PARTICLE INTERACTION AND RHEOLOGY OF ILLITE-IRON OXIDE COMPLEXES

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Abstract—The Bingham yield stress for suspensions of illite-iron oxide complexes is examined as a function of pH and iron oxide content. Addition of iron oxides to illite increased the yield stress over a pH range of 3 to 10. With increasing pH the yield stress decreased for the complexes with iron oxides of 2 and 5% while the complexes with iron oxides of 7, 10, and 20% exhibited the maximum yield stresses at pH values from 6 to 8. The iron oxides which are not associated with the illite enhanced the yield stress more than the iron oxides precipitated on the illite surfaces. The yield stress for the complexes was correlated with their zeta potential, and the higher yield stress is considered due to smaller interparticle repulsion.

Key Words—Bingham yield stress, Morphology, Illite, Iron oxide, Particle interaction, Zeta potential.

INTRODUCTION

Iron oxides (embracing oxides, oxyhydroxides, and hydrated oxides) in close association with the surface of soil clay particles contribute to the structural stability of soils. Significant correlations between free iron oxides and aggregate stability (El-Swaify and Emerson, 1980) and clay colloidal stability (El-Swaify, 1976) have been obtained. Electron microscopy (Greenland and Oades, 1968) and the study of charge characteristics of soil materials after removal of iron oxides by chemical treatment (Sumner, 1963) support the view that iron oxides affect soil structure through the interaction of their positive charges with the negatively charged clay particles.

Other studies on the association of iron oxides with clay particles have been conducted using laboratory-prepared complexes of pure clay minerals and synthesized iron oxides (Follett, 1965; Greenland and Oades, 1968; Greenland, 1975; Saleh and Jones, 1984). It was shown from these studies that the iron oxides were precipitated onto the kaolinite surfaces only when precipitation occurred under acid conditions, thereby leading to a reduction of the total net negative charge of the clay particles. The association of the iron oxides

with the kaolinite has been explained in terms of the pH-dependency of the surface charge of iron oxides. Electrophoretic measurements (Rengasamy and Oades, 1977; Kavanagh and Quirk, 1978) indicated that the net charge on clay surfaces became strongly positive at low pH values as a result of adsorption of iron oxides.

The role of iron oxides as cementing agents has been studied with respect to the behavior of sensitive marine clays. Selective dissolution procedures on remolded marine clays revealed that removal of up to 4% amorphous material, primarily iron and silica compounds, was associated with large decreases in the liquid limit and plasticity index (Hendershot and Carson, 1978). Reduction in the remolded shear strength of sensitive clays after removal of amorphous iron and aluminum with acid and base solutions has been attributed to the exposure of negative charges on clay particles resulting in a development of net repulsive forces between the clay particles (Yong *et al.,* 1979). The iron mineralogy of sensitive marine clays was assessed by Mössbauer spectroscopy. A decrease in the yield stress following citrate-dithionite and acid-base extraction of iron oxides has been demonstrated. (Torrance, 1984; Torrance *et al.,* 1986).

To develop a better understanding of the role of iron oxides in natural clays, the Bingham yield stress (Yong and Ohtsubo, 1987) and consistency limits (Ohtsubo and Wada, 1988) have been studied for kaolinite-iron

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oxide complexes in relation to morphology and charge characteristics. The Bingham yield stress and the liquid limit have been used in a relative way to assess the effects of iron oxides on clay behavior in pastes and suspensions. The present work was undertaken to provide more information concerning the electrostatic interaction of iron oxides with clay particles vis-a-vis clay behavior in suspension. The Bingham yield stress of the complexes of illite and synthetic, poorly-ordered iron oxides is examined as a function of pH and iron oxide contents. Particle interactions in the suspensions are assessed with the aid of electron microscopy and zeta potential determinations.

MATERIALS AND METHODS

The clay used in this study is 70% <2-μm clay fraction and consists mainly of illite accompanied by a small amount of kaolinite. Iron oxide solutions were prepared by adding saturated sodium bicarbonate solution dropwise to a solution of 20 g anhydrous ferric chloride ($FeCl_3$) in 140 ml water until the pH reached 1.5. Excess salt in the iron oxide solutions was removed with dialysis. The pH of the iron oxide solutions after dialysis was 3.8. The X-ray diffraction patterns of the prepared iron oxides indicate the presence of poorly crystallized akaganéite ($\beta FeOOH$).

