

EFFECT OF WETTING AGENTS ON THE DEFORMATION BEHAVIOR OF KAOLINITE-WATER SYSTEMS¹

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ABSTRACT

An experimental technique was developed for studying the deformation properties of kaolinite-water mixtures, and a study was made of the effects of different wetting agents on the deformation behavior of these mixtures. Particular care was taken to minimize physical effects that could be attributed to preferred orientation of clay particles. Evaluation of different compositions was made in terms of stress-strain diagrams obtained by means of a simple compression plastometer test. Auxiliary studies included sedimentation and filtration experiments of kaolinite-water mixtures containing wetting agents.

The various classes of wetting agents investigated, viz., anionic, cationic and nonionic wetting agents, were found to affect the deformability of clay-liquid mixtures independently of the surface tension of the liquid phase. As compared with water alone, cationic and nonionic reagents decreased and anionic reagents increased the deformability of clay-liquid mixtures.

In general, the sedimentation and filtration properties of kaolinite-water mixtures containing various wetting agents were consistent with the results of the deformation experiments.

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INTRODUCTION

Studies of the rheological properties of clay-water systems have proceeded along several lines. Many attempts have been made to discover how variations in clay mineral composition, non-clay mineral composition, electrolyte type and concentration, particle size distribution, and water content affect various rheological properties. These works have been directed toward obtaining information which would be useful to the clay technologist and mineralogist. Although many factors affecting the flow behavior of various clay-liquid systems have been well established, there is lack of agreement among many investigators regarding the effects of specific chemicals upon certain rheological properties. This disagreement can be attributed in part to differences in methods of testing and purity of materials. One of the more important factors frequently overlooked in studies of the plastic behavior of clays is the effect of particle orienta-

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tion. The orientation which is effected by various forming processes can be very great and unless this effect is evaluated results due to purely chemical processes may be biased. Orientation as a result of various forming processes has been studied by Williamson (1954, p. 129-143; 1947, p. 645-662; 1941, p. 280-292) and has been considered by Buessem and Nagy (1954, p. 489-491) in connection with their researches on the deformation behavior of clay-water systems. These latter workers were concerned primarily with the physical effects produced by orientation. A study of the chemical aspects of the deformation behavior of clay-water systems in which particle orientation was controlled was therefore indicated.

The effects of various types of polyelectrolytes upon the properties of clay-liquid systems have been studied by various workers in the fields of soil science and soil mechanics (e.g., Ruehrwein and Ward, 1952, p. 485-492). These researchers have been interested in materials which would stabilize soils or produce soils of improved tilth. It was found that certain types of chemicals (polycations) produced an open structure (flocculation) in the soils whereas other types (polyanions) produced a more dense structure (deflocculation). These results are consistent with those of Moilliet and Collie (1951, p. 123-129) and Reiner (1954, p. 61) who described the chemical or electrochemical effects produced by surface-active materials. Other researchers (Schwartz, 1952, p. 43; Kingery and Francl, 1954, p. 602) have reported that surface-active agents affect the plastic behavior of clay-water systems in a manner which is dependent on the original surface tension of the liquid phase and that little or no chemical effect is produced by different classes of surface-active substances. It seems

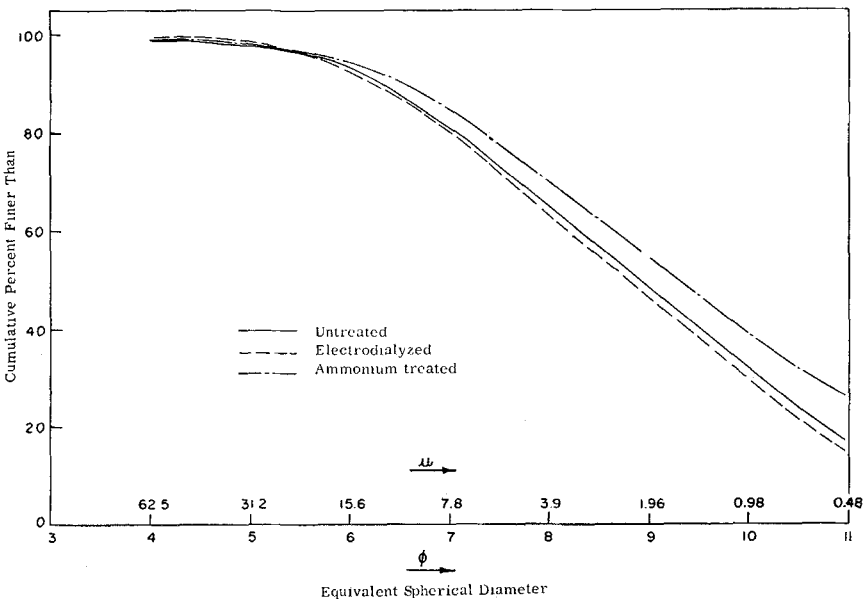


FIGURE 1.— Particle-size distribution curves for Georgia kaolinite.

unusual that there should be a certain specific chemical effect with respect to flocculation-deflocculation behavior with no correlation in plastic behavior. For this reason, further studies of the effects of wetting agents on the plastic behavior are justified.

The objectives of this investigation were to: (1) develop a method for studying the deformation behavior of clay-liquid systems in which particle orientation was controlled, (2) study the effect of a wide variety of wetting agents on the deformation behavior, and (3) study the filtration and sedimentation behavior of clays treated with solutions of wetting agents in order to see if there is a correlation between plastic behavior and flocculation-deflocculation behavior.

EXPERIMENTAL PROCEDURE

Raw Materials

Georgia kaolin, the basic raw material used throughout this investigation, was selected because previous studies (Sutton, 1954, p. 46-76; Auskern, 1954, p. 37-62) had shown it to be relatively free from contaminating materials, well crystallized, and fairly workable when mixed with water. Further characterization of this clay was made by x-ray analysis, particle-size analysis and base-exchange determinations. X-ray analysis showed only reflections that could be attributed to kaolinite. Base-exchange determinations by the manganese saturation method (Bower and Truog, 1940) gave a value of 6.4 meq Mn^{2+} per 100 g of clay. Base-exchange determinations by the titration method (Sutton, 1954) (after electro dialysis) gave a value of 5.0 meq of Na^+ per 100 g of clay. The fair agreement between these two values indicates that there were no drastic changes in chemical reactivity of the clay as a result of electro dialysis. The absolute value of the exchange capacity is of the order of magnitude to be expected for kaolinite. Particle-size analyses (Fig. 1) indicate a fairly uniform gradation of particle sizes with a fairly large proportion of particles finer than two microns (equivalent spherical diameter).

The clay was purified by an electro dialysis procedure similar to that described by Henry (1936, p. 19) and Prabhu (1950, p. 69-71). The electro dialyzed clay was carefully dried and ground to pass 80 mesh and stored in tightly closed glass jars.

