

STUDIES IN FRACTIONATED MONTMORILLONITE SUSPENSIONS

by

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ABSTRACT

Four natural bentonites, from Texas, Wyoming, Mexico, and Puerto Rico, have been fractionated by use of a super-centrifuge. The fractions have been investigated for base exchange capacity, apparent density, X-ray diffraction character and gel strengths of their suspensions.

Based on (001) spacings from X-ray diffraction and cation composition from ammonium acetate base exchange data, it was found that upon fractionation, clays of heterogeneous cation composition divide into two groups. Fractions larger than 0.150 micron contain the divalent cations Ca^{2+} - Mg^{2+} , while the finer fractions contain the monovalent cation Na^+ . Based on indirect evidence provided by X-ray diffraction, particle size fractionation, and gel strength, and correlation of the data with the literature, it is concluded that Na^+ clays exist as unit layers in suspensions while Ca^{2+} - Mg^{2+} particles are aggregates of a few layers.

Base exchange capacity and density were found to be independent of particle size.

A new structure is postulated and proposed for aqueous montmorillonite gels. This structure, descriptively called "hinge," comprises clay particles oriented randomly to form a network in which each particle is hinged to other particles through sharing of bound particle-water.

INTRODUCTION

One important use of montmorillonites is in drilling fluids. In order better to understand the gel properties of drilling fluids, it is essential to know such fundamental properties as particle size, base exchange capacity, and cation composition of the constituent clays. Although similar studies have been reported in the literature, these studies have covered pure Na^+ or Ca^{2+} systems. The following experiments were conducted on natural bentonites which present heterogeneities in both structure and composition.

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EXPERIMENTAL

The bentonites as received were in 1-5 in. lumps. They were ground to pass through a No. 200 sieve and dried in a 50°C oven for a week prior to any testing.

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Experimental procedure has been described in detail (Mungan, 1962, pp.12-21) and will be given here in brief.

Density Determination

Accurately calibrated pycnometers and pure benzene were used to obtain density of the dry bentonite samples and their fractions.

Particle Size Distribution

From each clay, 1000 g were suspended to form one per cent by weight suspensions which were allowed to hydrate for two weeks. The suspensions were then washed in a super-centrifuge at 50,000 rev/min (about 65,000 G) a number of times to remove soluble salts. The solids were resuspended in distilled water ($R = 300,000$ ohms) to form suspensions of about 0.75 per cent concentration. Particles larger than 44 microns were removed by wet screening through a No. 325 sieve. Sedimentation-decantation was used to obtain 44-to-1 micron fractions. The super-centrifuge was used to obtain submicron fractions. Each fraction was resuspended and refractionated five times to assure nearly monodisperse fractions. Approximate concentration of the suspensions was about 0.01 per cent during centrifugation.

The resulting fractions were dried and ground. A portion from each fraction was refractionated as above to note any particle size change due to drying and grinding.

Two 5.0-0.4 micron fractions were converted into pure Ca^{2+} and pure Na^+ clays in resin exchange columns. Subsequent fractionation of the suspensions of these clays, prepared in different concentrations and subjected to various mixing times, was carried out to study natural coagulation tendencies of the particles.

X-Ray Diffraction

To study cationic compositions of the fractions, oriented slides were prepared by settling about 100 mg of clay (from 0.5 per cent suspensions) on horizontally mounted 1×3 in. slides. As the slides dried slowly, solid matter settled homogeneously. The slides were weighed before and after preparation and if the weight difference did not conform to within 100 ± 5 mg, they were rejected. All X-ray work was carried out at 52 per cent RH (relative humidity) using copper $K\alpha$ radiation, nickel filter, 35 kVP and 16 mA. During a run, the position of the slide was changed three times to check the (001) intensity. If the intensities varied more than 5 per cent, the slide was rejected as being non-uniform in solid thickness.

Quantitative estimates for each mineral have been made from X-ray intensities.

