ELECTROKINETIC PROPERTIES OF LIME-TREATED BENTONITES*

by

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ABSTRACT

Zeta-potentials of Na- and Ca-bentonites treated with varying amounts of $Ca(OH)_2$ were measured by a Northrop–Kunitz horizontal cell and non-polarizing $Zn–ZnSO_4$ electrodes. Influences of other factors such as particle size, clay concentration, and salt concentrations were also studied.

The results indicate a four-stage change in zeta-potential and viscosity when $Ca(OH)_2$ is added in increasing amounts to Na-bentonite suspensions:

In the first stage, the addition of small amounts of lime caused no change in zeta-potential suggesting a counteracting effect of Ca^{++} adsorbtion and reaction of OH^- ions to increase the negative surface charge with only a slight change in viscosity. In the second stage, the addition of more lime resulted in a rapid decrease in zeta-potential accompanied by a rapid increase in viscosity and appearance of flocs. In the third stage, additional lime led to a slower decrease in zeta-potential but a continued rapid increase in viscosity and the formation of distinct large flocs. Apparently in all three stages the plentiful OH^- ions caused dissociation of weakly acidic groups to provide additional negative sites for linking the clay particles by Ca^{++} ions. The dissociation of weakly acidic groups probably reached its full capacity by the end of the third stage, termed the "lime retention point". In the fourth stage, the additional $Ca(OH)_2$ in excess of the lime retention point caused a slight change in zeta-potential and a slight decrease in viscosity. In this stage free lime was available for slow pozzolanic reaction.

In the Ca-bentonite–$Ca(OH)_2$ system, the first stage was an increase in zeta-potential due to dominant influence of OH^- potential-determining ions. The second stage was a rapid decrease in zeta-potential and increase in viscosity, corresponding to the third stage in treatment in the Na^+-clay. The end of the second stage is the lime retention point, after which excess lime is used for pozzolanic reaction.

INTRODUCTION

Soils have been stabilized with lime since ancient times, and lime is now being used in road building throughout the world. Addition of hydrated lime, $Ca(OH)_2$, to plastic clays rapidly reduces their plasticity and facilitates handling. The montmorillonitic clay soils, which are common in the Midwest, are most improved by treatment, even though in the natural state they are usually already calcium saturated.

Earlier work by Hilt and Davidson (1960) showed that montmorillonite

* Contribution No. 63–19 of the Soil Research Laboratory.

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clay soils retain $Ca(OH)_2$ far in excess of their cation exchange capacities, as measured at pH 7. This higher requirement must be satisfied before any lime is available for a long-term pozzolanic reaction to form new cementitious compounds. The higher lime requirement is indicated by a levelling off of the plastic limit vs. lime content curve. Later studies by Ho and Handy (1963) showed that slurry viscosity and floc size also reach maxima at this high point, termed the "lime retention point". At this point, the $Ca(OH)_2$ utilized in the lime retention reaction is no longer present, as shown by X-ray and DTA curves. The reaction was found to be pH-dependent, requiring a pH above 11.0. It was therefore suggested that lime retention is a cation adsorption phenomenon resulting from an increase in clay negative charge, perhaps by dissociation of weakly acidic OH groups in a strongly alkaline environment.

The present study was initiated to learn the effect of $Ca(OH)_2$ on zeta-potentials of Na- and Ca-bentonites.

Smoluchowski (1914) showed that the electrophoretic mobility μ of a particle moving through a liquid of viscosity η and dielectric constant D, under the influence of a homogeneous electric field, is given by

$$\mu = \frac{\varsigma\ D\ E}{4\ \pi\ \eta} \tag{1}$$

where ς is the zeta-potential, and E is the potential gradient of electromotive force. This equation is for large insulating particles, or for large cylinders moving with their axes perpendicular to the electrode, provided the radius of curvature at all points on the surface is much greater than the thickness of the double layer.

Booth (1948) and Henry (1948) considered the corrections necessary when the surface conductivity is taken into account. Henry shows that for an insulating particle:

$$\mu = \frac{\varsigma\ D\ E}{4\ \pi\ \eta} \cdot \frac{\lambda_0}{\lambda_0 + \dfrac{\lambda s}{a}} \tag{2}$$

where λ_0 = specific conductivity of the medium
λ_s = surface conductivity of the particles
a = radius of particle.

