Physical Chemistry

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Abstract

Full Text

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STUDIES IN THE PHYSICOCHEMICAL MECHANICS OF AQUEOUS DISPERSIONS OF CLAYS TREATED WITH CALCIUM HYDROXIDE

The study of the features of the processes of coagulation structure formation in aqueous clay dispersions is of great importance for explaining a number of surface phenomena that occur in drilling clay suspensions when they are treated with various chemical substances. One type of such treatment is the inhibition of clay suspensions with calcium hydroxide.

A number of authors believe (^{1}) that the action of calcium hydroxide on aqueous clay dispersions consists mainly in ion-exchange substitution of clay sodium by calcium. We have established, however, that when clay suspensions are treated with $Ca(OH)_2$ (Table 1), under ordinary conditions of pressure and temperature the process of chemical interaction of lime with the surface of clay particles predominates (^{2}), while the ion-exchange substitution of clay sodium by calcium, occurring upon the introduction of the first portions of lime, plays a considerably smaller role in changing the properties of the suspension.

Table 1

Structural-mechanical characteristics of aqueous clay dispersions

Clays	Concentration, %	Amount of $Ca(OH)_2$, mg per 100 g of sample	$E_1 \cdot 10^{-3}$, dyn/cm^2	$E_2 \cdot 10^{-3}$, dyn/cm^2	P_{k1}, dyn/cm^2	$\eta_1 \cdot 10^{-5}$, poise	λ	$\left\lvert \frac{P_{k1}}{\eta_1} \right\rvert \cdot 10^6$, sec^{-1}	θ_1, sec	$K_y = \varepsilon_0/C$	Structural-mechanical type
Askanian	10.0	–	3.75	8.0	10	125	0.320	8.0	3830	2.23	O
Askanian	10.0	450	35.0	9.1	36	25	0.735	14.6	343	0.52	U

Clays	Concentration, %	Amount of $Ca(OH)_2$, mg per 100 g of sample	$E_1 \cdot 10^{-3}$, dyn/cm^2	$E_2 \cdot 10^{-3}$, dyn/cm^2	P_{k1}, dyn/cm^2	$\eta_1 \cdot 10^{-5}$, poise	λ	$\left\|\frac{P_{k1}}{\eta_1}\right\| \cdot 10^6$, sec^{-1}	θ_1, sec	$K_y = \varepsilon_0/C$	Structural-mechanical type
Chasov-Yarskaya	24.2	–	13.50	8.0	55	25	0.629	22.0	498	0.51	U
Chasov-Yarskaya	24.2	120	32.60	20.0	18	35	0.621	5.3	117	0.34	U
Khablovskaya	60.0	–	100.00	15.0	180	142	0.662	12.6	1092	0.11	U
Khablovskaya	60.0	30.0	27.20	13.6	15	23	0.670	6.5	256	0.10	U

At the same time it has been shown that, on the X-ray diffraction patterns of clays treated with $Ca(OH)_2$, additional sharp reflections appear, belonging to a new phase characterized by a highly symmetric structure and good crystallinity. The diffraction pattern of the newly formed material indicates the presence of two crystalline forms: calcite—$CaCO_3$—and calcium hydrosilicate—$6CaO \cdot 3SiO_2 \cdot 2H_2O$. The surface character of the formation of calcium hydrosilicate and the absence of any significant bulk destruction of the clay particles during liming is demonstrated by the invariance of the external configuration of the shapes of the clay flakes in electron-microscopic photographs and by the preservation of the lines corresponding to these minerals on the X-ray diffraction patterns before and after liming.

The study, by methods of physicochemical mechanics of disperse systems (^{3}), of the features of the coagulation structures formed in aqueous clay dispersions made it possible for the first time to elucidate the mechanism of the action of calcium hydroxide on them. The studies were carried out on samples of montmorillonite, monotermite, and a polymineral mixture of kaolinite and hydromica, differing from one another in mineralogical composition and physicochemical properties.

The dimensions of individual crystals of montmorillonite from the Askanian deposit of the Georgian SSR lie within the range 0.02–0.15 μ. The total cap—

the cation-exchange capacity is 61 mg-eq/100 g of sample, the heat of wetting with water Q is 10.8 cal/g, and the effective specific surface area S is 389 m^2/g.

Montmorillonite suspensions at low concentrations of the solid phase (10%) are characterized by low values of the conditional instantaneous modulus of elasticity E_1, the modulus of elasticity E_2, and the conditional static yield stress P_{k_1}, and by elevated values of the greatest plastic viscosity η_1. Owing to the small size of individual crystals and the presence of a considerable number of particles per unit volume, the system develops large elastic conditional instantaneous deformations ε_0' (^{4}). The values of its structural-mechanical characteristics (elasticity λ, plasticity P_{k_1}/η_1, and the period of true relaxation θ_1) indicate the development of stable coagulation structures (Table 1) (^{15}).