For Bingham yield stress determinations six sets of illite suspensions were prepared in distilled water at a solid concentration of around 8% by weight.

To assess the role in Bingham yield stress determinations between those oxides precipitated on illite surfaces and those present as a separate phase from illite particles, two types of illite-iron oxide mixtures were prepared as follows:

(1) Adding iron oxide solutions to illite, nine sets of illite-iron oxide mixtures containing iron oxides of 2, 5, 7, 10, and 20% by weight were all adjusted to pH = 3.0 using HCl.

(2) Mixing iron oxide solutions (pH 9.5) with illite suspensions of pH 9.5, nine sets of illite-iron oxide mixtures containing iron oxides of 2, 7, 10, and 20% by weight were prepared.

Each of the suspensions was adjusted to a required pH value using HCl and NaOH. The mixtures prepared in (1) and (2) are referred to as illite-iron oxide complexes of initial pH 3.0 and 9.5, respectively. Measurements of the pH were always taken after equilibration for 24 hr, the equilibrium pH values being measured in the suspensions. The final solid and sodium concentrations of the suspensions of illite and illite-iron oxide complexes for Bingham yield stress determinations were adjusted to 7% by weight and 0.005 M, respectively, by adding concentrated NaCl solutions.

For electron microscopy, drops of dilute suspension were spotted onto plastic micro grids and examined in a JEOL 100B electron microscope.

The samples for electrophoretic measurement were prepared at a solid concentration of 0.7% by diluting the Bingham yield stress suspensions using 0.005 M NaCl. The electrophoretic apparatus was equipped with a flat, rectangular cell following the procedure described by Mori *et al.* (1980). Measurements were performed by focusing on one of the stationary levels within the cell and timing the motion of a minimum of 5 particles, first in one direction and then on reversing the polarity of the applied field in the opposite direction. The results obtained have been expressed as the zeta potential. Calculations of the zeta potential are based on the following Helmholtz-Smoluchowsky's formula (Hiemenz, 1977; Mori *et al.,* 1980):

$$\zeta = \frac{4\pi\eta}{D} \cdot \frac{1}{t} \cdot \frac{c}{i} \cdot s \times 300^2 \times 10^{-1}$$

in which ζ = zeta potential, in mV; η = coefficient of viscosity of the liquid, in poise; D = dielectric constant of the liquid; l = migration distance of particles, in μm; t = time required for particles to migrate distance l, in sec; c = electrical conductance of suspensions, in μS/cm; i = electric current flow in the cell, in μA; s = cross sectional area of the rectangular cell perpendicular to an electrical gradient, in cm².

The Bingham yield stress of the suspensions was measured using a rotating cylindrical viscometer. Flow curves were recorded at increasing and decreasing shear rates, equilibrium having been attained at each rate. There was evidence of hysteresis in some suspensions. Therefore, the Bingham yield stresses obtained from the flow curves of increasing shear rates were adopted.

MORPHOLOGY OF THE COMPLEXES

Electron micrographs of illite-iron oxide complexes at initial pH 3.0 and 9.5 are shown in Figures 1 and 2, respectively. At pH 3.0 for the complexes with 7% iron oxide (Figure 1a), fine "pepper" iron oxide particles and masses of acicular particles appear to be entirely associated with the face surfaces of the illite, not the edge surfaces. Raising the pH of the complexes from 3.0 to 6.0 (Figure 1b), and further to 9.0 (Figure 1c) produced no observable separation of the iron oxides from the illite. It would appear that once formed, the illite-iron oxide complexes are extremely stable.

