

# SPATIAL RELATIONS BETWEEN AIR BUBBLES AND FLOCCULATED KAOLINITE AND DICKITE\*

*by*

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## ABSTRACT

The optical microscope revealed that when air-saturated dilute aqueous suspensions of coarse kaolinite and dickite crystals were evacuated, negatively charged bubbles formed on and between the particles, which showed characteristic spatial relations to the bubbles and to each other.

Crystals leached with HCl developed edge-to-face flocculation over a wide acid pH range and presented their edges to the bubbles, indicating positive edge-charges. The addition of Na-montmorillonite reduced the number of particles adhering to the bubbles and impeded the edge-to-face flocculation.

In slightly acid suspensions, the particles became adlinedated to form chains linking bubbles together or dependent from them.

At pH <3 or >7 the bubbles retained relatively few particles probably because the negative charge density on bubbles decreased at pH <3, while the crystals lost their positive edge charges at pH >7. At pH >7 crystals were often retained by their basal surfaces.

Crystals saturated with Ca<sup>2+</sup> or Pb<sup>2+</sup> showed face-to-face flocculation and tended to present their basal surfaces to the bubbles. The relatively large amounts of Ca- and particularly of Pb-clay secured by the bubbles may be associated with the lessened wettability caused by these cations.

The mantles of adherent particles affected the stability of the bubbles, both by preventing the coalescence of neighbors, and by lengthening the diffusion paths for dissolved air passing from smaller to larger bubbles.

## INTRODUCTION

CRYSTALS of flocculated kaolinite are said to develop edge-to-face or face-to-face arrangements in response to changes in the concentration of appropriate electrolytes in the ambient solution. The evidence is largely dependent on the interpretation of alterations in viscosity or sedimentation volume, or on arguments from the presence or absence of streaming birefringence (Schofield and Samson, 1954). In addition, viscometric studies led

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Street (1956) to postulate adlineated floccules. During the present studies of flocculated coarsely crystallized kaolinite and dickite, all the suggested particle-arrangements were observed and photographed through the optical microscope. Moreover, the spatial relations between crystals and negatively charged air-bubbles revealed the presence or absence of positive edge-charges.

## MATERIALS AND THEIR PREPARATION

The materials are listed in Table 1. The clays A, B, and C were converted, where appropriate, to H-, H,Al-, Na-, Ca-, or Pb-forms. H-forms were obtained by rapid leaching with *N* HCl (cf. Harward and Coleman, 1954) and were examined soon after preparation. H,Al-forms were made by leaching with 0.1 *N* HCl (Harward and Coleman, *op. cit.*) or by electro-

TABLE 1.—CHARACTERISTICS OF MATERIALS USED

Code letter	Mineral	Morphology	Approx. diam.	Source
A.	Dickite	Hexagonal plates and thick booklets	10–100 $\mu$	Near Scranton, Pennsylvania
B.	Kaolinite	Platelets and booklets with some mica-plates	2–80 $\mu$ (+323 mesh)	Georgia
C.	Kaolinite	Kaolinite	2–44 $\mu$ (–325 mesh)	Georgia
D.	Muscovite	Cleavage-flakes	–325 mesh	New England

dialysis. Na-, Ca-, and Pb-forms were prepared by leaching with 1.0 *N* NaCl + 0.001 *N* HCl (Schofield and Samson, 1954), 1.0 *N* CaCl<sub>2</sub> and 1.0 *N* PbCl<sub>2</sub> respectively. The samples prepared by leaching with solutions of HCl or of metallic chlorides were washed with water to remove Cl<sup>–</sup>.

## PROCEDURE

Air bubbled through KOH solution was used to saturate distilled water at atmospheric pressure. Amounts of HCl or NaOH appropriate to pH values between 2 and 12 then added. Twenty mg of air-dried clay were suspended in 250 ml of the solution.