A list of wetting agents selected for study is given in Table 1. These wetting agents were prepared as solutions on a weight percent basis (0.125, 0.25, 0.50 and 1.00 wt. percent), and pH and surface-tension determinations were made. The values of pH were measured with a Beckman glass-electrode pH meter and the surface tensions were measured with a Cenco du Nouy tensiometer. From the results (Table 1) certain compositions and types were chosen which have widely varying chemical constitution with comparable surface tensions and pHs.

Testing Procedure

The experimental method developed by Buessem and Nagy (1954) was used as a model in devising experiments for evaluating the stress-strain behavior of clay-liquid mixtures. A simple compression plastometer was used and special

TABLE I. — PROPERTIES OF WETTING AGENTS AND WETTING AGENT SOLUTIONS

Reagent class	Name	Composition	Source ¹	Concentration (wt. percent)											
				0.125		0.25		0.50		1.00					
				pH	S.T. ²	pH	S.T.	pH	S.T.	pH	S.T.	pH	S.T.		
Anionic	Alkanol B	alkyl naphthalene sodium sulfonate	1	6.00	43.75	6.75	40.80	6.9-7.15	33.70	7.7-8.0	32.60				
	Neomerpin N	alkyl naphthalene sulfonic acid	1	2.90	38.75	2.65	34.25	2.42	34.72	2.08	31.00				
	Duponol WA	fatty alcohol sodium sulfate	1	6.82	31.85	7.46	30.20	8.45	30.90	8.80	29.20				
	Duponol 80	sodium octyl sulfate	1	6.00	49.70	7.22	42.78	7.88-7.92	35.80	10.15	30.50				
	Petrowet WN	saturated hydrocarbon sodium sulfate	1	5.95	48.15	6.80	43.75	6.80	34.35	9.20	25.12				
	Petrowet R	saturated hydrocarbon sodium sulfate	1	4.52	49.00	4.28	42.30	3.96	36.18	3.65	31.48				
	Santomerse D	alkyl aryl sodium sulfonate	2	5.12	31.30	4.71	33.98	5.10	33.98	6.24	33.60				
	F-126	chiefly perfluorocaprylic acid	3	5.58	35.80	4.40	28.80	5.17	21.30	5.20	18.12				
	Victawet 35B	surface-active phosphorous compound	4	6.72	23.70	6.70	22.80	6.68	23.10	6.60	22.90				
	Victawet 58B	surface-active phosphorous compound	4	6.58	29.92	6.62	25.60	6.60	23.60	6.48	24.00				
Cationic	Aerosol 18	N-octadecylidiodium sulfosuccinamate	5	6.40	43.38	6.85	38.75	7.05	34.35	7.45	36.46				
	Retarder LV	cationic surface-active composition	1	3.67	35.50	3.42	33.49	3.30	32.52	3.20	31.75				

Product QB	1	6.00	34.15	6.10	31.00	5.45	29.72	5.50	29.53
long chain surface-active product									
Victamine C	4	5.76	23.40	5.71	23.40	5.71	23.60	5.75	23.80
surface-active phosphorous compound									
Victamine D	4	5.35	33.86	5.55	32.22	5.05	32.41	5.91	34.05
surface-active phosphorous compound									
Nopocide K	6	5.20	36.38	5.00	36.55	4.62	35.60	4.51	35.30
dodecylacetamido dimethyl benzyl ammonium chloride									
Nonionic Nonisol 100	7	5.12	32.22	5.03	32.03	5.10	31.10	5.50	32.52
polyoxyalkylene fatty ester type									
Nonisol 200	7	4.40	35.30	4.21	33.77	4.50	33.33	6.18	32.90
polyoxyalkylene fatty ester type									
Nonisol 250	7	3.91	33.00	3.92	33.20	3.71	33.10	4.69	33.95
polyoxyalkylene fatty ester type									
Alrodyne 315	7	4.00	39.25	3.87	39.70	3.58	38.48	—	—
polyoxyalkylene fatty ester									
Surfynol 82	7	5.55	54.25	5.85	51.10	5.9-6.0	47.40	6.00	43.00
dimethyl octynediol									
Surfynol 102	7	5.55	43.00 (0.1%)	6.10	38.30 (0.2%)	5.7-5.75	34.00	—	—
similar to 82 (larger aliphatic groups)									
Surfynol 104	7	5.85	38.10 (0.03%)	5.95	34.30 (0.06%)	—	—	—	—
similar to 82 (larger aliphatic groups)									
Dimethyl Hexynediol	7	5.95	60.2	5.71	57.6	6.05	54.5	6.50	51.00
dimethyl hexynediol									
Victawet 12	4	4.02	26.40	3.75	26.48	3.41	26.30	3.32	26.10
surface-active phosphorous compound									

1 1—E. I. duPont de Nemours and Co., Wilmington, Delaware; 2—Monsanto Chemical Co., St. Louis, Mo.; 3—Minnesota Mining and Mfg. Co., St. Paul, Minn.; 4—Victor Chemical Works, Chicago, Ill.; 5—American Cyanamid Co., N.Y., N.Y.; 6—Nopco Chemical Co., Harrison, N.J.; 7—Geigy Chemical Corp., N.Y., N.Y.

² S.T. = surface tension (dynes/cm).

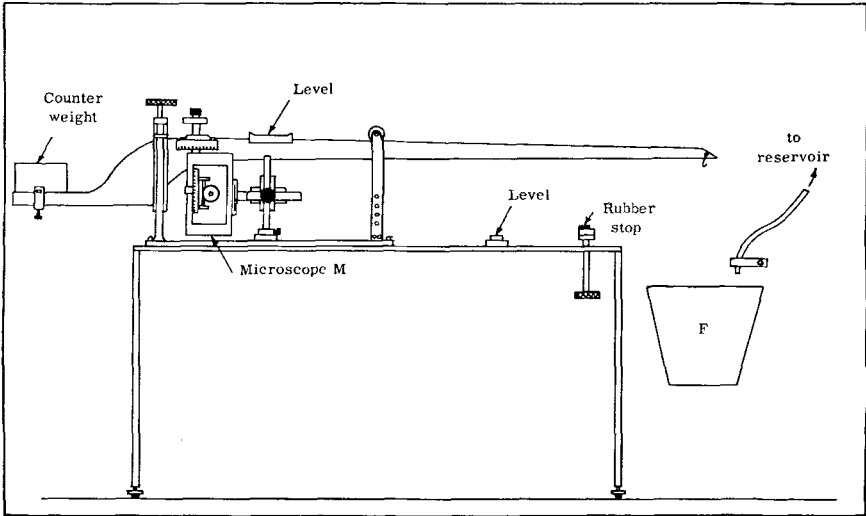


FIGURE 2.— Schematic drawing of apparatus used for deformation experiments (not to scale).

care was taken in sample preparation in order to avoid excessive orientation of clay particles. A compression test was selected because such a test offered the following advantages: (1) specimens could be made uniform in composition and accurately cut to the dimensions chosen, (2) test results were more consistent, and (3) there was no problem of gripping ends (of specimens).