Street (1957) showed that surface conductivities of kaolinitic particles in KBr solutions of 0.05 N to 0.0083 N concentrations had the values of 1.33×10^{-9}/ohm^{-1} and 3.55×10^{-9}/ohm^{-1}, respectively, or very low.

The effect of relaxation, arising from deformation of the oppositely charged diffused double layer, has a retarding force on the particles. In an applied electric field the charge of the diffuse double layer is displaced

in a direction opposite to the movement of the particle. This not only retards the electrophoresis by its movement, but also by the resulting dissymmetry of the double layer, it sets up a retarding potential difference. A correction has been suggested by Booth (1950).

In the following studies, Smoluchowski's equation was used with the following assumptions:

1. The electric field does not deform the double layer, or the magnitude of relaxation effect can be neglected.

2. The surface conductivity of bentonite particles is negligible.

Samples

All the samples used were of natural Ca-saturated Aberdeen Panther Creek bentonite and Na-saturated Volclay (the American Colloid Co.). Both contained about 90 per cent $<5\mu$ montmorillonite. The cation exchange capacities determined by the NH_4–Ac method at pH 7.0 were 83 and 88 m.e./100 g for the Ca-bentonite and the Na-bentonite respectively.

METHODS AND MATERIALS

Zeta-potential

A horizontal Northop–Kunitz cataphoresis apparatus (Arthur A. Thomas Co.) was used to determine the zeta-potential. The complete apparatus consists of the cataphoresis cell, and a right-hand and a left-hand electrode vessel with non-polarizable c.p. zinc electrodes. One-tenth normal zinc sulfate solution was used to fill the vessel for salt bridges.

The movements of the clay particles were observed by an ordinary Bauch & Lomb microscope equipped with dark field condenser and external illumination to eliminate the heating effect from a substage lamp. The total magnification used was of the order of $420\times$, a combination of a $20\times$ micrometer eyepiece and a $21\times$ objective lens. For each measurement the passage of at least 7 particles in each direction across 92.4μ on the ocular scale was timed by means of a stop watch.

To measure the true electromobilities independent of any electro-osmotic effect, it is necessary that the correct stationary layers in the cell be observed. A relatively simple calculation shows that these layers are located at 21.1 per cent of the total height from each inner wall for an infinitely wide cell (Abramson, 1934). A very wide cell was therefore used, and measurements were made at these stationary levels. The conductivity of the sample solution was measured separately with a conductivity bridge. Current through the cell was measured with a microammeter with $0–160\mu A$ scale and 1 per cent accuracy. The d.c. potential was supplied by dry cells, and a switch was included in the circuit to reverse the polarity without

effecting the reading on the ammeter. Thus the potential gradient E in equation (1) can be calculated as follows:

$$E = \frac{i}{A \bar{L}}$$

where i = current (amps)

A = cross-section area of the cell (0.0679 cm²)

$\bar{L}$ = specific conductance of the suspension (ohm⁻¹ cm⁻¹).

Viscosity

Relative viscosities of freshly prepared Na-bentonite–Ca(OH)$_2$ mixtures were measured with a Stormer paddle-type viscosimeter after 1 hr equilibration with shaking at 25°C. The paddle was actuated by a 25 g weight; results are expressed in minutes required for 100 revolutions of the rotor. Details of the method are presented elsewhere (Ho and Handy, 1963).

X-ray Diffraction

X-ray diffraction inspections were made of the dried Na-bentonite–Ca(OH)$_2$ suspensions. One-half ml samples were pipetted on clean glass slides and were dried slowly in the air. Then the samples were placed in a 60°C oven for 3 to 4 days, until the 001 d-spacing of the Na-bentonite had decreased to about 12Å. The dry slides were then transferred into a vacuum desiccator containing a 45 per cent CaCl$_2$ solution, which gives 30 to 35 per cent relative humidity at 24°C. The desiccator was evacuated for 15 min by means of an aspirator, and the slides were allowed to equilibrate for 3 days before being X-rayed. A diffraction unit (General Electric XRD-5) with copper Ka radiation was used with incident beam angle 4°, detector slit 0.2°, beam slit 1°, scan rate 2° per min, and time constant 3 sec.

PRELIMINARY STUDIES

Relation between Particle Size and Zeta-potential

About a 2 per cent Na-bentonite suspension was agitated for at least 8 hr with an electric stirrer. Particles of different sizes ranging from 0.5 to 12μ were pipetted after settling (Steele and Bradfield, 1934). Then 1 ml of each size fraction was re-suspended in 100 ml of 0.0029 N NaCl solution, which was used for conducting current during electrophoretic measurement.

