

FLOCCULATION OF SELECTED CLAYS BY VARIOUS ELECTROLYTES

by

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ABSTRACT

The flocculation behavior of clay specimens from altered basalt, altered granodiorite, and a transported (?) deposit in Latah County, Idaho, was investigated in order to determine if flocculation behavior would be an aid in characterizing clay samples in a way that could be related to the origin and history of the clays. The clay minerals are of the kaolinite group.

As flocculants, various chlorides differ one hundred-fold and sodium salts twenty-fold in the concentrations necessary to flocculate a clay to a fixed settling rate. The concentrations of individual chlorides necessary to flocculate different clays vary three-fold and the concentrations of individual sodium salts vary ten-fold. In all cases the higher the valence of the cation the lower is the concentration required for flocculation; the relative effectiveness, however, varies with the clay. The relative effectiveness of the anions as flocculants varies greatly with the clay and no definite order of effectiveness is apparent.

Halloysite requires less electrolyte for flocculation and has a larger settling volume than kaolinite. Well crystallized kaolinite has a smaller settling volume than poorly crystallized kaolinite.

Wide differences of flocculation behavior may provide a valuable, rapid method of classifying the clays of a district.

INTRODUCTION

A study of the flocculation behavior of various clay samples is being made as part of a broad investigation of the clay deposits in and around Latah County, Idaho. The study was undertaken primarily to determine if flocculation behavior would be an aid in characterizing clay samples in a way that could be related to the origin and history of the clays, and possibly to add to the general understanding of flocculation phenomena.

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EXPERIMENTAL PROCEDURE

Clay Samples

For the first part of the work three clay samples known to differ in origin or history were chosen.

Sample A was obtained about half a mile north of Helmer, Idaho. The clay had washed from a steep bank and settled from suspension in a tiny pond at the foot of the bank. The sample was almost pure clay and showed fine stratification evidently produced by successive rain storms. The clay bank is stratified and does not show relic structures of importance so is thought to be a transported deposit (Hubbard, 1957). The apparent source of the clay is altered granodiorite from the nearby Thatuna batholith and altered Permian volcanic rocks from Potato Hill (Mount Deary).

Sample B is highly altered Columbia River basalt.

Sample C is highly altered granodiorite. Samples B and C came from the same location in the Benson deposit (Hubbard, 1957) northeast of Troy. Locally the granodiorite is overlain by about 6 ft of basalt. The highly altered zone is more than 20 ft thick. The samples were taken about 18 in. apart just above and below the basalt-granodiorite contact.

X-ray diffraction and electron microscope examination of the clay from these specimens showed the transported (?) clay, A, to be a mixture of metahalloysite and poorly crystallized kaolinite; the basaltic clay, B, to be metahalloysite; and the granitic clay, C, to be well crystallized kaolinite. Plate 1 is the electron micrographs of these specimens.

Flocculants

The flocculating reagents were chosen to represent a range of valences, ion size, and calcium salt solubility which are known to affect their efficiency (Searle and Grimshaw, 1959, pp. 438-444). The final choice, however, was arbitrary. The chlorides used to study the effect of the cations were NaCl, CaCl₂, FeCl₂, AlCl₃, and SnCl₄. The sodium salts used to study the anion effect were NaCl, NaF, NaOH, Na₂SO₄, Na₂CO₃ and Na₂HPO₄.

Experimental Procedure

The clay suspensions were prepared by dispersing sufficient sample in distilled water with a malted-milk mixer to give about 4 percent solids. The suspensions were allowed to settle for 20 min (enough essentially to remove the $> 10 \mu$ fraction), then diluted to give suspensions containing 1 and 2 percent solids.