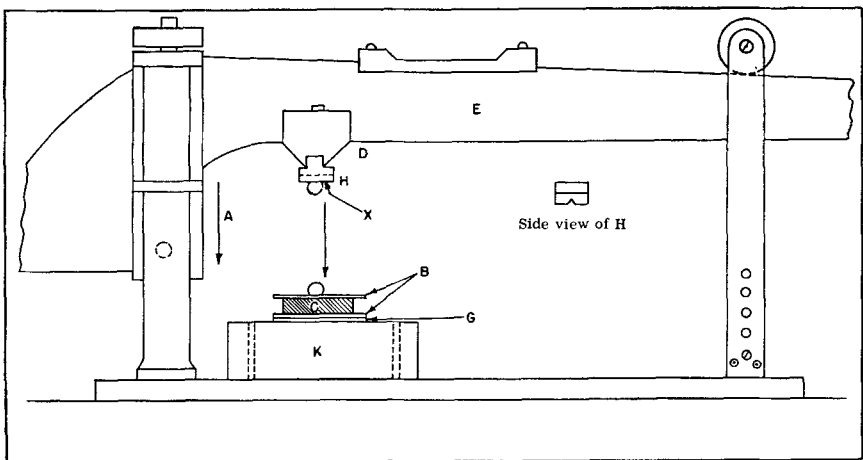


FIGURE 3.— Schematic drawing of loading arrangement details (not to scale.)

Samples were prepared by weighing 370 g of electrolyzed clay into a polyethylene bag, adding 130 g of liquid, aging one week in a humidified atmosphere, and kneading by hand. The clay-liquid mixtures were thoroughly worked (wedged and homogenized) on a Teflon sheet and carefully formed into a ball-shaped mass. The specimens were then put in plastic bags and stored an additional two days in a humidified atmosphere. After the second period of aging the samples were removed from the plastic bags and cylindrical specimens were extracted from the center of the ball by means of a cork borer and wire cutter. A carefully machined miter box was used in slicing the samples in order to control height and parallelism of the surfaces of the samples. Three samples were cut from each ball and run separately.

The samples, $5/16$ inch high by $7/8$ inch diameter, were tested in the apparatus shown in Figures 2 and 3. A clay specimen *C* (Fig. 3) is deformed continuously by the application of a force through *D*. The load is applied by adding

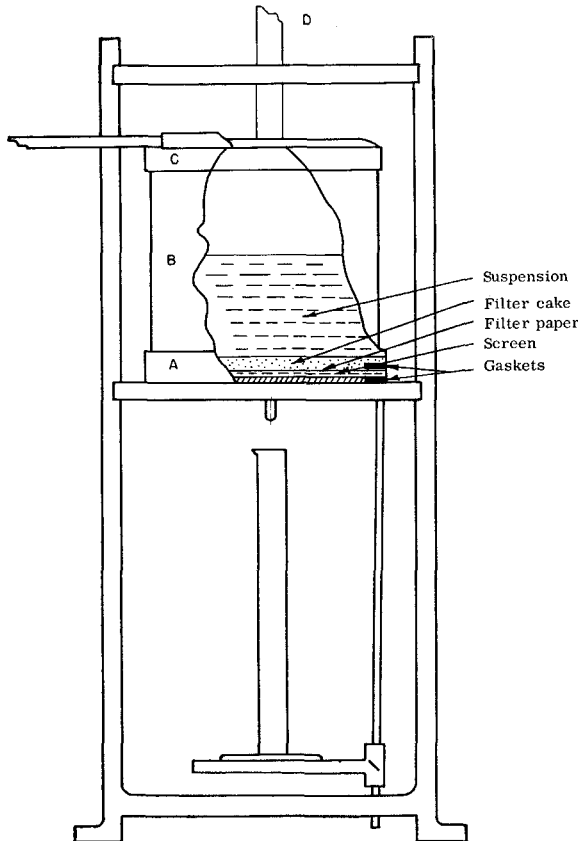


FIGURE 4. — Schematic drawing of water loss apparatus (not to scale).

water at a constant rate to bucket *F* (Fig. 2) which causes a force to be applied through lever arm *E*. Initial positioning of the sample is very important for accuracy and precision of measurement. Circles with the same diameters as the undeformed specimens were scribed on the aluminum discs *B* used for capping. These discs were coated with adhesive-backed Teflon in order to minimize sticking of the clay and to facilitate handling of the specimens after completion of the compression tests. A centering disc *G* was carefully centered and cemented on block *K* to aid in positioning samples. The design of block *H* permitted application of the deforming force at a point. Tendency for horizontal movement of discs *B* and specimen *C* was prevented by use of a ball-bearing contact and v-groove arrangement.

The deformation of the clay specimen was followed by means of a travelling microscope *M* sighted on point *X*. The decrease in height of the specimen was measured during the course of deformation. A notation of the elapsed time was made for each height reading. The stress-strain relations were readily computed from the original height, loading rate, and time corresponding to any given decrease in height.

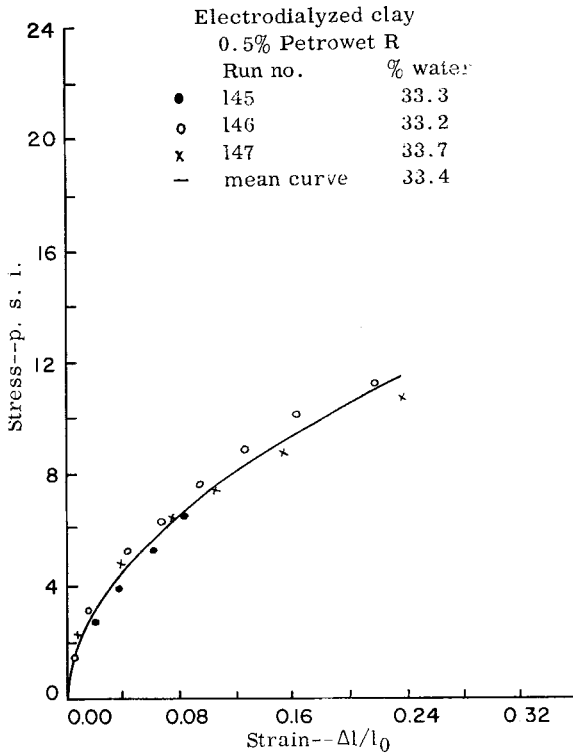


FIGURE 5. — Illustrating the variability of test results.

Deformation Experiments

Water. — Tests were made on samples of electrodyalyzed clay at water contents of 29.9, 31.8, 34.1, 36.1 and 38.7 wt. percent (dry weight basis). Each test was made in triplicate. These tests were essential since they provided a reference point for water containing various additives, as well as indicating the degree of reproducibility which could be obtained under the conditions of the test.

Wetting agents—class variable. — Three classes of wetting agents, i.e., non-ionic, anionic and cationic, were tested in various concentrations, based on surface tension and pH. Attempts were made to select those combinations which would give essentially constant surface tension and pH values, regardless of ion type. The reagents chosen within each class were as follows: Cationics: Victamine D, Nopocide K, Product QB, Retarder LV. Anionics: Duponol WA, Santomerse D, Petrowet R. Nonionics: Nonisol 200, Nonisol 100.

