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Fig. 1

Figure 1: Fig. 1

Abstract

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THE ACTION OF ULTRASOUND ON COAGULATION STRUCTURES OF AQUEOUS DISPERSIONS OF KAOLINITE AND MONOTHERMITE

In previous communications (1) we presented the results of investigations of the influence of ultrasonic oscillations on the process of coagulation structure formation in aqueous dispersions of montmorillonite and a natural palygorskite-montmorillonite mixture. In the present communication, on the basis of the concepts and methods of the physicochemical mechanics of disperse systems (2) and their application to dispersions of clay minerals (3), studies are considered of ultrasonic effects on the character of deformation processes (Fig. 1) and on the stability of aqueous dispersions of Glukhovets kaolinite and Chasov Yar monothermite (4).

Fig. 1. Dependence of the rapid elastic ε'_0, slow elastic ε'_2, and plastic $\varepsilon'_1\tau$ deformations and of the conditional modulus of deformation $E_{\varepsilon\,\text{cond}}$ on the time of ultrasonic treatment of aqueous clay dispersions.
a –Glukhovets kaolinite; *b* –Chasov Yar monothermite

Glukhovets kaolinite

The results of structural-mechanical, X-ray structural, and electron-microscopic analyses lead to the following considerations regarding the mechanism of action of ultrasonic oscillations on the formation of coagulation structures of kaolinite.

Figure 2: Electron-microscopic images of clays

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In the initial period of time (0–1 min), the impact action of the ultrasonic wave, intensive oscillations of particles, and their collisions with one another cause cavitational rupture of the bonds between the disperse phase and the dispersion medium and lead to a more uniform distribution

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Fig. 2. Electron-microscopic images of clays. **1** –Glukhovets kaolinite; **2, 3, 4, 5, 6** –Glukhovets kaolinite sonicated respectively for 1, 3, 12.5, 15, and 30 min; **7** –Chasov-Yar monotermite; **8, 9, 10** –Chasov-Yar monotermite sonicated respectively for 3, 6, and 15 min. 30,000×.

of the dispersed phase and the formation of more perfect hydrate shells. At the same time, a certain dispersion of the particles takes place (Fig. 2, 1 and 2; see inset to p. 853). Owing to this, the system is characterized by a decrease in the development of rapid elastic ε_0' and plastic $\varepsilon_1'\tau$ deformations and by an increase in slow elastic ε_2' deformations (Fig. 1). Such a suspension is characterized by a fall in the structural-mechanical constants, the period of true relaxation θ_1, the plasticity Pk_1'/η_1, the conditional deformation modulus $E_{\varepsilon\,\mathrm{cond}}$, the stability coefficient ε_0'/c, and by an increase in elasticity λ. In the deformation process, slow elastic deformations predominate, and the system passes into the second structural-mechanical type (Fig. 1) (^{5}).

Further sonication of aqueous kaolinite suspensions (3–12.5 min) causes the formation of a new coagulation structure of increased strength. In this time interval, subsequent dispersion of kaolinite particles occurs, new, stronger aggregates of the dispersed phase are formed, and a coagulation structure is created along new contacts and surfaces (Fig. 2, 3). Correspondingly, the development of rapid elastic deformations increases, while slow elastic and plastic deformations decrease (Fig. 1). In this time interval the system is characterized by a decrease in the structural-mechanical constants, the period of true relaxation, the conditional deformation modulus, the stability coefficient, and by a fall in elasticity and plasticity (Table 1).