Base-Exchange Capacity

Base-exchange capacity determinations were made by exchanging each whole clay with a solution of 3 N ammonium acetate and determining ions in

the solution as well as ammonium adsorbed on the clay. One gram of clay was weighed into a 250 ml polyethylene bottle and 50 ml of 3N ammonium acetate solution added. The bottles were gently agitated for 24 hr. Suspensions were then centrifuged to separate the supernatant fluid. To the solids, a fresh 50 ml of ammonium acetate solution was added and the cycle repeated. The combined 100 ml of solution was analyzed for Na^+ , Ca^{2+} , Mg^{2+} , and K^+ ions in a Zeiss flame spectrophotometer. To test if the exchange reaction had been carried to completion, the above cycle was repeated with the same solids. Analyses indicated less than 0.03 meq total additional Na^+ , Ca^{2+} , Mg^{2+} , and K^+ . Analyses are summarized in Tables 1 and 2.

A representative number of the collected fractionated solids were analyzed for nitrogen by the Kjehldahl method to check the total exchange capacity.

TABLE 1.—EXCHANGE CAPACITY, meq/100 g OF DRY CLAY

Sample No.	Size, in microns	Apparent Density g/ml	Exchange Capacity from Flame Photometer					Kjehldahl Exchange
			Na^+	Ca^{2+}	Mg^{2+}	K^+	Total	
1		2.51	30	30	25	3	88	85
1.E	1-0.4	2.50	20	40	23	3	86	
1.F	0.4-0.3	2.52	21	40	23	2	86	
1.G	0.3-0.15	2.51	22	35	24	2	83	
1.L	0.15-0.05	2.52	39	27	25	1	92	
1.N	0.05-0.02	2.51	50	20	32	1	103	
13		2.50	8	45	19	0	72	75
13.E	1-0.4	2.51	5	46	29	0	80	
13.F	0.4-0.3	2.50	6	45	32	0	83	
13.H	0.3-0.2	2.55	5	44	34	0	83	
13.K	0.2-0.1	2.49	6	47	33	1	86	
13.M	0.1-0.05	2.50	5	46	36	1	83	
13.N	0.05-0.02	2.51	6	46	40	1	93	

Gel Strength and Viscosity

Viscosities were measured by a variable speed, rotational viscosimeter, the Fann V-G meter, at two angular speeds, 300 and 600 rev/min. Gel strengths were measured at the end of zero and 30 min rest time.

RESULTS AND DISCUSSION

X-ray analyses indicated that impurities concentrated in the fractions larger than one micron in all the clays fractionated. Therefore, our discussion is concerned with the sub-micron fractions only, which were montmorillonitic clays. Occasionally, however, cristobalite, talc, quartz and calcite were found in as small a size as 0.150 micron (Mungan, 1962, p.32).

TABLE 2.—EXCHANGE CAPACITY, meq/100 g OF DRY CLAY

Sample No.	Size, in microns	Apparent Density g/ml	Exchange Capacity from Flame Photometer					Kjehldahl Exchange
			Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Total	
14		2.70	78	19	12	1	109	82
14.E	1-0.4	2.68	45	21	10	0	76	
14.F	0.4-0.3	2.68	45	24	12	1	82	
14.H	0.3-0.2	2.71	49	22	15	1	87	
14.K	0.2-0.1	2.72	49	20	20	2	91	
14.M	0.1-0.05	2.70	60	15	21	2	98	
14.N	0.05-0.02	2.70	65	14	20	3	102	
17		2.55	58	34	18	1	111	
17.E	1-0.4	2.50	19	38	27	1	85	70
17.F	0.4-0.3	2.51	21	34	30	1	86	88
17.H	0.3-0.2	2.55	24	31	31	1	87	
17.K	0.2-0.1	2.52	29	30	32	1	92	
17.M	0.1-0.05	2.55	35	25	34	1	95	
17.N	0.05-0.02	2.54	42	23	30	1	96	90

Density

Apparent densities of the dry clay fractions, determined pycnometrically in benzene are given in Tables 1 and 2. Densities were found not to change with particle size. In the fractions larger than one micron, densities varied somewhat due to accessory minerals.

Particle Size Distribution

Particle size distributions are given in Table 3. The bentonites No. 1, 13, 14, and 17 are from Mexico, Texas, Wyoming, and Puerto Rico, respectively.