Wetting agents—concentration variable. — One reagent from each class was tested at various concentrations. Nopocide K (cationic) was run at concentrations of 0.85, 0.50 and 0.05 wt. percent. Nonisol 200 (nonionic) was run at

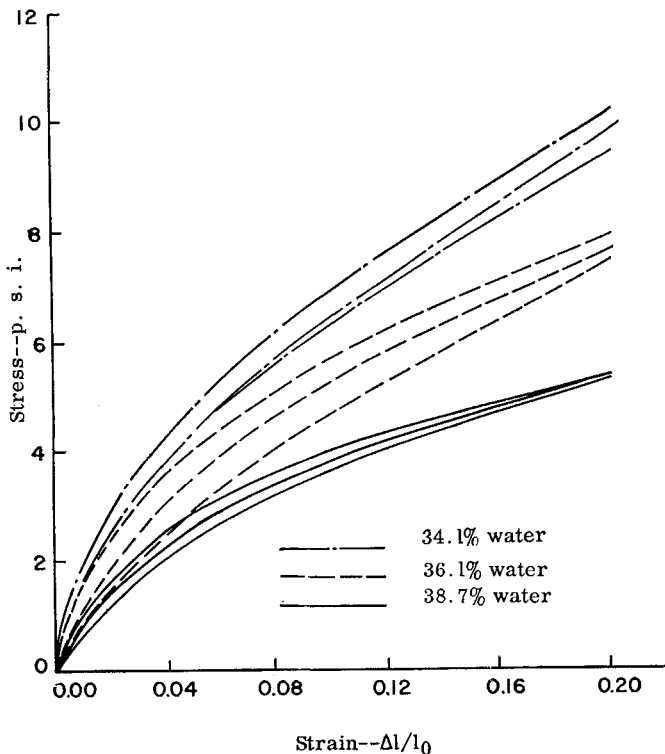


FIGURE 6. — Relation between stress and strain for three different water contents. Three runs made at each water content.

TABLE 2. — LEAST SIGNIFICANT DIFFERENCES (5 PERCENT LEVEL) OBTAINED FROM ANALYSIS AT INDIVIDUAL STRAIN VALUES

Strain	L. S. D. _{0.05} (p.s.i.)
0.02	0.785
0.04	0.879
0.06	0.892
0.08	0.787
0.10	0.721
0.12	0.782
0.14	0.600
0.16	0.578

concentrations of 0.95 and 0.50 wt. percent. Petrowet R (anionic) was run at 0.85 and 0.50 wt. percent.

Wetting agents—different types within classes.—The following reagents within each class were tested. Cationic: Victamine D, Retarder LV, Product QB, and Nopocide K. Anionic: Santomerse D, Petrowet R, and Duponol WA. Non-ionic: Nonisol 100, Nonisol 200, and Nonisol 250.

Sedimentation Experiments

Sedimentation tests were made using all the wetting agents listed in Table 1. The procedure for determining sedimentation volumes was as follows:

Ten grams (± 0.05 g) of electrodyalized clay was placed in a Nessler tube. (50 ml capacity) containing 40 ml of the desired reagent (0.50 percent by weight) and thoroughly agitated by hand shaking. The tube was then lightly stoppered, placed in the Nessler tube rack and allowed to sediment. The volume of the sediment was measured after various intervals of time. This procedure was repeated for each of 25 reagents and distilled water. The pH and surface-tension values of the solutions had been previously determined. The pH of each suspension was determined after the sedimentation tests were completed.

Filtration Experiments

The water-loss test is a common experiment performed in evaluation of drilling mud. Rogers (1953, p. 112-116, 266-277) describes the method and principles involved in the application of this test to drilling muds. This test was applied to some of the clay liquid compositions under consideration because it offered a means of obtaining information relative to clay-water interaction.

Essentially, the filterability of a clay suspension is tested. The apparatus is constructed in such a manner that the rate of filtration depends on the structure and density of the filter cake formed. For any given system the type of structure formed will depend on the clay-liquid interaction (flocculation-deflocculation behavior).

Suspensions were prepared by weighing 62.5 g of electrodyalized clay into a 500 ml Erlenmeyer flask containing 250 ml of water or a 0.95 wt. percent solution of the wetting agent being investigated. The flask was then tightly stoppered and agitated in a reciprocating type shaker for a period of 8 hours. A represen-

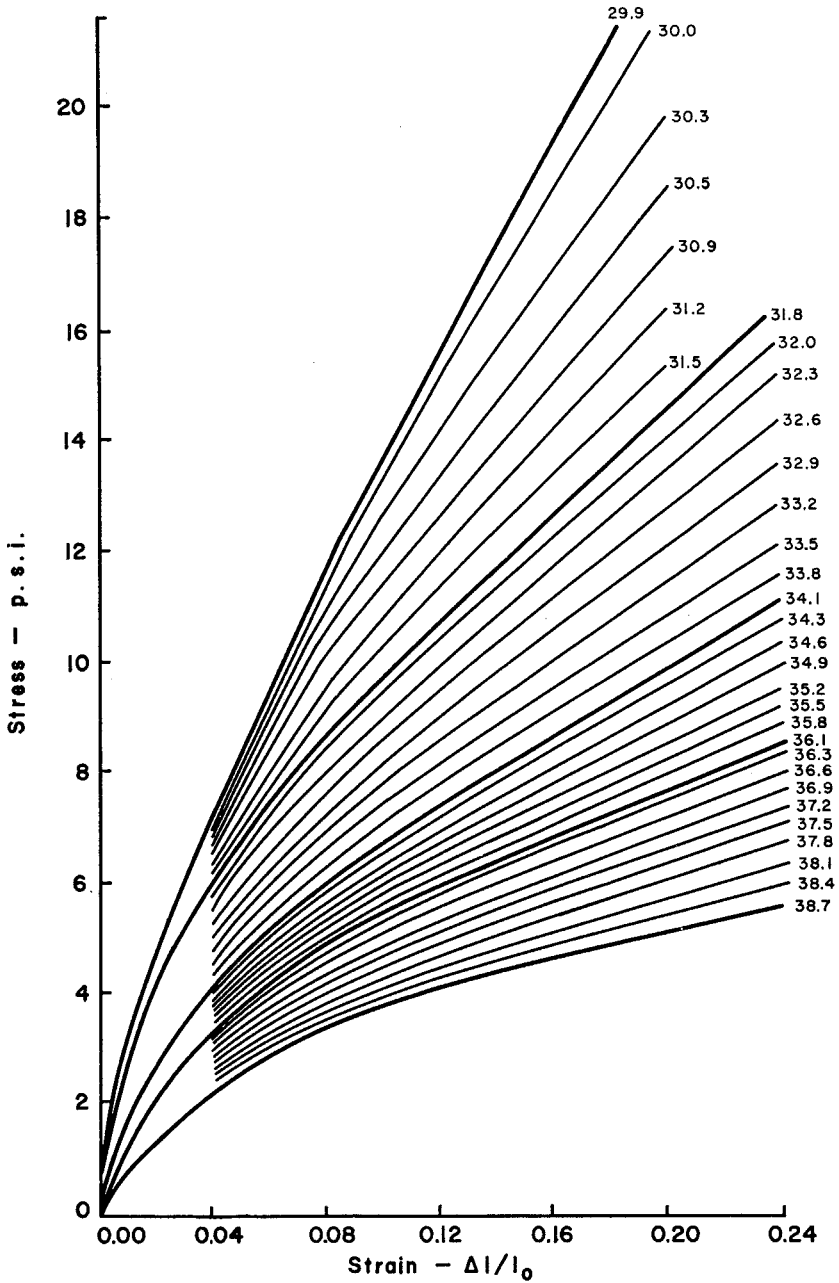


FIGURE 7. — Relation between strain and stress for various water contents (electrodialyzed clay).