The zeta-potential and particle size in the particular range studied showed a linear relationship (Fig. 1). The absolute value of zeta-potential tended to decrease slightly with an increase in particle size.
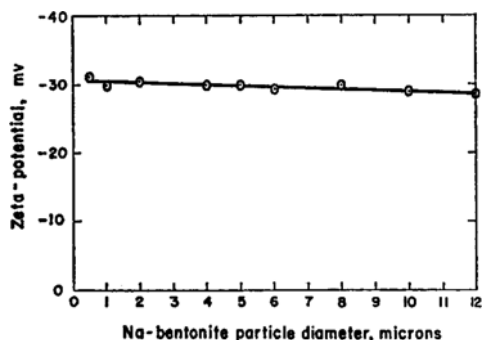
FIGURE 1.—Effect on zeta-potential of particle size calculated from settlement analysis.

Effect of Clay Concentration on Zeta-potential

The zeta-potentials of well-dispersed Na-bentonite and Ca-bentonite in suspensions ranging from 0.003 to 0.05 g/100 ml in 0.0029N NaCl solutions were determined (Fig. 2). The zeta-potential of Na-bentonite was not effected significantly by its concentration in the range studied.
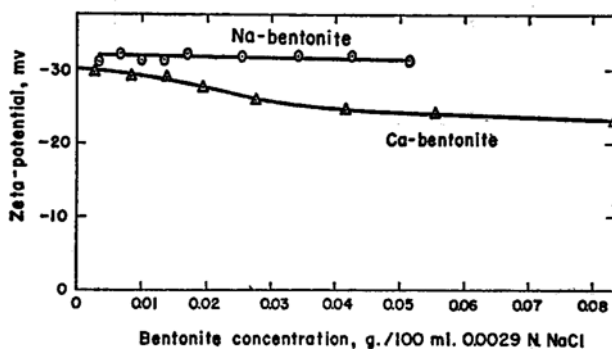

FIGURE 2.—Effect of bentonite concentration on zeta-potential in dilute NaCl solution.

In the Ca-bentonite suspensions, absolute values of zeta-potential decreased with clay concentration, particularly in the range of 0.003 to 0.03 g/100 ml. Since the Ca-bentonite concentrations were very low compared with the total amount of Na^+ ions present in the medium, some ion exchange reaction may have caused this change.

RESULTS

Effects of NaCl *and* CaCl$_2$

Preliminary zeta-potential measurements were made on bentonites suspended in sodium and calcium chlorides of various concentrations (Figs. 3, 4). The zeta-potential of Na-bentonite (CEC=0.018 m.e./100 ml suspension) decreased sharply from 44.5 to 32 mV as the NaCl concentration was raised from zero to 0.1 m.e./100 ml. The decrease was probably due to compression of the diffuse double layer of Na$^+$ ions upon addition of excess Na$^+$. The zeta-potential then levelled off with further addition of NaCl. The zeta-potential of Ca-bentonite (CEC=0.0126 m.e./100 ml suspension) increased sharply from 17 to 27 mV in the same range of
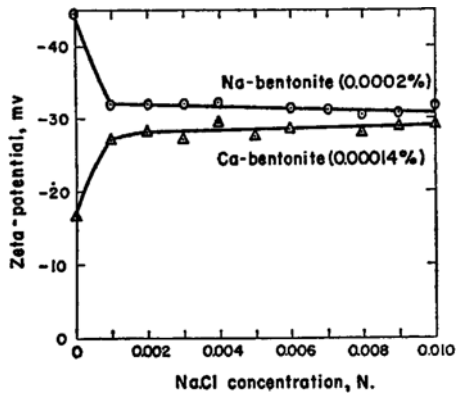
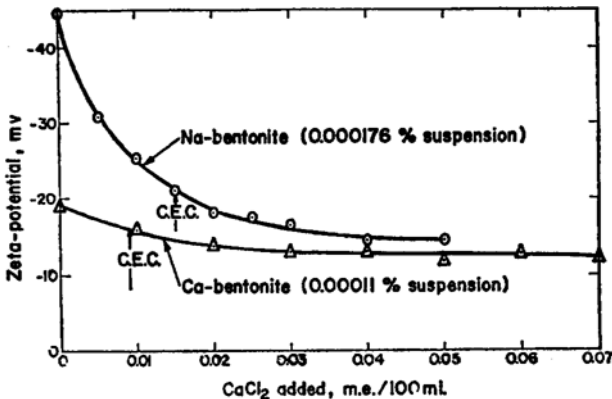FIGURE 3.—Effect of NaCl concentration on zeta-potential of bentonites.