TABLE 3.—PARTICLE SIZE DISTRIBUTION

No.	Size, in microns	Percentage of Fraction in Bentonite			
		1	13	14	17
A	> 1	58.7	70.3	15.4	17.5
E	1-0.4	8.5	9.3	8.6	16.0
F	0.4-0.3	8.5	10.5	8.6	15.0
G	0.3-0.15	4.9			
H	0.3-0.2		4.6	10.2	14.0
K	0.2-0.1		3.7	14.0	15.0
L	0.15-0.05	6.8			
M	0.1-0.05		1.4	9.5	6.0
N	0.05-0.02	12.5	0.5	12.5	10.0
P	< 0.02	0.0	0.0	21.6	10.0

Due to five repetitive fractionations of each size from very dilute suspensions, in which particle interaction is negligible, monodispersed fractions had probably been obtained. Subsequent drying at 50°C and regrinding to pass a No. 200 sieve, did not alter particle size, as was verified by refractionating a portion of each clay fraction.

Several authors have noted that Ca²⁺ clay particles are thicker (in *c* direction) than Na⁺ particles. (For example, Bradley and Grim, 1948, p.1407; van Olphen, 1958, p.196.) Table 4 shows the effect of concentration and mixing time on Na⁺ and Ca²⁺ clays. Na⁺ clay particle size is sensitive to concentration but does not change when the suspension is subjected to prolonged mixing. This means that Na⁺ particles are unit layers in dilute suspensions, but at concentrations higher than 1 per cent particle interference causes them to flocculate into aggregates. Ca²⁺ clay shows a pronounced decrease in particle size with prolonged mixing to indicate that particles are broken into unit layers. Aggregation in Ca²⁺ clays has been evidenced in the X-ray patterns also as will be discussed below.

X-Ray Diffraction

The X-ray patterns are given in Figs. 1-4. Only the X-ray pattern of the original bentonite and (001) peak of selected fractions are presented. For complete patterns, see Mungan (1962). The following observations are made:

1. For the bentonites from Wyoming, Mexico, and Puerto Rico, the Ca²⁺-Mg²⁺ concentrate in the coarser fractions, while Na⁺ concentrates in the finer fractions. This is concluded from shifting of the (001) peak from 15 Å to 12.6 Å at 52 per cent RH as particle size decreases. This observation agrees well with the base exchange data. (See Tables 1 and 2.) For the Texas clay, which is all Ca²⁺-Mg²⁺ montmorillonite, no shift in the (001) is noted.

2. For all the clays studied, the intensity of (001) increased as particle size decreased. This is interpreted to mean that in the finer fractions the alternating sequence of water and oriented silicate layers is repeated many more times than in the coarser fractions. This would be the case if the particles dissociate down to individual silicate layers. Further, the intensity increase for divalent clays was greater. It appears, therefore, that although Ca²⁺ particles are

TABLE 4.—PERCENT OF SAMPLE BELOW 1 MICRON

Clay	Mixing Time: 1 Hour Concentration				Concentration: 1 per cent Mixing Time			
	0.5 %	1.0 %	1.5 %	3 %	1 hr	5 hr	15 hr	20 hr
Ca ²⁺	28	27	27	25	27	30	35	50
Na ⁺	75	70	60	45	70	72	72	75

thicker than Na^+ in the larger sizes, as particle size decreases the thickness of the clay particles approaches that of a unit layer in both the Ca^{2+} and the Na^+ montmorillonites.

3. The (001) peaks are sharp and narrow for both the very coarse fractions (> 1 micron) and the very fine fractions (< 0.100 micron). In between these two sizes, the peak appears as a composite of the two peaks, suggesting random interstratification of the 12.4 Å and 15.4 Å layers. The 12.4 Å layers dominate

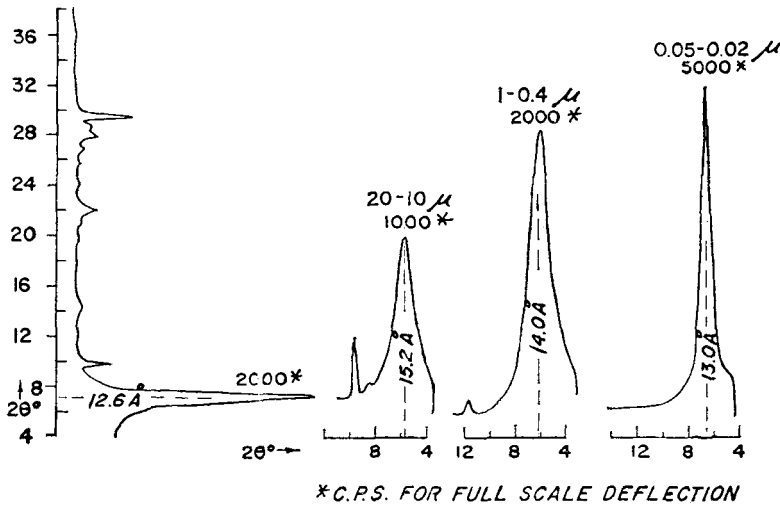


FIGURE 1.—X-ray diffractometer records for a Mexican bentonite (Sample no. 1).