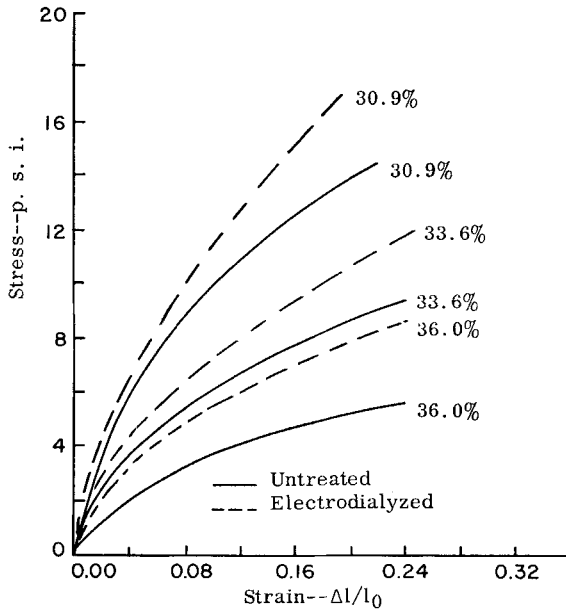


FIGURE 8. — Effect of water content on the deformation behavior of Georgia kaolinite. Water content—as indicated.

tative member of each class of wetting agents was tested; i.e., Santomerse D (anionic), Victamine D (cationic) and Nonisol 200 (nonionic).

The procedure followed in making the water-loss test is described with reference to Figure 4. The cup assembly (parts *A*, *B*, *C*) is removed from the rack and disassembled. The screen, filter paper (Whatman no. 50) and upper gasket are carefully placed in part *A*. Part *B* is screwed onto part *A* and the two placed in the rack. The thoroughly mixed clay suspension is poured quickly into the cup and a timer is started; cup *C* is quickly positioned and the compressed air is turned on to the desired pressure. Readings of the volume of water lost are taken at intervals until 25 ml has been removed from the suspension. Results are plotted as cumulative water loss versus the square root of the time in minutes.

RESULTS AND DISCUSSION

Method of Analyzing Results and Moisture Content Adjustments

Each composition tested was run in triplicate. Figure 5 gives results obtained for electrodialyzed clay treated with an aqueous solution of Petrowet R (anionic reagent). Data from each of three separate runs on this composition are plotted along with a mean curve. These results are typical for most of the runs made and give a qualitative indication of the experimental error inherent in the method.

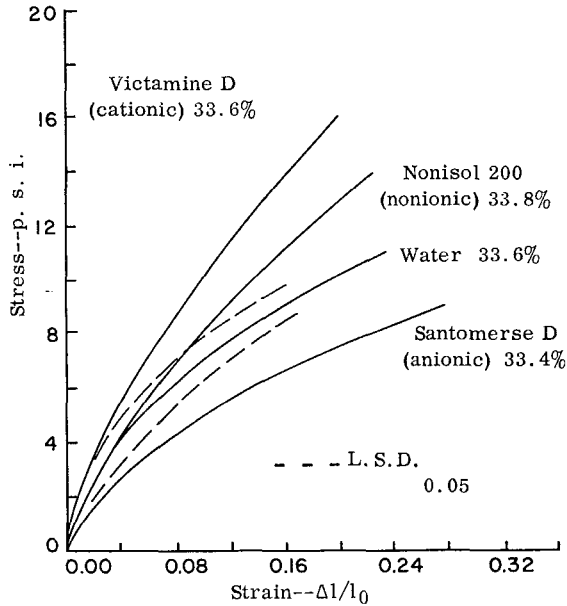


FIGURE 9. — Effect of anionic, cationic, and nonionic wetting agents on the deformation behavior of Georgia kaolinite. Water contents—as indicated. Wetting agent concentration—0.95 percent.

Figure 6 gives results of tests made on electrodyalized clay containing 34.1, 36.1 and 38.7 percent water. These tests were made in order to evaluate the experimental error. The variation in stress at arbitrarily chosen strain values was analyzed for all moisture contents, and calculations were made in order to determine the limits of precision at each of eight strain values. These limits of precision ("least significant differences"—L. S. D.) were determined by analyzing the variability of the results using conventional statistical procedures (Snedecor, 1946, p. 214-252, 406; Cochran and Cox, 1950, p. 47-102; Dixon and Massey, 1951, p. 119-132).

The least significant difference values obtained from the error as indicated from analysis of variance tests are listed in Table 2. These values were used to determine whether or not a given clay-liquid composition differed significantly from clay with water alone in its stress-strain behavior. Experimental results with different clay-liquid compositions were compared with the behavior of clay-water mixtures having a comparable liquid content.

In order to obtain comparable results, moisture-content adjustments were sometimes necessary. These adjustments were made using a set of calibration curves (Fig. 7) which gave the relationship between stress and strain for electrodyalized clay over a wide range of moisture contents. In Figure 7, curves for 29.9, 31.8, 34.1, 36.1 and 38.7 percent water represent mean experimental curves whereas intermediate curves were obtained graphically.

Deformation Experiments

The dependence of the stress-strain behavior on the water content has been well established (Henry and Siefert, 1941, p. 282; Russell and Hanks, 1942, p. 21-23), and is further illustrated in Figure 8. This figure also shows the effect of electro dialysis on the deformation properties of mixtures containing different amounts of water. At all water contents the untreated clay was more deformable than the electro dialyzed clay. This difference in behavior is probably due to the presence of adsorbed alkali ions in the untreated clay. Clay-water mixtures composed of electro dialyzed clay are generally conceded to offer more resistance to deformation than mixtures containing clay treated with alkali ions (Sullivan and Graham, 1940, p. 48-50; Speil, 1940, p. 35).

Results of deformation experiments made with wetting agent additions (Figs. 9 to 15) illustrate the effects of reagent class, different reagents within classes, and concentration.

Characteristic behavior was noted for different classes of wetting agents (Fig. 9). All clay-liquid mixtures containing cationic and nonionic reagents produced bodies which were less deformable and all anionic reagents produced bodies which were more deformable than comparable clay-water mixtures. Solutions used in these tests had similar surface tensions, concentrations and pHs.