The pH of the point of zero charge (PZC) of iron oxides ranges between 7 and 9 without any marked difference between the various mineral forms (Schwertmann and Taylor, 1989). Therefore the iron oxides are predominantly positively charged at a pH of 3. This leads to the adsorption of iron oxides to negatively charged face surfaces of illite at pH 3.0. The adsorption of iron oxides onto the illite surfaces at pH 3.0 would be expected to confer positive charges. Raising the pH while neutralizing this positive charge does not materially affect the surface of iron oxide particles already
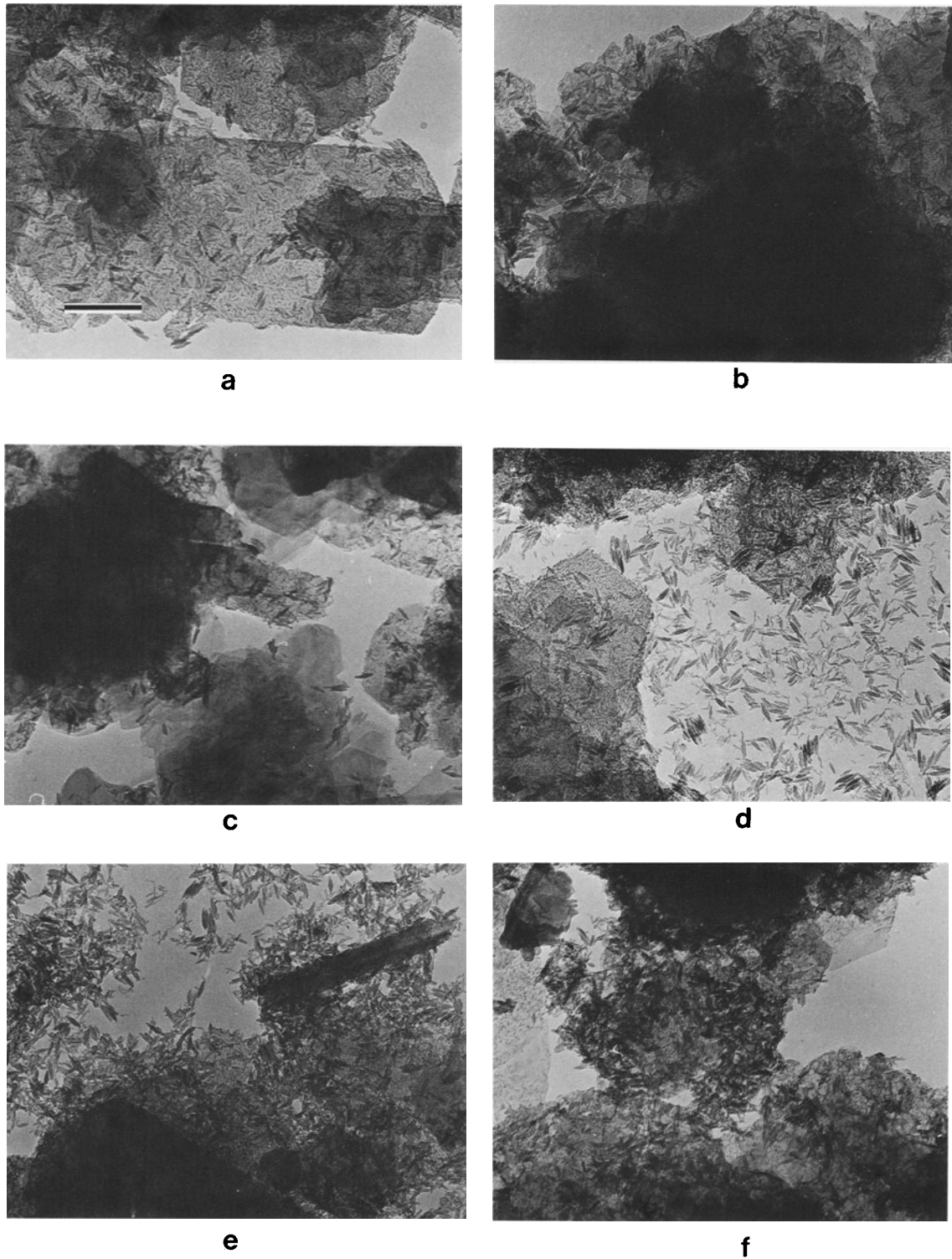