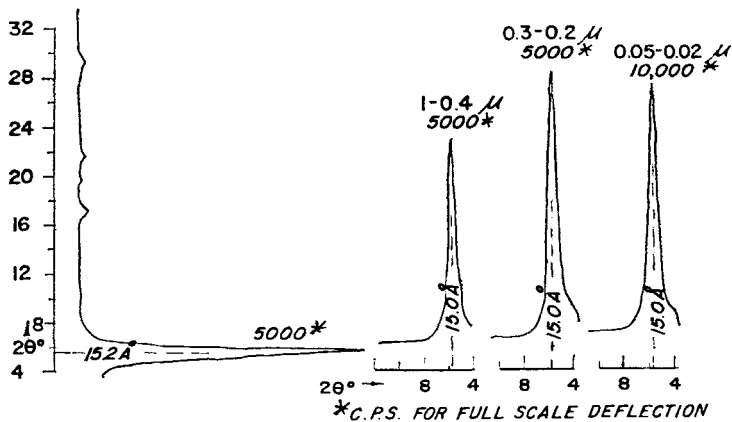


FIGURE 2.—X-ray diffractometer records for a Texas bentonite (Sample no. 13).

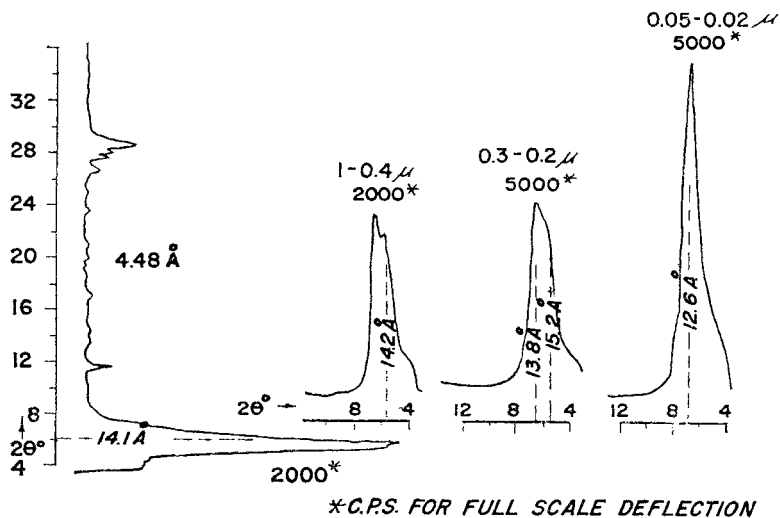


FIGURE 3.—X-ray diffractometer records for a Wyoming bentonite (Sample no. 14).

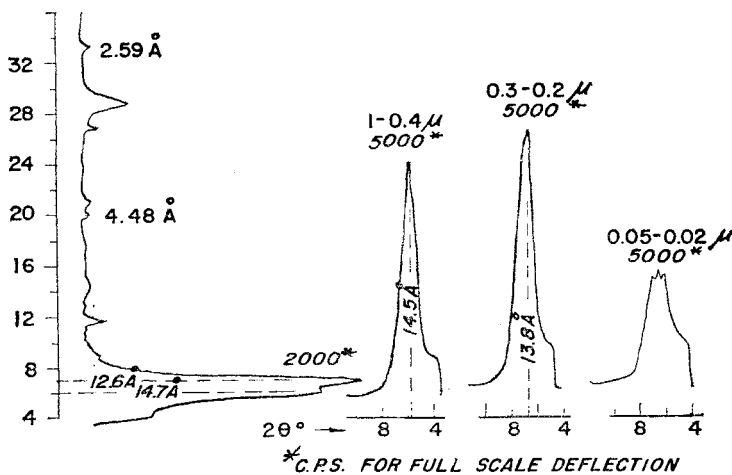


FIGURE 4.—X-ray diffractometer records for a Puerto Rican bentonite (Sample no. 17).

as particle size approaches 0.1 micron. This has been observed previously (Jessen and Mungan, 1959, p.458; and McAtee, 1958, p. 281).