Table 1

Structural-mechanical characteristics of sonicated aqueous dispersions of clays

Sonication time, min	$E_1 \cdot 10^3$, dyn/cm^2	$E_2 \cdot 10^3$, dyn/cm^2	$E \cdot 10^3$, dyn/cm^2	$Pk_1 \cdot 10^{-1}$, dyn/cm^2	$\eta_1 \cdot 10^5$, poise	λ	$\frac{Pk_1'}{\eta_1} \cdot 10^{-6}$, sec^{-1}	θ_1, sec	$E_{\varepsilon\,\mathrm{cond}} \cdot 10^{-2}$, erg/cm^3	ε_0'/c	Structural-mechanical type
Glukhovets kaolinite, $C = 58\%$											
–	1150	560	376	162	4500	0.673	3.6	1200	2150	0.32	V
1	750	145	121	180	1500	0.838	12.0	1240	700	0.16	II
3	800	360	192	200	2600	0.690	9.5	1095	1200	0.27	V
5	940	435	297	230	2700	0.683	8.5	910	1520	0.27	V
12.5	1520	790	520	370	5700	0.660	6.5	710	2980	0.34	V
15	715	380	248	170	2200	0.654	7.7	885	1220	0.20	V
30	1100	420	304	210	1220	0.725	17.2	402	940	0.15	V
Chasov Yar monotermite, $C = 15\%$											
*	14	8.0	5.1	5.5	25	0.636	22.0	490	17.0	0.50	IV
1.5	15	19	8.4	1.6	78	0.4441	2.05	930	40.6	1.8	IV
3.0	18	20	9.5	1.6	128	0.474	1.23	1345	54.6	2.02	IV
4.5	16	29	10.3	4.1	150	0.358	2.73	1455	61.8	2.44	IV
6.0	13	30	9.1	2.1	221	0.303	0.95	2430	64.5	3.25	III
8.0	8.6	12	5.0	1.5	106	0.417	1.42	2120	34.1	2.64	III
10.0	10	13	5.7	1.0	108	0.434	0.93	1890	37.2	2.48	III
15.0	11	15	6.4	1.0	133	0.424	0.75	2080	43.0	2.62	III

* $C = 24.2\%$.

With 12.5-min treatment by ultrasound (Fig. 2, 4), the kaolinite–water system shows the maximum development of rapid elastic deformations and minimum plastic deformations. High values of the conditional deformation modulus indicate the great strength of the coagulation structure. Aqueous dispersions of kaolinite at this sonication time are characterized by the maximum value of the structural-mechanical constants, the period of true relaxation, the stability coefficient, and by minimum values of elasticity and plasticity.

With further treatment of the suspensions, a secondary process of destruction of the previously formed aggregates begins; this is well confirmed by the sharp drop in the conditional deformation modulus in the interval 12.5–15 min and by the whole pattern of mechanical and electron-microscopic data (Fig. 2, 5).

At the same time, new aggregates are formed, connected with one another by fragments of kaolinite crystals with weaker molecular interaction. This third, as it were reticulate, structure (30 min; Fig. 2, 6) is characterized by a very considerable development of plastic deformations owing to higher moduli of elasticity and resilience, and by the lowest values of the highest plastic viscosity. The kaolinite dispersion becomes more elastic and highly plastic.

Thus, when aqueous dispersions of kaolinite are treated with ultrasound, in them there occurs (1 min) a rupture of the structural bonds between the disperse phase and the dispersion medium and destruction of the primary aggregates of the disperse phase, and a certain dispersion of the kaolinite particles begins. Then the ultrasonic action, as a result of dispersion, the liberation of a large amount of free surface energy, and the distribution of particles and hydrate films, causes the gradual formation of a new, more compact and stronger structure. In turn, after the completion of its formation (12.5 min), i.e., after the formation of aggregates of definite size and strength, this second structure, owing to the impossibility for kaolinite of forming stronger aggregates with completion of the crystalline structure, is also destroyed. A third coagulation structure arises, with an ordered arrangement of the structural network, very elastic and plastic. Under conditions of limited strengths of the aggregates of the disperse phase, this structure evidently most effectively resists the action of ultrasonic oscillations. Undoubtedly, the parameters of the suspension (particle sizes and their spatial distribution) and the parameters of ultrasonic action are inseparably connected with one another.

Chasov-Yar monothermite. Under the action of ultrasonic treatment in the initial period of time, particles of Chasov-Yar monothermite are intensively dispersed (Fig. 2, 7) with separation of kaolinite and hydromica. The outlines of the destroyed crystals are more sharply cut, which is clearly seen in electron-microscopic photographs. Such mechanical dispersion increases the number of disturbances in the crystalline structure and the number of structure-forming elements per unit volume. In accordance with this, the system is characterized by a gradually increasing development of rapid elastic deformations, an increase in the structural-mechanical characteristics, and a transition into the region of the fourth structural-mechanical type.

In the time interval 1.5–3 min, rupture of molecular bonds between the clay mineral and water takes place, as well as redistribution and formation of new, more uniformly distributed solvate shells. This process reaches its greatest development with 3-min treatment (Fig. 2, 8). In this case the system is characterized by comparatively increased elasticity and reduced plasticity. Subsequently (3-6 min), owing to the further dispersion of the particles (Fig. 2, 9), there is a decrease in the thickness of the solvate shells, which is accompanied by a decrease in the development of slow elastic and plastic deformations.