FIGURE 4.—Effect of CaCl$_2$ concentration on zeta-potential of bentonites.

NaCl concentrations, and then levelled off, probably as a result of ion exchange and expansion of the double layer (Fig. 3).

The zeta-potential of Na-bentonite decreased drastically from 45 to 20 mV upon the addition of $CaCl_2$ equivalent to its CEC (Fig. 4). The zeta-potential then continued to decrease gradually as more $CaCl_2$ was added, with no break in the curve. This suggests that an initial rapid cation exchange took place owing to the preferential adsorption of available Ca^{++} ions; but complete cation exchange occurred only when $CaCl_2$ in excess amounts was added.

Addition of $CaCl_2$ to Ca-bentonite changed its zeta-potential only slightly, even when the addition of $CaCl_2$ was more than twice its CEC. The slight decrease in zeta-potential with $CaCl_2$ was probably caused by further compression of the diffuse double layer of Ca^{++} ions.

Effects of $Ca(OH)_2$ on Zeta-potential and Viscosity

Na-*bentonite*.—Various amounts of reagent grade $Ca(OH)_2$ were added to 100 ml of 2 per cent well-dispersed Na-bentonite suspension in 125 ml Erlenmeyer flasks, and thoroughly mixed. Then the flasks were tightly stoppered with rubber stoppers, and the mixture was allowed to cure at 24°C for one year. At the end of the curing period, 1 ml of each suspension was withdrawn and mixed with 100 ml volume of distilled water in a volumetric flask. (The reason for using distilled water instead of 0.0029 N NaCl was to avoid any complications due to cation exchange. Preliminary results showed that cation exchange effected the zeta-potentials.) The large flocs which formed as a result of the addition of lime were dispersed in 1 to 2 min with a 1 kW ultrasonic generator to give particles in the desired size range, i.e. from 0.5 to 12μ. The electrophoretic movement of particles was observed at 23°C room temperature after at least 4 hr equilibration.

Experiments were also performed with freshly prepared Na-bentonite–$Ca(OH)_2$ mixtures. In these tests sample mixtures were allowed to cure at 23°C for 2 days with mechanical shaking and for 1 additional day without stirring.

The addition of $Ca(OH)_2$ to Na-bentonite suspensions resulted in a four-stage change in zeta-potential, and the viscosity changes follow an inverse trend (Fig. 5). In the first stage, addition of $Ca(OH)_2$ up to 2 per cent (54 m.e./100 g) causes essentially no change in zeta-potential. This phenomenon is contrary to that observed in the Na-bentonite–$CaCl_2$ system at pH around 7, indicating that the potential determining OH^- ions at high pH are playing a major role in increasing the negative surface charge of the clay crystals, counteracting the effect of Ca^{++} adsorption and exchange. The viscosity is low at this stage, suggesting that Ca^{++} adsorption may be mainly on the internal exchange sites.

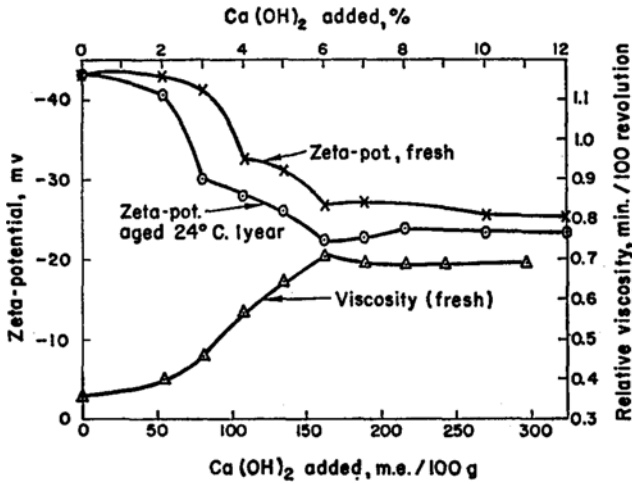In the second stage, additional $Ca(OH)_2$ up to 3 per cent (81 m.e./100 g)

FIGURE 5.—Effect of Ca(OH)₂ content on zeta-potential and viscosity of Na-bentonite before and after curing.

in the aged sample, and up to 4 per cent (108 m.e./100 g) in the freshly prepared samples caused a rapid decrease in zeta-potential accompanied by a considerable increase in viscosity and the appearance of flocs. Here Ca⁺⁺ ions apparently played the dominant role in depressing the diffuse double layer and increasing the intermicellar attractive force.