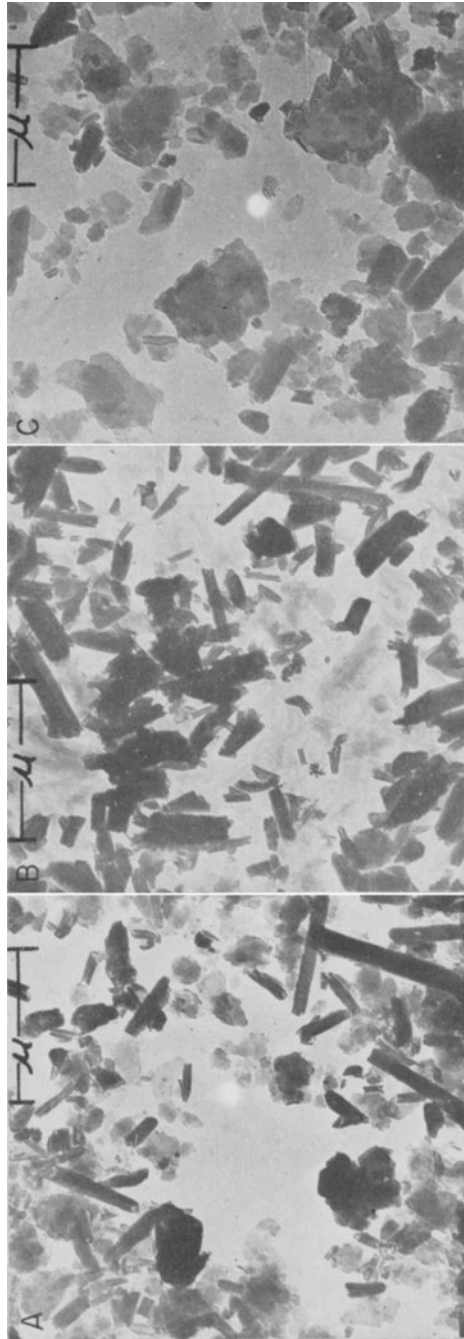


PLATE 1.—Electron micrographs. (*A*) transported (?) clay, sample A. (*B*) basalt clay, sample B. (*C*) granitic clay, sample C.

The clay was flocculated by adding sufficient reagent solution of appropriate strength to give about 30 ml of clay suspension containing just under 1 percent solids.

Settling time was taken as the time for a sharp boundary to appear between the settled floc and the liquid. Settling volumes were measured at this time. Preliminary tests in which the white-light transmission of the liquid was measured showed that there was essentially no change in transmission after the end of settling as determined by the development of the sharp interface. This, plus reasonable reproducibility, indicates good reliability for the method of determining settling times.

All work was done at room temperature because tests at 13°, 25°, and 54 °C showed no significant dependence of the flocculation rate on temperature. A dependence of flocculation behavior on solids concentration was observed but eliminated as a variable by working with suspensions of uniform strength. Because the size distribution of the clay particles is characteristic of the sample the entire < 10 μ fraction was used in each case, although more details of the flocculation process might have been gained by using closely sized material.

The pH of the flocculated suspensions in all cases changes by less than half a unit through the concentration ranges investigated. The pH at which rapid flocculation first occurred with any one reagent varied as much as one unit from sample to sample. The pH data are summarized in Table 1.

TABLE 1.—pH OF FLOCCULATED SUSPENSIONS

	NaCl	CaCl ₂	AlCl ₃	SnCl ₄	Original Suspension
Clay A	6.6	6.6	5.8	4.6	6.4
Clay B	7.4	7.2	5.6	5.1	7.6
Clay C	7.1	7.0	5.2	4.1	7.2

RESULTS AND DISCUSSION

The settling time versus electrolyte concentration curves for the three clay samples and six cation chlorides are shown in Fig. 1 and the settling volume curves in Fig. 2. The effectiveness of a reagent is clearly a function of the valence of the cation. Although the curves shift slightly from one clay sample to another the dependence on the clay is fairly small. The ratios of concentrations of the reagents at which the settling time curves level off are given in Table 2. The similarity between the ratios for clays B and C and the difference between these and the ratio for clay A suggest that factors in the environment other than the parent rock are the most effective in determining cation flocculation behavior. It should also be noted

that these ratios are very different from those reported by other workers (Michaels, 1958, p. 29; Brindley, 1958, p. 19). The anomalous effectiveness of ferrous iron relative to calcium, and the unusual settling time settling