When aqueous dispersions of montmorillonite are treated with calcium hydroxide, the pattern of the deformation process changes sharply; this is apparently connected with the process of autocoagulation, accompanied by a decrease in the number of structure-forming particles per unit volume due to aggregation of the system. This is confirmed by the decrease in hydrophilicity ($Q = 8.3$ cal/g) and in the effective specific surface area ($S = 332$ m^2/g) of the dispersed phase (^{6}).

Consequently, the introduction of $Ca(OH)_2$ contributes, through the formation of calcium hydrosilicate, to a reduction in the number of hydrogen bonds and to the blocking of active centers of the external and internal surfaces of montmorillonite, thereby hindering ion-exchange processes and causing aggregation of the particles of the system. The latter is confirmed by the decreased development of elastic conditional instantaneous deformations and by the increased development of plastic ε_1', τ. The stability coefficient K_y of the limed suspension decreases by more than a factor of four (Table 1).

The presence of hydrophobization and aggregation processes is confirmed by the sharp increase (with the exception of the greatest plastic viscosity) in the structural-mechanical constants, elasticity, and plasticity, and by the decrease in the period of true relaxation; moreover, the values of the structural-mechanical characteristics of coagulation structures once again indicate the development of autocoagulation phenomena.

The monotermite from the Chasov-Yar deposit of the Ukrainian SSR consists predominantly of an aggregate of kaolinite and hydromica (^{2},^{7}). The latter is dioctahedral, with Al^{3+} in octahedral positions. Kaolinite has an imperfect structure, although elements of three-dimensionality are preserved in it. Electron-microscopic photographs also show a mixture of pseudohexagonal and isometric flakes belonging to different phases. The dimensions of kaolinite are 0.1–0.3 μ, and those of hydromica are 0.1–0.4–1.0 μ. Monotermite has a comparatively high cation-exchange capacity (44.5 mg-eq/100 g of sample), hydrophilicity ($Q = 5.0$ cal/g), and effective specific surface area ($S = 180$ m^2/g).

Monotermite suspensions at considerable concentrations of the dispersed phase (24.2%) develop small elastic conditional instantaneous deformations (^{8}). The comparatively low aggregate stability of these suspensions is indicated by the low values of the stability coefficient and the corresponding values of the structural-mechanical characteristics.

When the suspensions are treated with calcium hydroxide, there is an increase in the structural-mechanical constants, with the exception of a decrease in the conditional static yield stress. The aggregate stability of the system, compared with the initial suspension, decreases ($K_y = 0.34$). A decrease is observed in elasticity, plasticity, and the period of true relaxation. Coagulation structures develop somewhat smaller elastic conditional instantaneous deformations than the initial ones.

The changes described in the processes of coagulation structure formation once again point to phenomena of hydrophobization of clay particles due to the surface formation of calcium hydrosilicate. Limed

the Chasov-Yar clay is characterized by reduced hydrophilicity ($Q = 4.1$ cal/g) and effective specific surface area ($S = 147.7$ m^2/g).

The particle sizes of the monomineral constituents of the kaolinite–hydromica clay from the Khabl' deposit in Krasnodar Krai range within 0.3—0.5 μ. Among the clays studied, the Khabl' clay has the minimum cation-exchange capacity (22.7 mg-eq/100 g of sample), specific effective surface area ($S = 90$ m^2/g), and hydrophilicity ($Q = 2.5$ cal/g). Aqueous dispersions of this clay (60%), in comparison with those of the other clays, are characterized by maximum values of E_1, P_{k_1}, η_1. The system develops approximately equal magnitudes of elastic ε_2 and plastic deformations at small values of elastic instantaneous deformations. Its structural-mechanical characteristics indicate the formation of unstable coagulation structures. The aqueous dispersions possess comparatively high aggregative lability, as is confirmed by the low K_y.

The action of calcium hydroxide on suspensions of Khabl' clay, at their sufficiently high fluidity, is directed toward a significant decrease in the structural-mechanical constants (Table 1). The system is characterized by increased elasticity, decreased plasticity, and a decreased period of true relaxation. Owing to significant aggregation of the particles, as a result of the hydrophobization process ($Q = 2.2$ cal/g; $S = 73.1$ m^2/g), aqueous dispersions of Khabl' clay develop smaller elastic instantaneous deformations than the initial suspensions. In the system there is a further decrease in the stability coefficient and the formation of unstable coagulation structures.

As is evident from the data considered, treatment of aqueous dispersions of the clays studied with calcium hydroxide leads to a sharp change in their structural-mechanical characteristics. The nature of this change indicates autocoagulation occurring as a result of chemical interaction with the formation of calcium hydrosilicate, which causes hydrophobization of the system; this is accompanied by a regular decrease in hydrophilicity and in the effective specific surface area. Naturally, in this case the process of formation of coagulation structures occurs with a significantly smaller number of active structure-forming particles per unit volume, which is confirmed by the weak development of elastic instantaneous deformations.

All these processes are most pronounced in the treatment of montmorillonite suspensions with calcium hydroxide, which is explained by the special structure of the latter, associated with the presence of external and internal surface.

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