Figure 1.   Electron micrographs of illite-iron oxide complexes of initial pH 3.0 (a) Fe oxide:7%, pH 3.0 (b) Fe oxide:7%, pH 6.0 (c) Fe oxide:7%, pH 9.0 (d) Fe oxide:20%, pH 3.0 (e) Fe oxide:20%, pH 6.0 (f) Fe oxide:20%, pH 9.0 Scale bar indicates 500 Å.
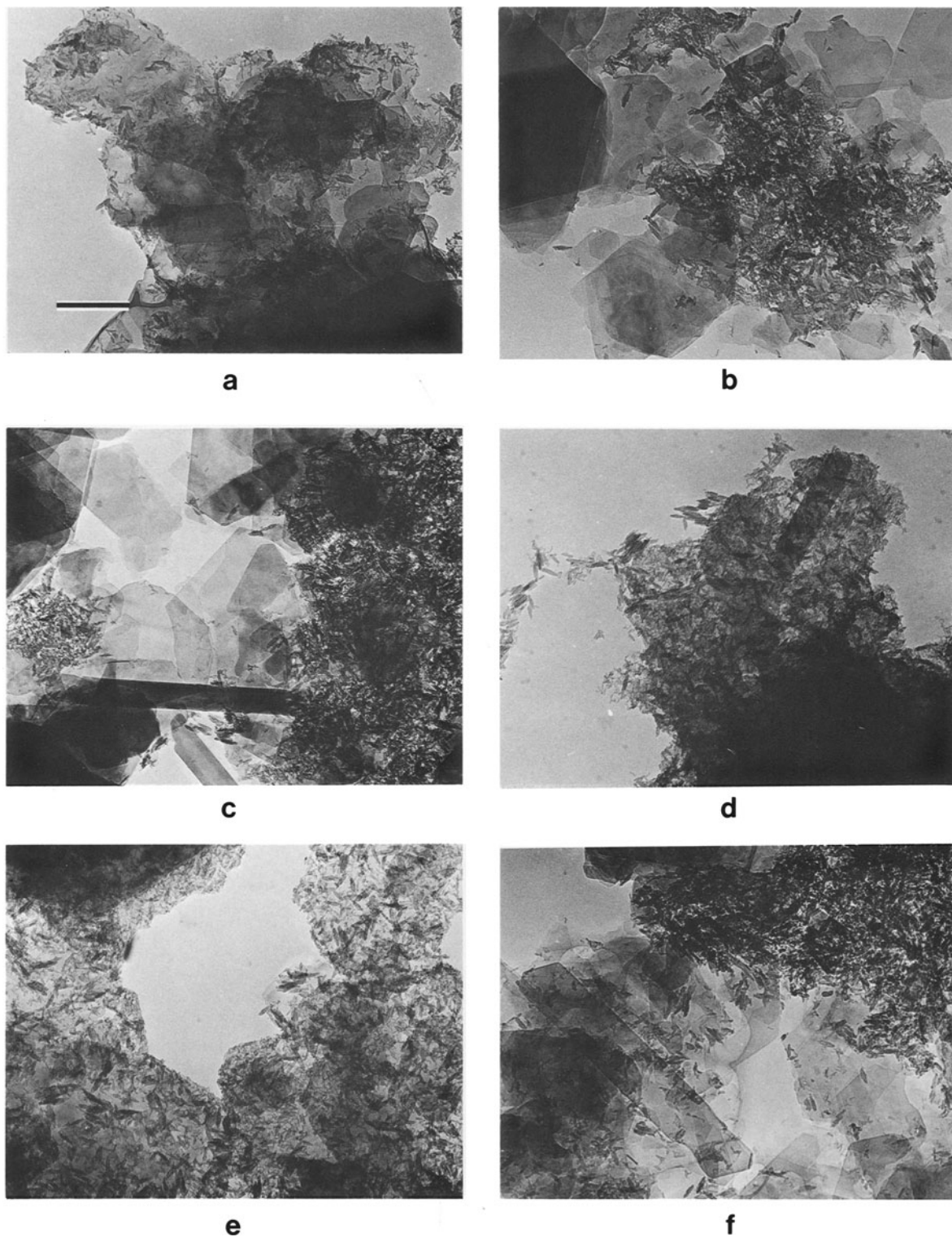
Figure 2.   Electron micrographs of illite-iron oxide complexes of initial pH = 9.5 (a) Fe oxide:7%, pH 3.0 (b) Fe oxide:7%, pH 6.0 (c) Fe oxide:7%, pH 9.0 (d) Fe oxide:20%, pH 3.0 (e) Fe oxide:20%, pH 6.0 (f) Fe oxide:20%, pH 9.0 Scale bar indicates 500 Å.
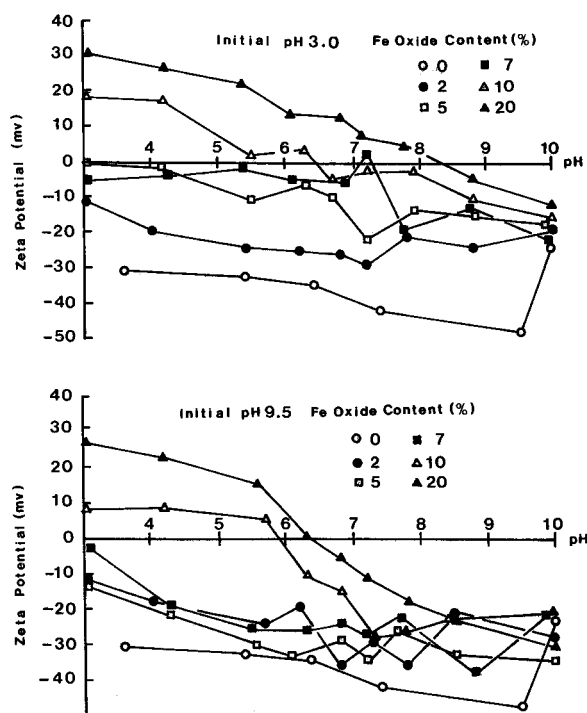
Figure 3. Zeta potential of illite-iron oxide complexes with different iron oxide contents as a function of pH. (a) Initial pH 3.0 (b) Initial pH 9.5.

