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Abstract

Full Text

PHYSICAL CHEMISTRY

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MECHANISM OF THE EFFECT OF ULTRASONIC OSCILLATIONS ON THE PROCESSES OF COAGULATION STRUCTURE FORMATION IN AQUEOUS DISPERSIONS OF CLAYS

Mechanical treatment is one of the most effective methods of influencing the processes of coagulation structure formation in aqueous dispersions of clays, the structural features of which determine their behavior in various technological processes ^(1,2). In the present communication we present the results of a study of ultrasonic effects on the mechanism of deformation processes and on the stability of aqueous clay dispersions, based on the concepts and methods of the physicochemical mechanics of disperse systems ⁽¹⁾.

The objects of study were clays that form aqueous dispersions with different coagulation structures and stability (Table 1).

Table 1

Structural-mechanical characteristics of ultrasonicated aqueous dispersions of clays

Ultrasonication duration, min	$E_1 \cdot 10^{-3}$, dyn/cm ²	$E_2 \cdot 10^{-3}$, dyn/cm ²	$E \cdot 10^{-3}$, dyn/cm ²	$P_{k1} \cdot 10^{-1}$, dyn/cm ²	$\eta_1 \cdot 10^{-5}$, poise	λ	$\frac{P_{k1}}{\eta_1}$, sec ⁻¹	θ_1 , sec	E_ϵ conventional, 10^{-2} , erg/cm ³ ₀ /C	Structural-mechanical type	
Cherkassy montmorillonite clay											
$C = 15\%$											
—*	26	16	9.9	17.5	11	0.620	159	111	10.8	0.11	V
7.0	6.2	5.0	2.8	1.5	22	0.551	6.81	785	12.3	1.33	V
8.5	50	83	31.2	7.0	460	0.376	1.52	1475	189	2.52	IV
9.5	22	27	12.1	4.4	110	0.449	4.00	910	58.4	1.78	IV
14	30	35	16.1	5.0	83	0.461	6.02	515	55.7	1.25	IV
18	25	23	12.0	8.0	50	0.521	16.0	416	36.2	0.97	V
Cherkassy palygorskite-montmorillonite clay											
$C = 10\%$											
—**	22	60.0	16.0	21.0	270	0.268	7.78	1680	101	3.17	III
1.5	5.0	12	3.5	2.8	80	0.294	3.50	2280	24.6	4.94	III
3.0	8.8	20	6.1	3.2	141	0.306	2.27	2310	42.8	4.86	III
6.0	9.6	22	6.7	5.0	205	0.304	2.44	3060	50.8	5.27	III
7.0	107	320	81	55	1860	0.251	2.96	3380	610	5.70	III

* $C = 38.2\%$

** $C = 14.5\%$

Ultrasonic treatment is characterized by the following data: oscillation frequency 19.5 kHz, amplitude of the alternating ultrasonic pressure 6 atm, amplitude of particle oscillations 2.42μ , amplitude of particle acceleration $3.6 \cdot 10^6$ cm/sec².

Cherkassy montmorillonite. The results of structural-mechanical, X-ray

Fig. 2. Electron-microscopic images of clays.

Figure 1: Fig. 2. Electron-microscopic images of clays.

Fig. 1

Figure 2: Fig. 1

structural, and electron-microscopic analyses lead to the following considerations concerning the mechanism of action of ultrasonic oscillations on the formation of coagulation structures of montmorillonite.

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Fig. 2. Electron-microscopic images of clays. **1** –Cherkassy montmorillonite; **2** –the same, ultrasonicated for 5 min; **3** –the same, ultrasonicated for 8.5 min; **4** –the same, ultrasonicated for 14 min; **5** –palygorskite-montmorillonite clay; **6** –the same, ultrasonicated for 1 min; **7** –the same, ultrasonicated for 3 min; **8** –the same, ultrasonicated for 6 min; **9** –the same, ultrasonicated for 7 min.

The instantaneous increase and decrease of pressure in the suspension under the action of a traveling wave, and the intense oscillations of the particles of the dispersed phase with very large accelerations, first of all cause cavitation rupture of the bonds between the dispersed phase and the dispersion medium and lead to a more uniform distribution of the dispersed phase and to the formation of more perfect hydrate shells. This is indicated by the growth of elastic ε'_2 deformations (Fig. 1) and by the decrease in the moduli and in the conditional static yield point P_{k_1} (Table 1). At the same time, the impact action of the ultrasonic wave, the intense oscillations of the particles, and their collisions with one another cause dispersion of the particles and a significant increase in the number of structural defects (Fig. 2, insert to p. 1364). This is accompanied by a sharp increase in the greatest plastic viscosity η_1 , in the elastic conditionally instantaneous ε'_0 deformations, and by a decrease in the plastic $\varepsilon'_1\tau$ deformations. Within 7 min the process of distribution of the hydrate films is completed and the elastic deformations reach their maximum development. The process of dispersion of clay particles continues for another 1.5 min. After 8.5 min, dispersion reaches its limiting development, at which the elastic conditionally instantaneous deformations become maximal. The coagulation structure formed possesses the highest value of bond energy and stability.