Figures 10 to 12 show the deformation behavior of clay-liquid mixtures containing different nonionic, cationic and anionic wetting agents. Solutions used in these tests had comparable concentrations but different surface tensions.

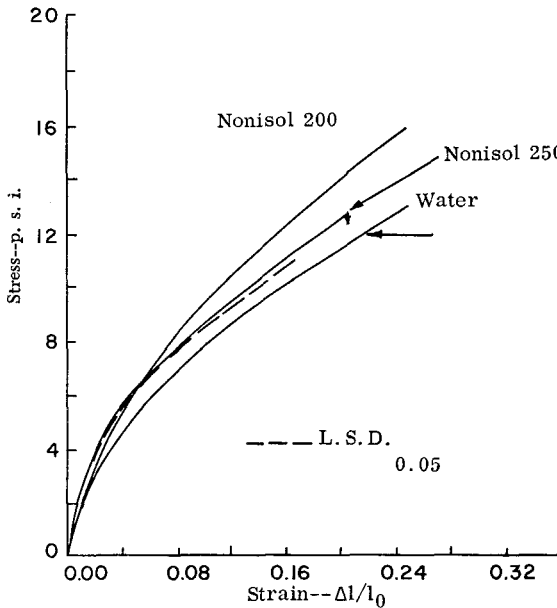


FIGURE 10. — Effect of nonionic wetting agents on the deformation behavior of Georgia kaolinite. Water content—33.1 percent. Wetting agent concentration—0.5 percent.

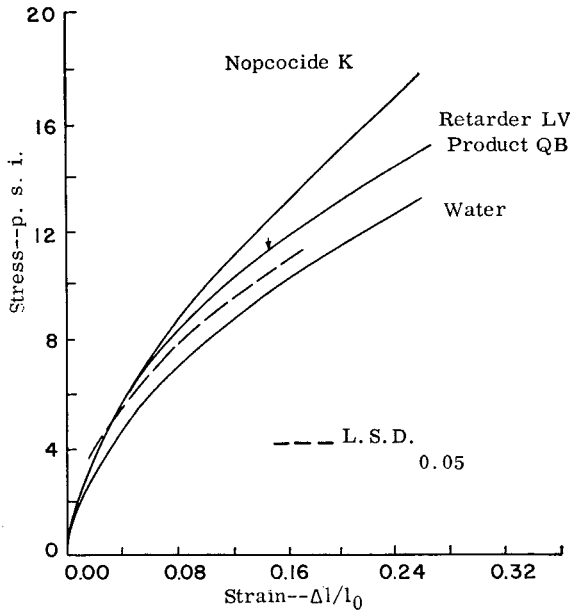


FIGURE 11. — Effect of cationic wetting agents on the deformation behavior of Georgia kaolinite. Water content—33.2 percent. Wetting agent concentration—0.5 percent.

Here again there was characteristic behavior for each class of reagent regardless of surface tension or pH.

The effect of reagent concentration is illustrated in Figures 13 to 15. Nonisol 200 in concentrations of 0.5 and 0.95 wt. percent produced a body which was less deformable than that produced with water at the same liquid content; Petrowet R at a concentration of 0.85 wt. percent produced a body which was more deformable than one with water, whereas at a concentration of 0.5 wt. percent no significant effect was noted; Nopcocide K at 0.85 and 0.50 wt. percent produced a body of decreased deformability whereas no effect was noted with this reagent at 0.05 wt. percent. These results illustrate the dependence of the deformation behavior on the concentration and suggest that there is no simple relation between deformation behavior and surface tension and pH.

Sedimentation Experiments

Results of the sedimentation experiments are given in Figure 16. All the cationic reagents produced sedimentation volumes that were larger than those produced with water alone whereas all the anionic reagents produced volumes less than or equal to the sedimentation volume with water. Compared with water, nonionic reagents gave both larger and smaller sedimentation volumes. Large sedimentation volumes are characteristic for a flocculated system and

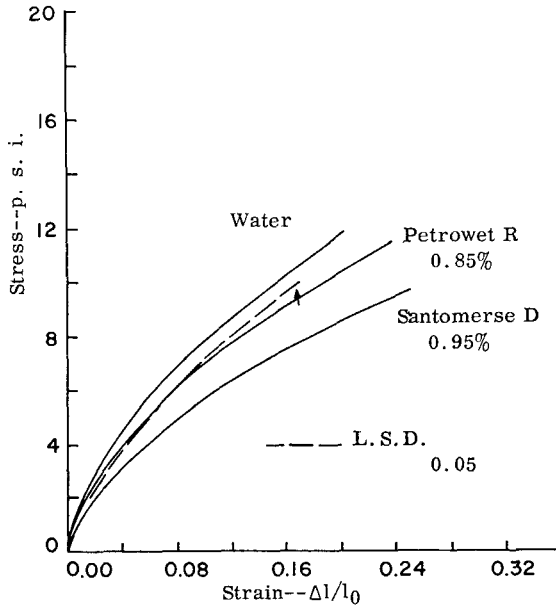


FIGURE 12. — Effect of anionic wetting agents on the deformation behavior of Georgia kaolinite. Water content—33.0 percent.

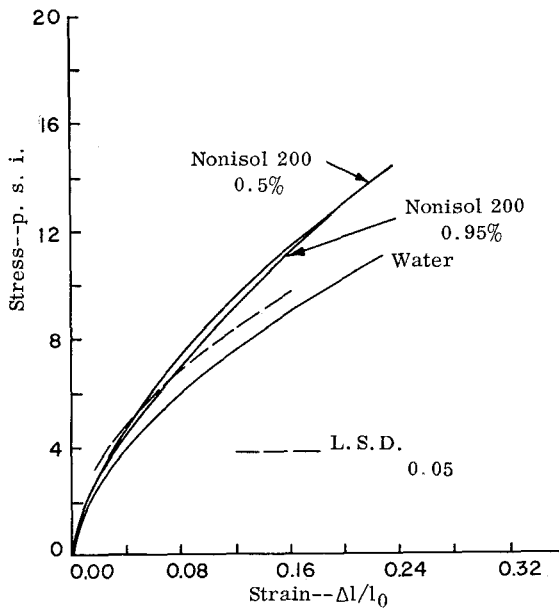


FIGURE 13. — Effect of wetting agent concentration on the deformation behavior of Georgia kaolinite. Water content—33.8 percent. Wetting agent concentrations—as indicated.