neutralized by the illite, and will not release the particles into suspensions.

At pH 3.0 for the complexes of initial pH 3 with 20% iron oxide (Figure 1d), a large proportion of acicular iron oxide particles are not associated with the illite, while the "pepper" iron oxide particles are precipitated on the illite surfaces. This suggests that negative charges on the illite surfaces are completely neutralized by the "pepper" iron oxides, resulting in the separation of the acicular iron oxide particles from the illite. At pH 6.0 (Figure 1e) or 9.0 (Figure 1f) the acicular iron oxide particles are observed to be aggregated, presumably due to a decrease of the interparticle repulsion of iron oxides.

At pH 9.0 for both the complexes of initial pH 9.5 containing 7 and 20% iron oxides (Figures 2c and 2f), the acicular iron oxide particles are seen as a separate phase, independent of the illite, with no observed adsorption of iron oxides onto illite surfaces. The iron oxides separated from the illite are present as aggregates because of a greater Van der Waals attraction than the electrostatic repulsion between the iron oxide particles. By lowering the pH to 6.0, a substantial proportion of the iron oxide particles are adsorbed on the illite surfaces for the complexes with 20% iron oxides (Figure 2e), while most iron oxide particles remain as a separate phase independent of the illite for the com-

plexes with 7% iron oxides (Figure 2b). At pH 3.0 (Figures 2a and 2d) the iron oxide particles in both complexes containing iron oxides of 7 and 20% are associated with the illite surfaces. This suggests that for iron oxides to be more fully associated with the illite surfaces, a lowering of the pH to levels around 3 would be needed.

ZETA POTENTIAL

The zeta potential is the electric potential in the double layer at the interface between a particle which moves in an electric field and the surrounding liquid. Although the Smoluchowsky equation does not exactly apply to the aggregated particles of illite-iron oxide complexes under consideration, the calculated zeta potential could be a relative index of the changes in the charge characteristics of illite through addition of iron oxides. Taking note of the fact that the zeta potential is directly related to the net charge of clays, Figures 3a and 3b show the zeta potential curves of illite and illite-iron oxide complexes of initial pH 3.0 and 9.5 as a function of pH. The face surfaces of illite possess permanent negative charge, and the pH-dependent edge change is small relative to the face surface charge (Greenland and Mott, 1978). The illite is therefore negatively charged over the pH range examined, and the net negative charge increases with increasing pH.

In Figure 3a, the complexes of initial pH 3.0 with iron oxides of 2, 5, and 7% are observed to be negatively charged over a pH range of 3 to 10. This suggests that the face surfaces of the illite in these complexes are partially neutralized by the iron oxides, retaining negative charge even after the adsorption of iron oxides. Charge reversal took place for the complexes with iron oxides of 10 and 20%. Electrophoretic mobility curves obtained by Rengasamy and Oades (1977) and Kavanagh and Quirk (1978) are similar. An isoelectric point value of 8.4 for the complexes with 20% iron oxides agrees well with the isoelectric point values of iron oxides presented by Schwertmann and Taylor (1989). This indicates that the adsorption of 20% iron oxide neutralized all the negative charges on the face surfaces of illite, and the electrokinetic behavior of the iron-coated illite particles is controlled by the charge characteristics of the iron oxides precipitated on the illite surfaces.