In many of the X-ray patterns diffraction effects other than the normal integral sequences characteristic of one basal spacing were observed. The $d = 4.48 \text{ \AA}$ and $d = 2.59 \text{ \AA}$ peaks in Figs. 3 and 4 are examples. These effects arise when the particles are thick or are aggregates and settle on the slides in positions other than flat. Figure 5 shows disappearance of flocculation features from Ca^{2+} clay upon prolonged mixing to indicate that particles have probably attained unit layer thickness.

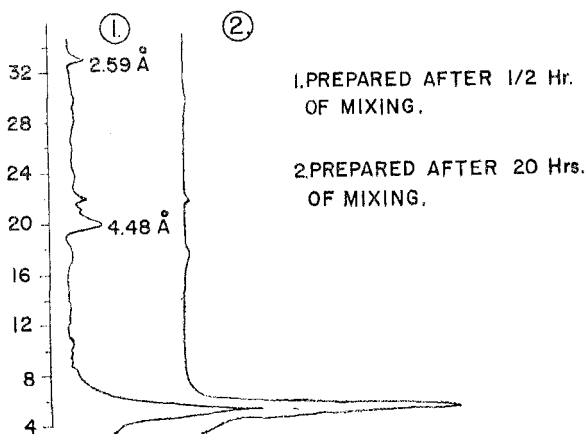


FIGURE 5.—X-ray diffractometer records for two preparations of slides from a 5-0.4 μ fraction of a Ca^{2+} clay.

Base Exchange

The exchange cations of each bentonite and each fraction are given in Tables 1 and 2. Total exchange capacity as determined by nitrogen analysis (Kjehldahl method) was always lower than the total obtained by the flame spectrophotometer analyses. The difference is partly inherent in the method and partly because fractions contained traces of accessory minerals. The results indicate the following:

1. Na^+ and Mg^{2+} increase in the finer fractions.
2. Ca^{2+} decreases in the finer fractions.

The reason for Mg^{2+} increase in the finer fractions is not known. Base exchange capacity does not change with particle size.

Rheology

The Bingham flow curves are shown in Fig. 6. Measurements were made at 300 and 600 rev/min with a Fann V-G meter as has been described by Savings and Roper (1954).

Although highly idealized, the Bingham model can be applied to the clay suspensions. The slope of the lines represents the plastic viscosity, η_p , and the y intercept represents yield stress, S_y . The equation of flow for a Bingham fluid is:

$$S = S_y + \eta_p R_S$$

where S is the shearing force and R_S is the rate of shear. In the Bingham model, yield stress represents a measure of interparticle forces while the plastic viscosity is a measure of mechanical interaction. Figure 6 shows that:

1. Ca^{2+} montmorillonites develop much lower yield stress and plastic viscosity than Na^+ montmorillonites of equal particle size. This can be explained on a simple basis by extension of Einstein's equation to the clay particles:

$$\eta = 1 + 2.5\phi$$

In suspension, Na^+ particles orient greater thicknesses of adsorbed water than Ca^{2+} particles, resulting in greater ϕ (volume fraction of particles) and thus greater η (relative viscosity).

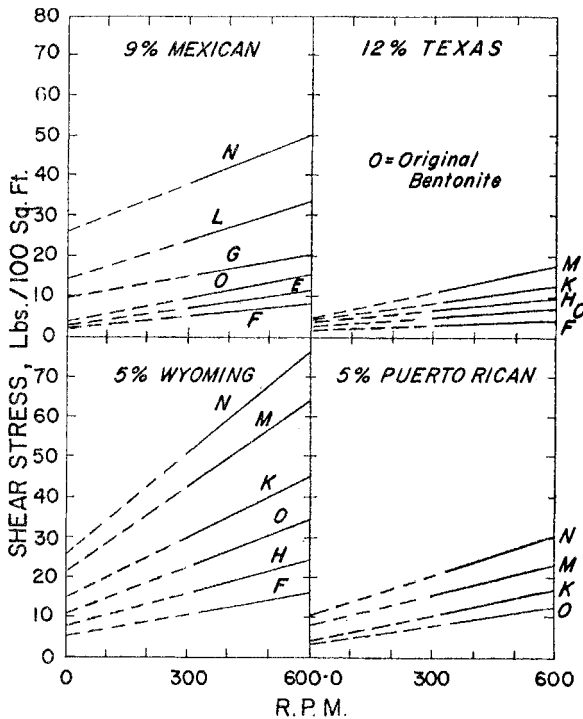


FIGURE 6.—Bingham flow curves for 4 bentonites.