In the third stage, addition of Ca(OH)₂ from 3 per cent (81 m.e./100 g)
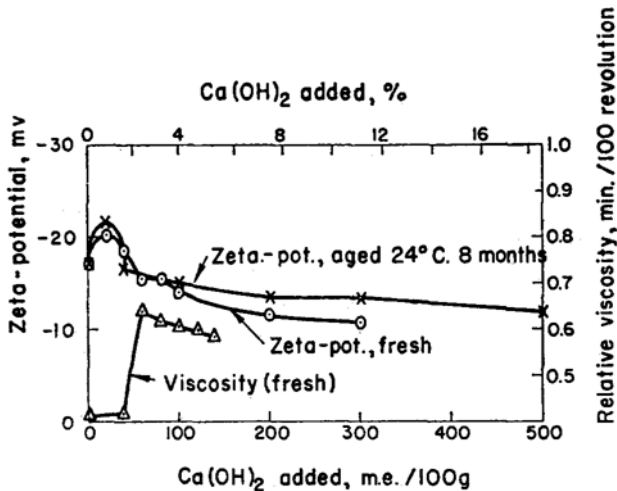

FIGURE 6.—Effect of Ca(OH)₂ content on zeta-potential and viscosity of Ca-bentonite before and after curing.

to 6 per cent (162 m.e./100 g) resulted in a slow decrease in zeta-potential, but with a continued fast increase in viscosity, which reached the maximum at about 6 per cent of $Ca(OH)_2$. Formations of distinct large flocs were observed at the same level of $Ca(OH)_2$ treatment. This, plus the relatively small change in zeta-potential, suggests that Ca^{++} ions and OH^- ions were counteracting in their effect on micellar charge, the Ca^{++} ions being adsorbed in such a way as to act as bridges linking the clay particles. The dissociation of weakly acidic sites by OH^- ions probably reached full capacity at the end of this stage, 6 per cent of $Ca(OH)_2$, indicated by the maximum increase in viscosity and formation of distinct large flocs.

In the fourth stage, which starts at the lime retention point, addition of $Ca(OH)_2$, from 6 to 12 per cent caused only a very slight change in zeta-potential. The relative viscosity decreased slightly, and was accompanied by the continued formation of distinct large flocs.

That the zeta-potential of the freshly prepared samples was higher than that of the aged samples at comparable level of lime content may be due to incomplete cation exchange in the freshly prepared samples.

Ca-*bentonite*.—Procedures for sample preparation were the same as those used for Na-bentonite–$Ca(OH)_2$ systems, except that 0.05 g/100 ml H_2O suspension was used for zeta-potential measurement.

The zeta-potential of Ca-bentonite increased rapidly from 17 to 21 mV upon addition of 20 m.e. $Ca(OH)_2/100$ g of clay, verifying the increase in negative surface charge at high pH (Fig. 6). Change in viscosity at this stage was negligible.

Addition of up to 60 m.e. $Ca(OH)_2/100$ g of clay caused a rapid decrease
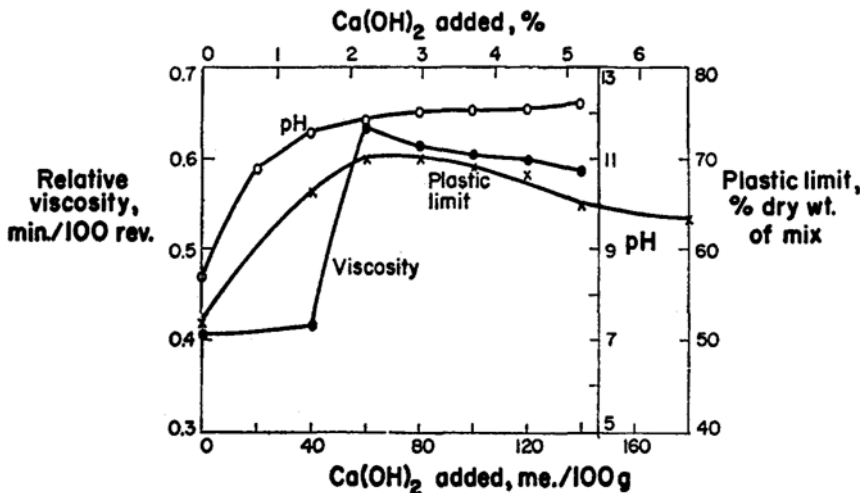