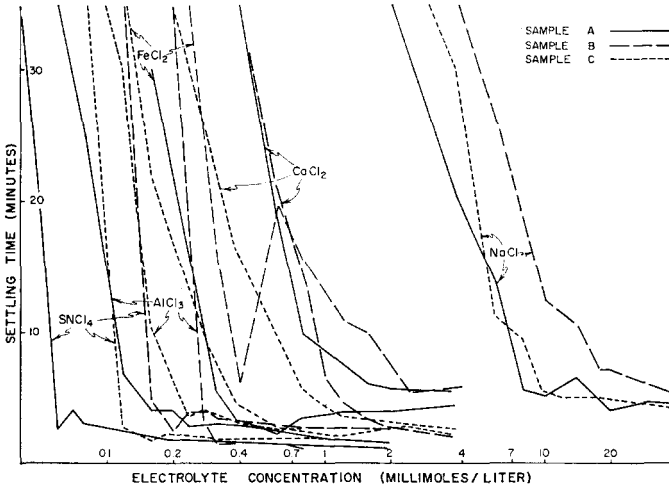


FIGURE 1.—Settling times with cationic flocculants.

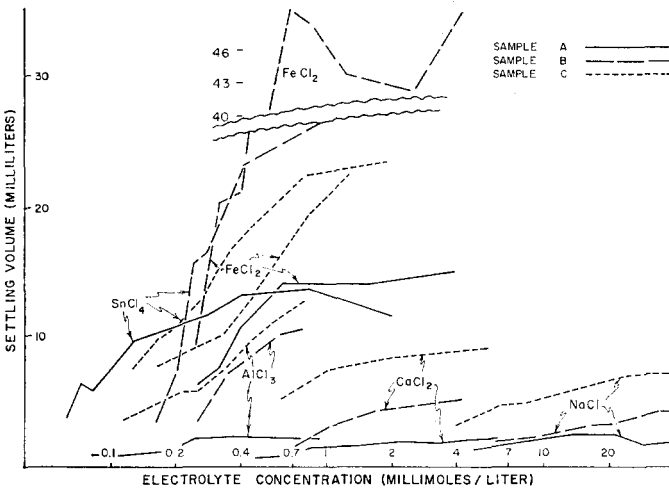


FIGURE 2.—Settling volumes with cationic flocculants.

volume behavior of clay B flocculated with ferrous chloride both invite further investigation. The high-concentration minimum in the settling time curve for clay B at a concentration ratio value close to that of CaCl₂ suggests it is a remnant of the effect of valence on the flocculation efficiency of the

ion; the position of the low-concentration minimum and the breaks in the curves for clays A and C must be explained on the basis of other factors.

The results of the anion flocculation experiments are shown in the settling time curves in Figs. 3 and 4, and some settling volumes in Fig. 5. The variation in behavior from one clay to another is much greater with the

TABLE 2.—CATIONIC FLOCCULANT CONCENTRATION RATIOS

	Na ⁺ : Ca ²⁺ : Fe ²⁺ : Al ³⁺ : Fe ³⁺ : Sn ⁴⁺ ::
Clay A	1.0 : 0.125 : 0.044 : 0.017 : 0.021 : 0.007
Clay B	1.0 : 0.086 : 0.029 : 0.020 : 0.021 : 0.013
Clay C	1.0 : 0.100 : 0.037 : 0.025 : 0.020 : 0.012

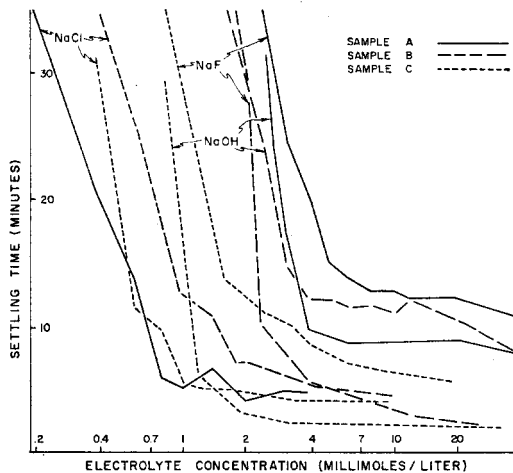


FIGURE 3.—Settling times with monovalent anionic flocculants

various anions than with the cations. This greater variation is not unexpected since the anions are not only adsorbed on the clay surface to a limited extent but also interact with the cations and influence their adsorption and the resulting flocculation of the clay (Grim, 1953, p. 146). On an empirical basis flocculation with the sodium salts of various anions seems to have considerable promise as a tool in clay investigations.