2. For both Na^+ and Ca^{2+} montmorillonite higher gel strength is developed as particle size decreases, cation composition of the fractions remaining the same. This is due to greater number of particles in suspension as particle size decreases, causing a greater mechanical interaction between particles. This is reflected in an increase in η_p .

GEL DEVELOPMENT

The structure of montmorillonite gels is, at best, still based mainly on inference. The recently favored theory is a scaffolding cubic structure with particles linking edge to surface. This is the so-called "house of cards" structure. Some arguments against such a structure are:

1. Clay particles are very thin in the c direction (one unit layer in Na^+ clay, 3 to 4 layers in Ca^{2+} clay) and at the same time they have great extensions in the a, b plane. The average lateral dimensions have been reported to range from 1000 Å to 5000 Å. It is, therefore, very unlikely that a particle only 10–50 Å thick, yet 1000–3500 Å long, can stand vertically on one edge against the surface of another particle and be stable in such a position.

2. Particles have a highly irregular outline in the a, b plane. A great many of the published electron micrographs of montmorillonite mineral specimens have indicated that particles would have only a small number of edge to surface contact points even if they should rest on their edge areas. The gel strength resulting from such a structure would have to be very low. Yet, very high gel strengths are observed.

3. The fundamental support for the "house of cards" structure is based on the fact that clay particles bear a net negative charge; but, due to broken bonds, the edges tend to be positive. Thus, the association is assumed to be a positive edge to a negative surface. This is indeed the case; however, electrostatic bond between edge and surface is rather weak and would result in a rather unstable association of particles. Furthermore, repulsive forces are dominant within clay suspensions and, hence, particles will, in the final structure, be located at positions dictated by repulsive forces. An electrostatic bond strong enough to hold edge to surface under dominant repulsive forces is not likely to be the case.

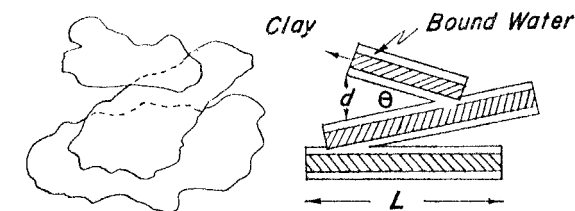
4. In gels, such as drilling fluids, clay concentration is usually 5 to 20 per cent by weight. Using a value of 10 per cent clay by weight (about 4 per cent by volume assuming clay density of 2.5) and two layers of bound water on each silica sheet, a particle 10 Å thick will hold to itself 10 Å (4 layers) of water. The remaining volume, 86 Å in this case, or 86 per cent, is free water. Bound water acts as an integral part of the particle. Clay particles which are at least 1000 Å long, therefore, do not have enough liquid volume allowed them to turn around and stand on edge for that would require free water of 1000 Å thickness at least. At 20 per cent clay concentration, free water per particle is only 72 Å in thickness.

HINGE STRUCTURE

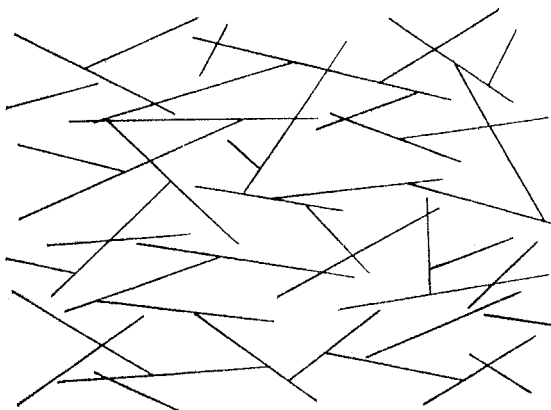
It is proposed that clay particles under the influence of all active forces will assume random positions in a gel, but nevertheless will maintain a bond with each other, thus forming a continuous solid phase. The nature of the bond is best explained through sharing of bound water or water of hydration between two particles. Each clay particle may adsorb 1, 2, or 3 water layers on each silica surface. Each water molecule has two protons that it can share. When two clay particles are in proximity along some point or line edge, the protons of the water from one particle will be shared by the other, thus forming a bond. The association can be between edge and surface or two edges.