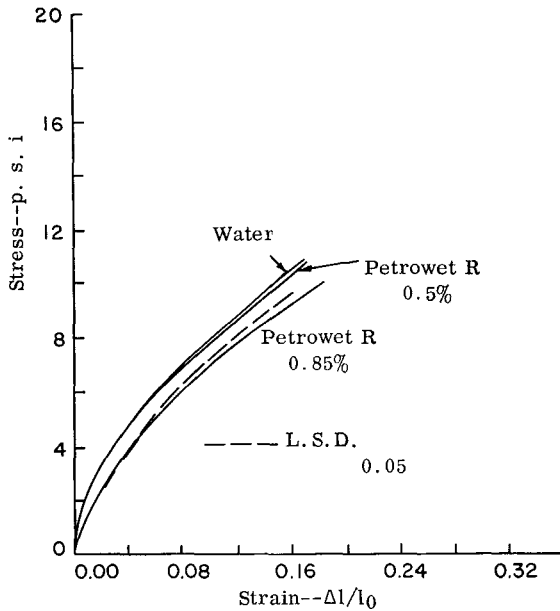


FIGURE 14. — Effect of wetting agent concentration on the deformation behavior of Georgia kaolinite. Water content—33.0 percent. Wetting agent concentration—as indicated.

small sedimentation volumes are typical of deflocculated systems. Volumes obtained with cationic reagents therefore indicate a high degree of flocculation whereas the volumes obtained for anionic reagents indicate that the systems were fairly well deflocculated. This behavior is consistent with the observed deformation properties since it is generally accepted that flocculated systems resist deformation more than deflocculated systems (Johnson and Norton, 1942, p. 338; Sullivan and Graham, 1940; Speil, 1940).

Filtration Experiments

The filtration behavior or permeability of filter cakes formed from suspensions containing wetting-agent additions is given in Figure 17. From this figure it is apparent that anionic reagents produce deflocculation and a slow filtering media whereas cationic and nonionic reagents produce flocculation and a faster filtering media. The behavior of clay-water mixtures lies between that observed for mixtures containing anionic additives and the behavior observed for materials containing cationic or nonionic additives.

From the foregoing results it is apparent that deformation behavior and related properties of clay-liquid systems are primarily dependent upon the chemical nature of the wetting agents added. Parameters such as surface tension seem to be of secondary importance.

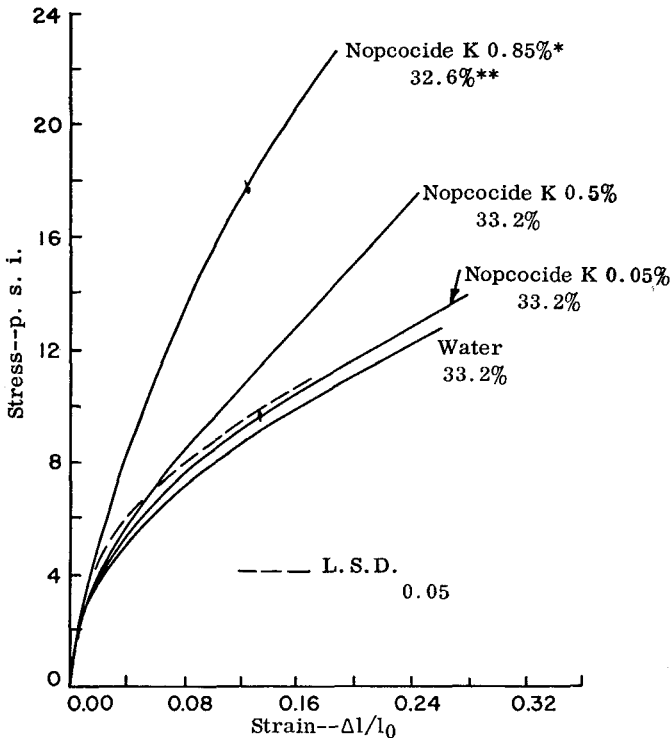


FIGURE 15. — Effect of wetting agent concentration on the deformation behavior of Georgia kaolinite. Water content—as indicated (**). Wetting agent concentration—as indicated (*).

SUMMARY

A study of some of the chemical factors affecting the deformation behavior of workable clay-water mixtures has been made. Property-determining factors, i.e., variations in chemical or mineralogical composition, particle shape, particle size distribution, impurity content, particle orientation and properties of the liquid phase were controlled. A single clay (kaolinite) was selected for study and a simple compression test was developed for determining the stress-strain behavior of this clay treated with various classes of wetting agents.

Particular emphasis was placed upon the evaluation of a method for estimating the effects of the various wetting agents. The analysis of variance technique was adapted to the problem of estimating differences between compositions and measuring the precision of these estimates.

The more pertinent results are summarized in Figure 18 and enumerated in the following paragraphs.

The physical properties of the liquid phase (namely, surface tension and pH) of wetting agents are of secondary importance in their effects on the stress-strain

behavior of workable clay-water masses. Variations in the surface tension of the liquid phase did not produce corresponding variations in the deformation behavior. Similarly, no systematic trends were noted with changes in pH. In general, anionic reagents caused an increase in the deformability; nonionic reagents produced little change or decreased the deformability; and cationic reagents decreased the deformability of clay-water masses.

The effect of concentration of various types of reagents was investigated. In the concentration ranges studied, increases in the concentration of reagents generally accentuated the effects produced.

The filtration and sedimentation behavior of clay-liquid systems containing wetting agents was also evaluated. The "filterability" of these mixtures increases according to reagent type in the following order: anionic < water < nonionic < cationic. In general, cationic wetting agents produced large, and anionic wetting agents produced small sedimentation volumes. As compared with water, suspensions of nonionic wetting agents with clay produced both larger and smaller sedimentation volumes.

In summary, reagents producing a more deformable mixture than clay-water mixtures give a smaller sedimentation volume and filter slowly. On the other

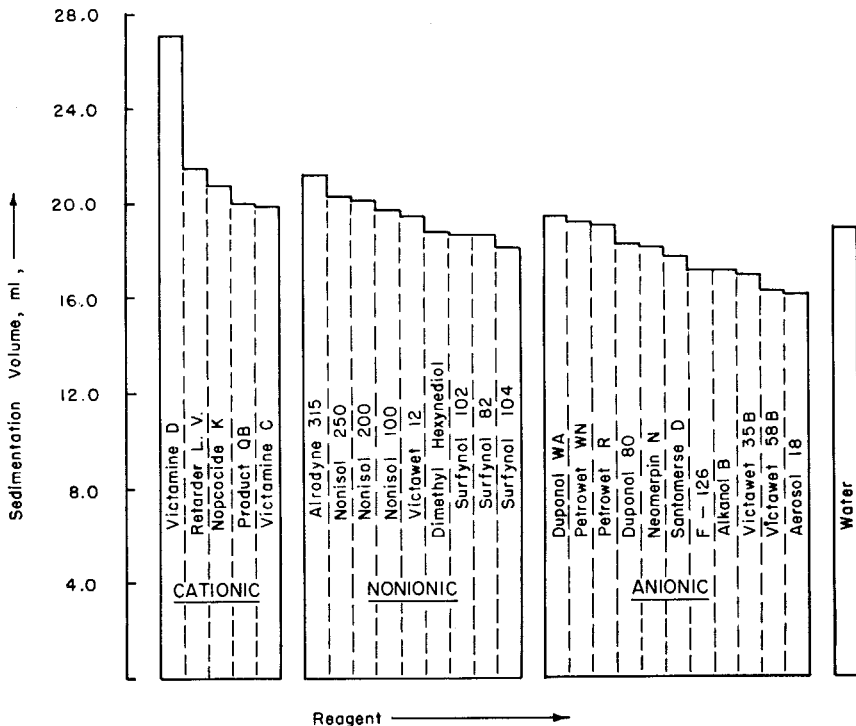


FIGURE 16. — Effect of wetting agents (0.50 percent by weight) on the sedimentation volume of kaolinite suspensions (25 percent solids).