FIGURE 7.—Changes in plastic limit and viscosity (30 per cent suspension) of Ca-bentonite with addition of $Ca(OH)_2$.

in zeta-potential from 21 to 15 mV, associated with a sudden increase in viscosity up to a maximum value. Therefore Ca^{++} ion adsorption must play a dominant role, balancing the now more highly negative clay charges and linking the clay particles. This stage was accompanied by the formation of distinct large flocs. Moreover, the plastic limit also reached the maximum at the same level of $Ca(OH)_2$ treatment, indicating the maximum occlusion of free water within the flocs (Fig. 7).

Additional lime caused only a slight decrease in zeta-potential, viscosity, and plastic limit. The zeta-potential of the freshly prepared samples in this last stage was lower than that of the aged samples, probably indicating removal of free $Ca(OH)_2$ through pozzolanic reaction in the aged samples. The conductivity data also indicated removal of Ca^{++} ions from the system.

Effect of $Ca(OH)_2$ on X-ray d-spacing

In the aged suspensions the d-spacings increased from 13Å for pure Na-bentonite to 14.7Å Na-bentonite treated with 2 to 4 per cent lime, indicating partial Ca^{++} saturation (Fig. 8). The spacing was 15.2Å in treatments exceeding 5 per cent lime, indicating complete calcium saturation. The shape of the peaks gradually became symmetrical with the increasing degree of calcium saturation. At higher lime contents, decrease in d_{001} diffraction intensity appeared due to lower preferred orientation of the highly flocculated clay particles.

The freshly prepared samples (2 days' equilibration) showed only a 14.7Å d_{001} spacing and unsymmetrical peaks regardless of the amounts of $Ca(OH)_2$ added, indicating that interlayer cation exchange was a slow process compared with the rate of flocculation.

DISCUSSION

Na-bentonite

The first addition of up to 2 per cent of $Ca(OH)_2$ (54 m.e./100 g) to Na-bentonite seems to have been used for partial interlayer cation exchange, indicated by the change in X-ray d_{001} spacing after equilibration at 35 per cent r.h. Yet the potential determining OH^- ions must play an important role in increasing the negative surface charge at high pH, to compensate for the depressing effect of the Ca^{++} ions. The slight increase in viscosity suggests that the energy of attraction between clay micelles remains very low.

In the second stage, which covers the range from 2 to 3 per cent lime in aged samples and up to 4 per cent lime in the freshly prepared samples, there was a rapid decrease in zeta-potential accompanied by a rapid increase in viscosity and the appearance of flocs. Although the Na-
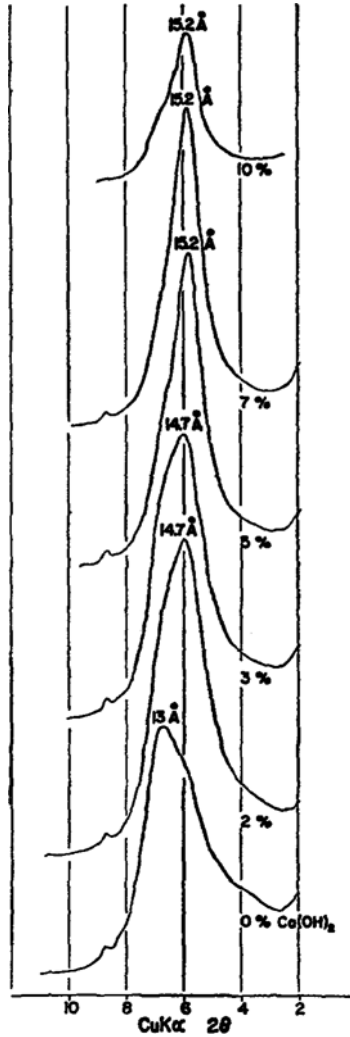
FIGURE 8.—Montmorillonite d_{001} spacings in aged Na-bentonite–Ca(OH)$_2$ mixtures after equilibration at 35 per cent r.h.

bentonite was still only partially saturated in the interlayer with Ca^{++} ions, indicated by the d_{001} spacing, and total Ca^{++} adsorption was high enough to play a dominant role in decreasing the zeta-potential. Furthermore, some of the available Ca^{++} ions must have been used for linking the clay micelles, since viscosity increased rapidly in this stage.