The maximum dispersion of aqueous dispersions of Chasov-Yar monothermite is revealed in electron-microscopic photographs after their 6-min treatment (Fig. 2, 9). The coagulation structure that is thereby formed belongs to the third structural-mechanical type. It consists of a large number of free crystals of kaolinite and hydromica with the smallest sizes of unit aggregates. The development of rapid elastic deformations in this structure is maximal, while that of slow elastic and plastic deformations is minimal. It is characterized by the largest values of the elastic modulus, the highest plastic viscosity, the period of true relaxation, the conditional modulus of deformation, and the stability coefficient.

With an increase in the sonication time to 8–15 min, aggregation of particles and the formation of new kaolinite-hydromica aggregates with increasing size are observed; this proceeds until the free crystals of kaolinite and hydromica completely disappear from the field of the electron microscope (Fig. 2, *10*). The formation of secondary aggregates leads to a decrease in the number of structure-forming particles per unit volume and, consequently, to a reduction in the development of rapid elastic deformations and to an increase in slow elastic deformations. All structural-mechanical characteristics in the system again decrease. A certain increase in the conditional deformation modulus in the sonication interval of 8–15 min should evidently be attributed to an increase over time in the number of kaolinite-hydromica aggregates. The coagulation structure that forms is characterized especially by the greatest development of slow elastic deformations, as if compensating for the low strength of the newly formed aggregates of the dispersed phase.

Thus, during ultrasonic treatment of monotermit dispersions, there first occurs (1-6 min) a rupture of the bonds between the dispersed phase and the dispersion medium, destruction of kaolinite-hydromica aggregates, and some dispersion of individual kaolinite and hydromica crystals. With 6-minute treatment this process reaches an optimum. The coagulation structure consists predominantly of individual small crystals of kaolinite and hydromica and becomes strong and stable.

More prolonged ultrasonic treatment (8–15 min), owing to the appearance of a large amount of free bond energy and the attainment of a critical particle size—particles which, evidently, are no longer destroyed under the specified parameters of the ultrasonic wave—leads to the formation of secondary kaolinite-hydromica aggregates, apparently of ordered composition, which form a third coagulation structure, compensating for the destructive action of the ultrasonic wave through maximal development of slow elastic deformations.

Kaolinite and kaolinite-hydromica minerals, when their aqueous dispersions are treated with ultrasound, first form coagulation structures of increased strength as a result of the destruction of their primary bonds and the dispersion of particles. Subsequently these structures pass into less strong but very elastic structures, in which equilibrium between the structure and the parameters of ultrasonic oscillations is established through large slow elastic deformations.

The natural mixture of kaolinite and hydromica, which is monotermit, changes the character of the formation of coagulation structures of its aqueous dispersions more intensively than pure kaolinite.

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CITED LITERATURE

1. N. N. Kruglitskii, V. V. Simurov, *Ukr. Khim. Zhurn.*, **30**, No. 8 (1964); N. N. Kruglitskii, V. V. Simurov, F. D. Ovcharenko et al., *Ukr. Khim. Zhurn.*, **30**, No. 12 (1964); N. N. Kruglitskii, V. V. Simurov, F. D. Ovcharenko et al., *DAN*, **159**, No. 6, 167 (1964).

2. N. V. Mikhailov, P. A. Rebinder, *Koll. Zhurn.*, **20**, 2, 105 (1955); P. A. Rebinder, *Proceedings of the Third All-Union Conference on Colloid Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1956, p. 7; P. A. Rebinder, *Physicochemical Mechanics—a New Field of Science*, 1958; P. A. Rebinder, *ZhVKhO im. D. I. Mendeleeva*, **8**, 2, 161 (1963).

3. S. P. Nichiporenko, *Basic Problems in the Theory of Treatment and Forming of Ceramic Bodies*, Publishing House of the Academy of Sciences of the Ukrainian SSR, 1960; F. D. Ovcharenko, *Hydrophilicity of Clays and Clay Minerals*, Publishing House of the Academy of Sciences of the Ukrainian SSR, 1961; F. D. Ovcharenko, S. P. Nichiporenko, *ZhVKhO im. D. I. Mendeleeva*, **8**, 2, 171 (1963).

4. Yu. A. Rus' ko, *Information Bulletin of the Academy of Sciences of the USSR, Geographic Department*, Publishing House of the Academy of Sciences of the USSR, 1961, p. 115.

5. F. D. Ovcharenko et al., *Colloid Chemistry of Palygorskite*, Publishing House of the Academy of Sciences of the Ukrainian SSR, 1963; N. N. Kruglitskii, *Ukr. Khim. Zhurn.*, **30**, 5, 115 (1964).

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