wetting ([12]) by water and benzene (Table 1) are somewhat overestimated for water, while for benzene they have the same order as the specific surface areas determined from sorption isotherms. This is explained by the fact that, when calculating the specific surface area by the BET method, we take into account only the adsorption of a monomolecular layer. When calculating the specific surface area from heats of wetting, we also carry out the calculation by formally taking into account only the interaction of a monomolecular layer of liquid with the adsorbent, whereas the thermal effect observed by us relates not only to the monomolecular layer but also to other layers formed during adsorption, and in the present case also to swelling of the samples.

The values of the specific surface areas calculated on the basis of the porograms* are very low (Table 1). This is associated with the distribution of the pore volume of the specimens according to their effective radii. On the differential structural curves obtained from benzene vapor sorption data, rises are clearly observed in the region of 20–50 Å and in the region of 13 Å (Fig. 2), characterizing the presence of developed porosity in the region of transitional pores and micropores.

Fig. 2. Differential structural curve of the distribution of pore volumes by radii for specimen No. 7. **1** –according to mercury porosimetry data, **2** –according to capillary condensation of benzene vapor data

Differential structural curves obtained from mercury porosimetry data do not cover the region of micropores and part of the region of transitional pores (Fig. 2), which mainly determine the magnitude of the specific surface areas of the specimens studied. When the pressure is increased to 1400 kg/cm^2, the walls of pores with radius < 50 Å do not withstand the mercury pressure and are destroyed. This is indicated by the rise of the differential structural curve at

$r < 50$ Å. The presence of macropores is observed in the region from 300 to 30,000 Å.

A comprehensive study of specimens of montmorillonite-containing trepel-like clays shows that they possess a bidisperse, and possibly polydisperse, structure and belong to the 4th structural type according to the classification of A. V. Kiselev (13). Comparison of the data obtained by different methods makes it possible to establish the limits and possibilities of their application. The adsorption-structural method makes it possible to characterize the structure of the clays studied in the region of micro- and transitional pores with radii up to 300 Å, while the mercury-porosimetry method characterizes the structure in the region of transitional pores with radii > 50 Å and in the region of macropores. The X-ray and electron-microscopic methods made it possible to give only a general characterization of the clays because of their polydispersity, in the presence of which some particles are superposed on others and the electron densities of particles or pores overlap one another, and also because of the imperfection of the method used (6).

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* The porograms were obtained with a PA-3m mercury porosimeter (^{9}).

Note: Figure translations are in progress. See original paper for figures.