In the third stage, addition of Ca(OH)$_2$ from 3 per cent to 6 per cent

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caused a slower decrease in zeta-potential, associated with the continued fast increase in viscosity and the formation of distinct large flocs. X-ray data indicated the completion of cation exchange, but the Ca++ ions adsorbed appeared to be far in excess of the CEC as measured at pH 7. Previous work by other workers (Schofield, 1949; Lin, 1959, p.19) has shown the pH dependence of the CEC. The increase in charge at high pH was ascribed to dissociation of weakly acidic terminal groups. Such an increase in clay charges would provide some sites for linking the bentonite particles by means of the bridging action of the extra Ca++ ions adsorbed, causing a rapid increase in viscosity, formation of large flocs, and probably occlusion of free water within the flocs, raising the plastic limit. These phenomena were not observed in either Na-bentonite–CaCl$_2$ or Na-bentonite–NaOH systems (Ho and Handy, 1963), indicating that both high pH and the availability of polyvalent cations are essential factors for this type of flocculation. Furthermore, flocculation took place before there was time for complete cation saturation upon addition of Ca(OH)$_2$ to Na-bentonite suspensions. The decrease in pH with time in the clay–lime mixtures further indicated the gradual consumption of OH− ions in pozzolanic reactions.

Similar results were obtained by Street and Buchanan (1956) in kaolinite–Ca(OH)$_2$ and kaolinite–Ba(OH)$_2$ systems. They explained the phenomena on the basis of bi-polar flocculation, which is caused by the attraction of separated positively and negatively charged areas on the kaolinite particles. However, this type of simultaneous presence of both positive and negative charges on the highly negative charged montmorillonite particles may be ruled out because of internal compensation (Schofield and Samson, 1953, 1954).

In the fourth stage, when more than 6 per cent of Ca(OH)$_2$ was added, there was only a slight change in zeta-potential, accompanied by the slight decrease in viscosity and continued formation of large flocs. Previous X-ray and DTA data show that this stage is characterized by the free Ca(OH)$_2$ which is available for slow utilization in pozzolanic reactions after the dissociation of the weakly acidic terminal groups reaches full capacity.

Ca-*bentonite*

In Ca-bentonite–lime systems, no cation exchange can take place on the permanent charge sites. Addition of small amounts of Ca(OH)$_2$ to the Ca-bentonite suspension increased negative surface charge and zeta-potential through the dissociation of weakly acidic terminal groups and did not affect viscosity. Upon further addition of lime, Ca++ adsorption reduced zeta-potential and greatly increased viscosity over that of Ca-bentonite at pH 7. The higher clay negativity and the Ca++ ion adsorption appear to be factors in this interaction. Simultaneously there was formation of large flocs, and the plastic limit attained a maximum at the same level

of $Ca(OH)_2$ added (60 m.e./100 g), indicating the occlusion of free water within the flocs.

CONCLUSIONS

1. Small amounts of $Ca(OH)_2$ added to bentonite increase negative charges on the clay particles, probably by dissociation of clay OH groups. The action is complicated in Na-bentonite by accompanying partial ion exchange.

2. Further additions of $Ca(OH)_2$ allow Ca^{++} adsorption to compensate the increased negative charge gradually and cause floc formation. Both a high pH and presence of polyvalent cations are required for this type of flocculation.

3. Complete Ca^{++} saturation is not necessary for this flocculation; flocculation and partial exchange occur rapidly, but complete interlayer cation exchange is comparatively slow and probably continues by diffusion.

4. Dissociation of clay OH groups, and accompanying adsorption of Ca^{++} ions to change viscosity and plasticity, reaches a maximum at the "lime retention point"—about 6 per cent $Ca(OH)_2$ for Na-bentonite, and about 2 per cent $Ca(OH)_2$ for Ca-bentonite. Lime added in excess of these amounts remains undissolved until needed to replenish the system as the dissolved lime is used up in slow pozzolanic reactions.

ACKNOWLEDGMENTS

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