The potential curves for the illite-iron oxide complexes with iron oxides of 5 to 20% prepared at initial pH 9.5 (Figure 3b) are located in lower positions compared with those of the complexes prepared at initial pH 3.0 for the same iron oxide content. This indicates that the particles in the complexes of initial pH 9.5 possess more negative charges at a given pH value. The electron micrographs in Figure 2 show that iron oxides in the complexes of initial pH 9.5 are not associated with the illite surfaces at pH values of 6 and 9. One

could therefore speculate that the higher negative charge developed in the complexes prepared at initial pH 9.5 could be due to the presence of negative charges on the face surfaces of illite particles which are not coated by the iron oxides.

BINGHAM YIELD STRESS

Clay suspensions in a coagulated state at low solid concentrations show flow curves which approximate the Bingham model. Bingham yield stress is a sensitive measure of the degree of coagulation and can be used as an index of change in the particle-interaction forces and modes of particle association. Figure 4 shows the Bingham yield stress curves tested at various pH values for the illite and illite-iron oxide complexes prepared initially at pH 3.0. The variation of yield stress with pH for a suspension of plate-like clay particles has been discussed by Van Olphen (1977), and Rand and Melton (1977). The likely model can be viewed in relation to the yield stress of the illite in Figure 4. The highest yield stress for the illite is obtained at pH 3.5 where edge-to-face association occurs. This is seen to decrease with changes in the particle configuration from edge-to-face to edge-to-edge, and finally to a dispersed structure.

Addition of iron oxides of 2 and 5% to the illite markedly increased the yield stress over a pH range of 3 to 10. Because the illite surfaces are partially neutralized by the adsorption of positively-charged iron oxides as shown in Figure 3a, the iron-coated illite particles possess both positive and negative charges on their surfaces in the lower pH range. Thus the electrostatic attraction between the residual negative charge on the illite surfaces and the positive charge of the iron oxide particles adsorbed on the illite surfaces would cause flocculation of face-to-face association. This leads to greater yield stresses for the complexes with iron oxides of 2 and 5% than for the illite (FIgure 4a). Higher yield stresses for the complexes with 5% iron oxide than for those with 2% iron oxide are ascribed to the greater interparticle attraction energy in the face-to-face configuration. Reduction in the yield stress with increasing pH for the complexes with iron oxides of 2 and 5% could be attributed to the decrease of attraction energy between the iron-coated illite particles resulting in a change in charge from positive to neutral.

In the case of the complexes with iron oxides of 7 and 10%, the yield stress increased with increasing pH, showing a maximum at pH values of 6 and 7.7, respectively. For the 20% iron oxide content the yield stress was almost zero below pH 6, but increased with rising pH without reaching the maximum. Smaller yield stresses in the low pH range can be explained in terms of repulsion due to the positive charge on the illite surfaces fully coated by iron oxides. With increasing pH the repulsion between the iron-coated illite surfaces
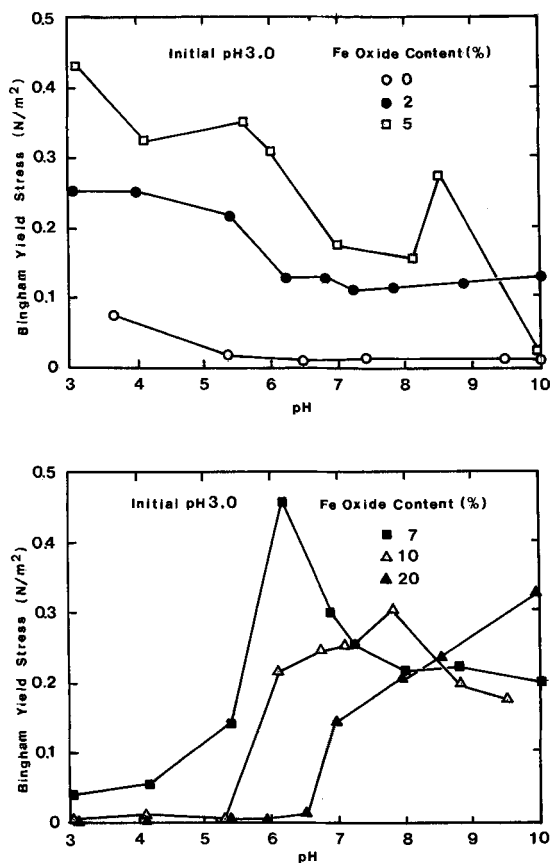