Measurement of settling volumes also seems to hold some promise as a research method. The curves in Fig. 2 show appreciable variation in settling volume from clay to clay. For example, clay B has a larger settling volume than clay C when flocculated with FeCl₂ or SnCl₄, but a smaller settling volume when flocculated with the other chlorides. Fig. 5 shows that clay B has a greater settling volume than clay C when flocculated with NaF, NaOH, or Na₂SO₄, although C has the greater volume when flocculated with NaCl.

In the application of flocculation studies to a geologic problem, tests have been made using anion flocculation in the study of two sets of clay samples. The first set consisted of four samples taken from a vertical section of a transported (?) deposit at depths of 37, 45, 52 and 59 ft. The apparent source of the clay is altered granodiorite. Structures in the clay suggesting relic feldspar cleavage fragments and pebbles, and considerable alteration of the basalt underlying the clay, seem to indicate considerable postdepositional alteration. The other set consisted of two samples of chalky, white clay identical in appearance, texture, diffraction patterns, and apparent source rock taken from locations 20 miles apart. Table 3

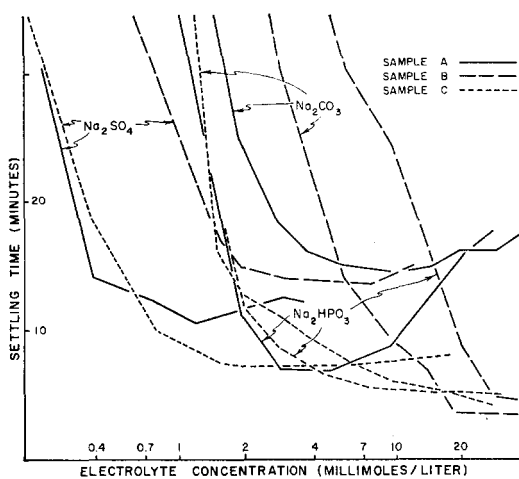


FIGURE 4.—Settling times with divalent anionic flocculants.

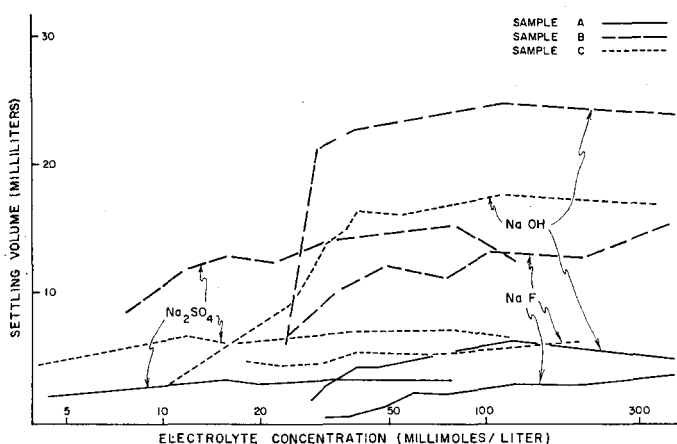


FIGURE 5.—Settling volumes with anionic flocculants.

gives the results of these tests in terms of reagent concentrations at which the settling time curves leveled off. Because the 45-ft sample in the first set would not disperse in distilled water it is not included in the table.

These results cannot be interpreted with certainty but they suggest for the first set of samples either that there was considerable difference in the different layers of clay or rock in the original deposit, or that the post-depositional alteration was not sufficient to produce uniformity. The results with set 2 show large differences in behavior where similarity was expected.

TABLE 3.—REAGENT CONCENTRATION IN MILLIMOL PER LITER FOR RAPID FLOCCULATION

	NaF	NaCl	NaOH	Na ₂ CO ₃	FeCl ₃
Sample					
37 ft	23	15	46	37	0.14
52 ft	23	7	46	320	0.14
59 ft	460	460	230	> 400	0.40
CW 1	230	15	145	250	0.14
CW 2	23	1	> 230	100	0.10

CONCLUSIONS

The experiments show that the response of different clay samples to flocculation by several electrolytes, especially with different anions, varies greatly but there are indications that to some extent the variations are systematic. The test is very sensitive but this sensitivity may make it impossible completely to interpret the experimental results until the theory of flocculation is more fully developed so that the effects of the variables can be clearly evaluated. As an empirical method of comparing clay samples, flocculation by electrolytes holds considerable promise.

Several phenomena were observed in the course of the experiments that do not seem to be explained by the present theories of flocculation. Further work is needed on these points.

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