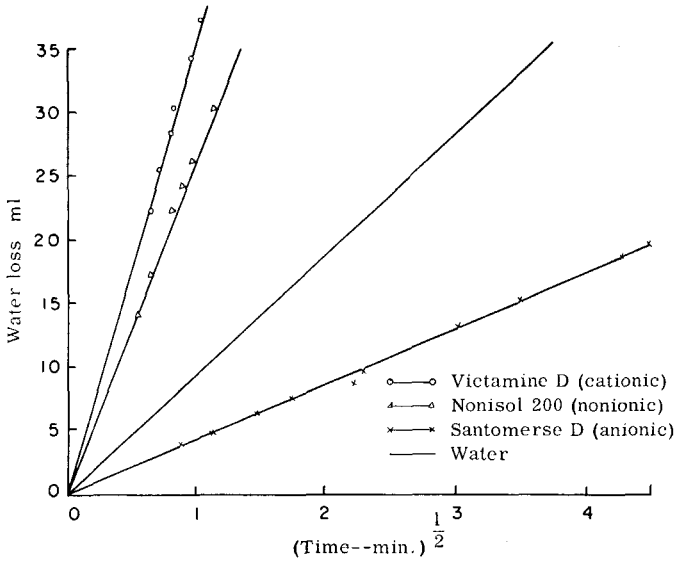


FIGURE 17. — Filtration behavior of kaolinite suspensions (25 percent solids) with wetting agent additions (0.95 percent by weight).

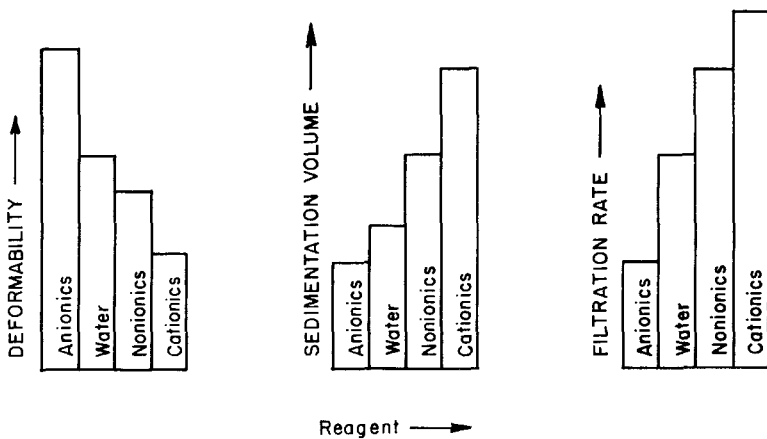


FIGURE 18. — Summary graph of deformation, sedimentation and filtration behavior (schematic).

hand, reagents that produce a less deformable mixture give a larger sedimentation volume (certain nonionics excepted) and filter more rapidly.

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REFERENCES

- Auskern, A., 1954, A study of clays by infrared absorption spectroscopy: M. S. Thesis, The Pennsylvania State University, 116 p.
- Bower, C. A., and Truog, E., 1940, Base-exchange capacity determination of soils and other materials: *Ind. Eng. Chem. (Anal. Ed.)*, v. 12, p. 411-413.
- Buessem, W. R., and Nagy, Bartholomew, 1954, The mechanism of the deformation of clay: in *Clays and Clay Minerals*, *Natl. Acad. Sci.—Natl. Res. Council Pub.* 327, p. 480-491.
- Cochran, W. G., and Cox, G. M., 1950, *Experimental designs*: John Wiley & Sons, New York, 454 p.
- Dixon, W. J., and Massey, F. J., Jr., 1951, *Introduction to statistical analysis*: McGraw-Hill Book Co., New York, 370 p.
- Henry, E. C., 1936, Acid and base-binding capacities and viscosity relations in certain whiteware clays: Ph.D. Thesis, The Pennsylvania State University, 46 p.
- Henry, E. C., and Siefert, A. C., 1941, Plastic and drying properties of certain clays as influenced by electrolyte content: *J. Amer. Ceram. Soc.*, v. 24, p. 281-285.
- Johnson, A. L., and Norton, F. H., 1942, Fundamental study of clay. III, Casting as a base-exchange phenomenon: *J. Amer. Ceram. Soc.*, v. 24, p. 337-344.
- Kingery, W. D., and Francl, J., 1954, Fundamental study of clay. XIII, Drying behavior and plastic properties: *J. Amer. Ceram. Soc.*, v. 37, p. 596-602.
- Moilliet, J. L., and Collie, B., 1951, Surface activity: D. van Nostrand Co., Inc., New York, 379 p.
- Prabhu, K. P., 1950, Anion exchange and viscosity phenomena in kaolinite, illite, and montmorillonite: Ph.D. Thesis, The Pennsylvania State University, 158 p.
- Reiner, M. (ed.), 1954, *Building materials, their elasticity and inelasticity*: North Holland Publishing Co., Amsterdam, 560 p.
- Rogers, W. F., 1953, *Composition and properties of oil well drilling fluids*: Gulf Publishing Co., Houston, Texas, 676 p.
- Ruehrwein, K. A., and Ward, D. W., 1952, Mechanism of clay aggregation by polyelectrolytes: *Soil Sci.*, v. 73, p. 485-492.
- Russell, R., Jr., and Hanks, C. F., Jr., 1942, Stress-strain characteristics of plastic clay masses: *J. Amer. Ceram. Soc.*, v. 25, p. 16-28.
- Schwartz, B., 1952, Fundamental study of clay. XII, A note on the effect of surface tension of water on the plasticity of clay: *J. Amer. Ceram. Soc.*, v. 35, p. 41-43.
- Snedecor, G. W., 1946, *Statistical methods (4th ed.)*: The Iowa State College Press, Ames, Iowa, 485 p.
- Speil, S., 1940, Effect of adsorbed electrolytes on properties of monodisperse clay-water systems: *J. Amer. Ceram. Soc.*, v. 23, p. 33-38.

- Sullivan, J. D., and Graham, R. P., 1940, Effect of exchangeable bases on torsion properties of clays: *J. Amer. Ceram. Soc.*, v. 23, p. 39-51.
- Sutton, W. H., 1954, Factors affecting the strength of clay bodies in the temperature range 110° C - 800° C: M. S. Thesis, The Pennsylvania State University, 97 p.
- Williamson, W. O., 1941, Some structures of unfired pottery bodies revealed by a new technique: *Br. Ceram. Soc. Trans.*, v. 40, p. 275-292.
- , 1947, The fabric, water distribution, drying-shrinkage, and porosity of some shaped discs of clay: *Amer. J. Sci.*, v. 245, p. 645-662.
- , 1954, The effects of rotational rolling on the fabric and drying shrinkage of clay: *Amer. J. Sci.*, v. 252, p. 129-143.