Figure 7 represents such an association and gives rise to the name "hinge" for the newly proposed mechanism of gel development. Accessory particles may cause expansion or contraction of the wedge formed at the "hinge" point.

A network of interlacing and randomly hinged particles form the gel structure. The strength of such a gel will be influenced mostly by the length of



PARTICLE ASSOCIATION



GEL STRUCTURE

FIGURE 7.—Schematic drawings of interparticle associations in the range of mud concentrations.

the hinge bond (L) by the distance (d) between the two ends of particles, and by electrostatic attraction forces. For a stable gel structure, it is visualized that most of the particles will hinge along line contacts. To accomplish this despite the highly irregular outlines, the angle θ will have to be very small, 2–10°.

The distance d between particle ends is a function of L and θ . For specific clay concentration, L becomes smaller as the particle size decreases. With far greater numbers of particles, the angle should also diminish. Consequently, increased gel strength should be expected.

The "hinge" structure can be used to explain known thixotropic properties and measured gel strength data.

1. The reversible nature of the thixotropic character of gel, from solid-to fluid-to-solid state, is readily explained by the "hinge" theory. When a gel sets, all particles have formed bonds with each other, in a random fashion, along points, or lines, sharing their bound water. The result is an interlacing network of solid particles forming a continuous network. In this network, there will be chambers occupied by liquid water. These chambers are not interconnected. As a result, the gel behaves like a solid. Under agitation, particle bonds are broken and some of the bound water is disrupted from surfaces. The liquid water volume is increased and water becomes the continuous phase, with the clay particles isolated from each other. If the agitation is stopped, some liquid water will orient on particle surfaces (become bound water), particles will form hinge bonds, and the gel will be restored.

2. Differences of gel strength between Ca^{2+} and Na^{+} clays follow from this theory. Na^{+} clay will develop higher gel strength because it attains smaller particle size, resulting in a greater number of particles in the gel and smaller (d) distances and θ between particles. Furthermore, Na^{+} clays hydrate to greater extent, resulting in a greater amount of bound water and, therefore, a larger volume fraction of the solid in suspension. Finally, Ca^{2+} clay particles tend to aggregate forming clusters or sandwiches, thereby decreasing the effective surface upon which water can bind itself.

3. If the clay concentration is decreased, there will be more liquid water available for each particle. Water will enter between particles, keeping them apart by greater (d) distances and larger angles, θ . A "house of cards" structure will form as the limiting case. However, to reach this state, the clay concentration will have to be low.

The "hinge" structure proposed will apply equally well whether the particles are considered to be flat plates, disks, or fibers, since the hinge bond can be around a mere point.

CONCLUSIONS

This study demonstrated the heterogeneous nature of natural bentonites and showed separation of two distinct groups upon size fractionation. Fractions smaller than the 0.150 micron size contain monovalent cation

(Na^+), while fractions larger than 0.4 micron contain mainly divalent cations (Ca^{2+} - Mg^{2+}). The fractions in between 0.4 and 0.15 micron contain randomly interstratified Na^+ and Ca^{2+} - Mg^{2+} layers.

For a pure Ca^{2+} clay, there were no particles smaller than 0.2 micron, while for a basically Na^+ clay, up to 56 per cent of the clay fell into the size bracket equal to or smaller than 0.2 micron. It would seem of interest to convert a natural bentonite to pure Na^+ and pure Ca^{2+} forms and study particle size distributions and compare them to the particle size distribution of the natural state.

Density and base exchange capacity of montmorillonites are not affected by particle size.

Bingham yield-stress slightly increased and plastic viscosity markedly increased with decreasing particle size, cation composition remaining the same. This is the result of greater numbers of particles in the suspension. When particle sizes were the same, Na^+ clay developed greater yield stress and plastic viscosity than Ca^{2+} clays. This is the result of different interparticle forces and hydration properties of the Na^+ and Ca^{2+} ions.

A new mechanism is postulated for the formation and final structure of aqueous montmorillonite gels.

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