Figure 4. Variation in Bingham yield stress with pH for illite-iron oxide complexes of initial pH 3.0 with different iron oxide contents.

would decrease due to the changes in iron oxide charge from negative to neutral, leading to a decrease of the yield stress. The maximum yield stresses at pH values of 6 and 7.7 for iron oxide contents of 7 and 10% could be attributed to the minimum electrostatic repulsion established between the particles. For complexes with 10% iron oxides, the pH value where the maximum yield stress occurs roughly agrees with the net isoelectric point determined from the zeta potential measurements (Figure 3a).

The Bingham yield stress curves for the complexes prepared initially at pH 9.5 are shown in Figure 5. It is noted that while the yield stress for a given iron oxide content varies in a similar way to the complexes of initial pH 3.0 (Figure 4), the increase in the yield stress by addition of iron oxides was greater for the complexes of initial pH 9.5.

The enhancement of the yield stress for the illite with added iron oxides can result from two basically different phenomena: (1) the electrostatic potential of the illite surfaces may be reduced to permit particle aggregation; or (2) the iron oxide particles may be adsorbed on more than one illite particle, and thus are
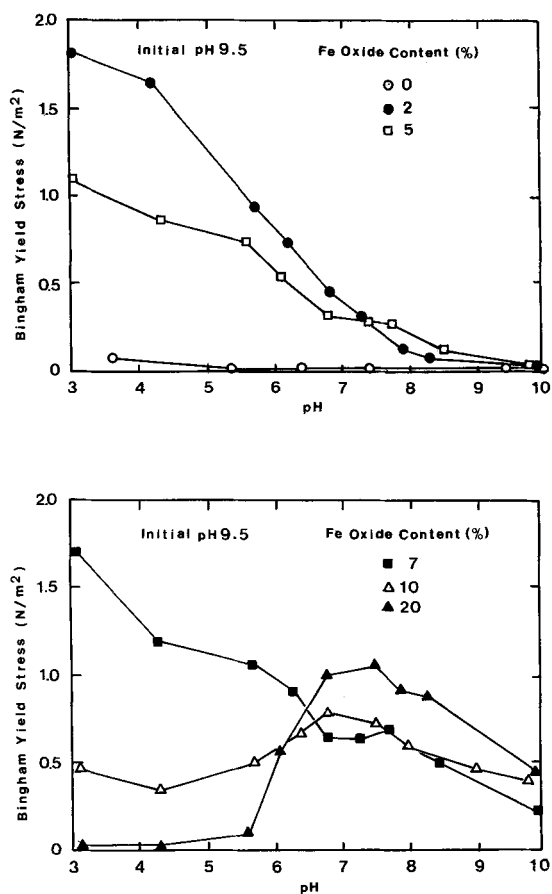
Figure 5. Variation in Bingham yield stress with pH for illite-iron oxide complexes of initial pH 9.5 with different iron oxide contents.

Figure 6. Relation between zeta potential and Bingham yield stress for illite-iron oxide complexes: (a) initial pH 3.0 (b) initial pH 9.5.

directly responsible for interparticle bridging (Michaels, 1954).

For the complexes prepared at initial pH 3.0, a reduction of electrostatic potential on the illite surfaces occurs since the iron oxide particles are adsorbed on the face of illite. The possibility of interparticle bridging by iron oxides would be very small. In the complexes prepared at initial pH 9.5, aggregates of dissociated iron oxide particles (due to their interparticle attraction), will be attracted to the face surfaces of more than one illite particle, therefore resulting in the formation of a bridge between illite particles. This serves to enhance the yield stress more for the complexes of initial pH 9.5 than for the complexes of initial pH 3.0.