Fig. 1. Dependence of the conditional deformation modulus E_ε , of the elastic conditionally instantaneous ε'_0 , elastic ε'_2 , and plastic $\varepsilon'_1\tau$ deformations on the time of ultrasonic treatment of aqueous clay dispersions.

a–Cherkassy montmorillonite; –Cherkassy palygorskite-montmorillonite clay

It should be assumed that ultrasonic oscillations, rearranging the structure of the suspension in accordance with their own characteristics, after dispersion

of the particles to a certain size and their corresponding arrangement in the volume, create so great an increase in the free surface energy (in the present case by a factor of 17) that the increased forces of molecular action begin to hinder further destruction of the crystals. At the same time, it is possible that a synchronicity of motion is created, determined by the frequency and amplitude of the oscillation, and by the size and distribution of the particles. Dispersion ceases. The coagulation structure obtained is the most perfect.

With further treatment of the suspensions, the process of coarsening of the particles, or so-called autocoagulation, begins. It is expressed in a decrease in the values of the structural-mechanical constants—the period of true relaxation θ_1 , the conditional deformation modulus E_ε , the stability coefficient ε'_0/c —and in an increase in elasticity λ and plasticity P_{k_1}/η_1 . At first there occurs a sharp, and then a more gradual, decrease in the development of elastic conditionally instantaneous deformations and a growth of plastic deformations. Destroyed particles with very-

with high surface energy, during collisions, in some cases—apparently during the completion of the structure—may join so firmly that subsequent ultrasonic waves are unable to destroy them. In the process of coarsening, the particles acquire distinct outlines, i.e., the crystalline structure of the particles is perfected; these particles become the basis for the formation of a new coagulation structure, the third in terms of structural-mechanical characteristics (Fig. 2).

Cherkasy palygorskite-montmorillonite clay. The results of ultrasonic treatment of the clays studied are analogous: a new coagulation structure is formed, stable with respect to ultrasonic action. However, the effect of ultrasound on the process of structure formation and on the properties of the structures formed differ markedly from one another. In a suspension of palygorskite-montmorillonite clay, in the first period of time (1.5 min), the primary aggregates are destroyed (Fig. 2) and the water envelopes are redistributed. This is accompanied by an increase in elastic deformations and a considerable decrease in the values of the structural-mechanical constants and the conditional modulus of deformation (Fig. 1). At the same time, dispersion of the montmorillonite packets begins, reaching their limiting destruction by the seventh minute and releasing, for the formation of a coagulation structure, about 60–80% of the total bonding energy that had not previously participated in the formation of the coagulation structure. In parallel, dispersion of palygorskite crystals proceeds, occurring predominantly along the channels on the C axis and, in turn, producing a large number of disturbances of the crystal lattice and additional reserves of bonding energy for the formation of a coagulation structure.

The separation and destruction of minerals and the ever-increasing imperfection of their surface create the possibility of forming new, more strongly bound aggregates capable of resisting the action of ultrasound; in their construction, particles of montmorillonite packets and palygorskite crystals that have been maximally destroyed (for the given frequency and amplitude of oscillations) take part, in ratios corresponding to the formation of the greatest number of contacts

and especially inclusion contacts. Possibly, these ratios are determined by the magnitudes of the effective surfaces participating in the formation of mineral aggregates. The significant number of free palygorskite crystals indicates that a considerably smaller amount of palygorskite participates in the construction of aggregates of the first type than in the aggregates of the primary structure. The stages of formation and growth of new aggregates as they accumulate are accompanied by a gradual increase in the structural-mechanical constants, the conditional modulus of deformation, elastic instantaneous deformations, and by a decrease in plastic ones. The continuing destruction of minerals, the continuous increase in the forces of molecular interaction, the deficiency of montmorillonite, and the excess of palygorskite lead to the formation of aggregates of the second type, with a predominance of palygorskite, for which a parallel arrangement of palygorskite crystals and a comparatively small number of montmorillonite particles are characteristic. The formation of aggregates of the first and second types subsequently occurs simultaneously, although the onset of formation of the former belongs to the third minute, and of the latter—to the sixth minute. The gradual accumulation of aggregates with a very strong coagulation structure by the seventh minute leads to a sharp qualitative jump: individual aggregates increase markedly and join into a common spatial structure with entirely new, considerably higher structural-mechanical characteristics.

Thus, acting on aqueous dispersions of clay minerals, ultrasound destroys their coagulation structures, promotes a uniform distribution of water envelopes, and disperses particles of the very

minerals (montmorillonite and palygorskite) and forms new mineral aggregates of increased strength, carrying out their selection and accumulation. The type of clay mineral and the degree of perfection of its crystalline structure, under the given parameters of ultrasonic action, determine the course of the process of change in the dispersed phase and the properties of the coagulation structure that is formed.

A clay mineral of imperfect structure—montmorillonite—forms two types of structures: one at the moment of the highest dispersion of the packets, distinguished by very high bond energy and stability, and a second after the formation of new montmorillonite crystals with lower structural-mechanical characteristics and stability. A natural mixture of palygorskite and montmorillonite forms two types of aggregates of the dispersed phase: the first with a predominance of montmorillonite and the second with a predominance of palygorskite. The coagulation structure formed by them possesses very high structural-mechanical characteristics and stability.

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