Response of the yield stress of illite by addition of iron oxides confirms the role of iron oxides in natural clays previously studied by Yong et al. (1979), Torrance (1984), and Torrance et al. (1986). They have indicated that citrate-dithionite and acid-base extractions of iron oxides decrease the shear strength and the yield stress for remolded post-glacial marine clays.
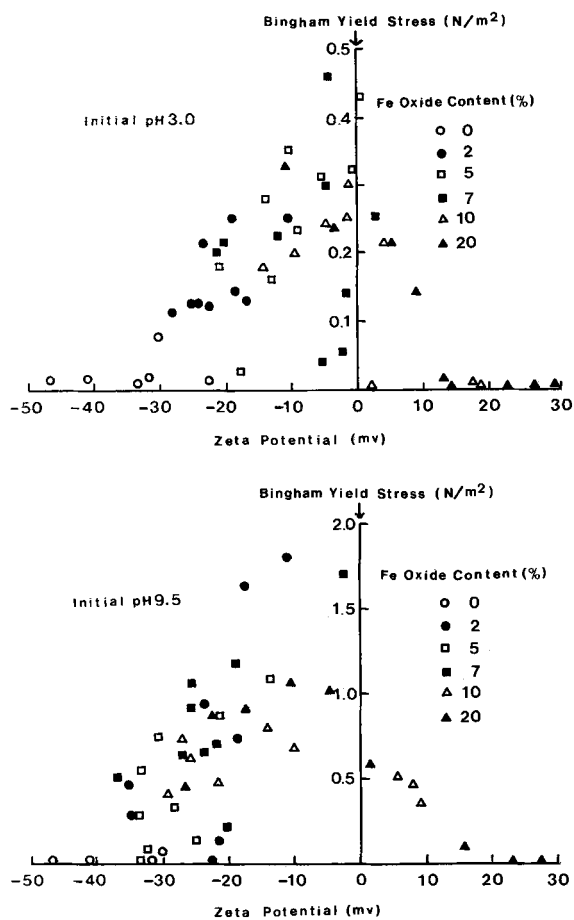
ZETA POTENTIAL VERSUS BINGHAM YIELD STRESS

The zeta potential, representing the electric potential at an unknown distance from the surface in the double layer, is not equal to the surface potential. It is to some extent comparable with the Stern potential, although it is not necessarily identical with that potential. Therefore, if the zeta potential is considered to be a measure of the particle repulsion, then a relation is expected to exist between the Bingham yield stress and the zeta potential.

This relation is presented in Figures 6a and 6b where the yield stress data for the complexes of both initial pH 3.0 and 9.5 are plotted against the zeta potential. The yield stress increased with decreasing negative zeta potential, showing a maximum at a zeta potential of zero, and subsequent decreases with increasing positive zeta potential. The maximum yield stresses at a zeta potential of zero for both the complexes prepared at initial pH 3.0 and 9.5 can be attributed to the minimum

electrostatic repulsion between particles. The complexes of initial pH 9.5 gave higher yield stresses than the complexes of initial pH 3.0 for the whole zeta potential range. This is thought to be responsible for the interparticle bridging between illite particles by the dissociated iron oxides in the complexes prepared at initial pH 9.5.

SUMMARY AND CONCLUSIONS

The iron oxides in the complexes prepared at initial pH 3.0 are retained on the face surfaces of illite when the iron oxide content is 7%, irrespective of subsequent increases in the pH of the complexes (up to 9.0). For 20% iron oxide content, excessive iron oxides not associated with the neutralization of negative charges on the illite surfaces are present as a separate phase from the illite. In the case of the complexes prepared at initial pH 9.5, the iron oxides are separated from illite at pH 9.0 when the iron oxide content is 7 and 20%. For the iron oxides to be fully associated with the illite surfaces, a lowering of the pH below 3.0 is needed.

For both complexes of initial pH 3.0 and 9.5, iron-coated illite surfaces are negatively charged over the pH range examined for iron oxide contents of 2, 5, and 7%, while charge reversal occurs for iron oxide content of 20%.

Addition of iron oxides to illite increases the Bingham yield stress over a pH range of 3 to 10. For both complexes of initial pH 3.0 and 9.5, the yield stress decreases with increasing pH for lower iron oxide content. The maximum occurs near pH values of the isoelectric point of iron oxides for higher iron oxide contents. The yield stress for the complexes is correlated with the zeta potential, and the higher yield stress is considered due to smaller interparticle repulsion.

Changes in the yield stress of illite by addition of iron oxides are different depending on whether or not the iron oxide particles in the complexes are associated with illite surfaces. The iron oxides which are not associated with illite enhance the yield stress more than the iron oxides precipitated on the illite surfaces.

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