The air-saturated suspension, in a horizontal glass tube (6 mm I.D.) closed at one end, was placed on the stage of the microscope, where it

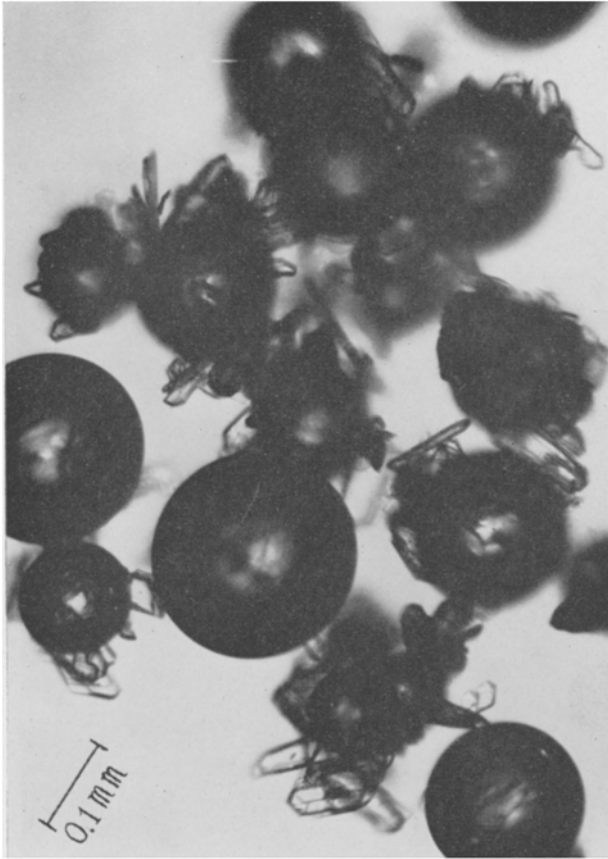


PLATE 1.—H,Al-dickite (+325 mesh) at pH 4.7. The crystals present their edges to the bubbles and themselves show edge-to-face flocculation.

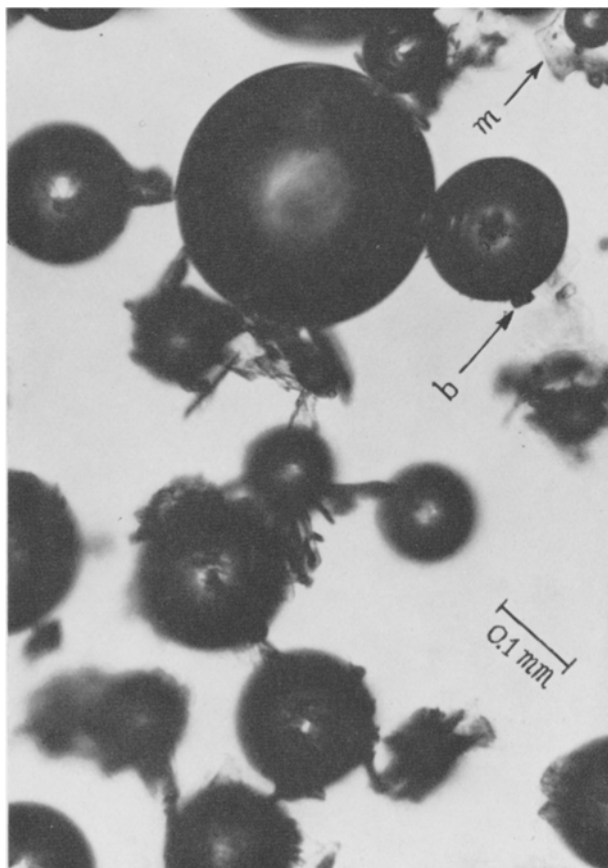


PLATE 2.—H,Al-kaolinite (+325 mesh) at pH 4.7 The crystals, and a book (b), present their edges to the bubbles and the crystals show edge-to-face flocculation. A mica-flake (m) presents its basal surface to a bubble.

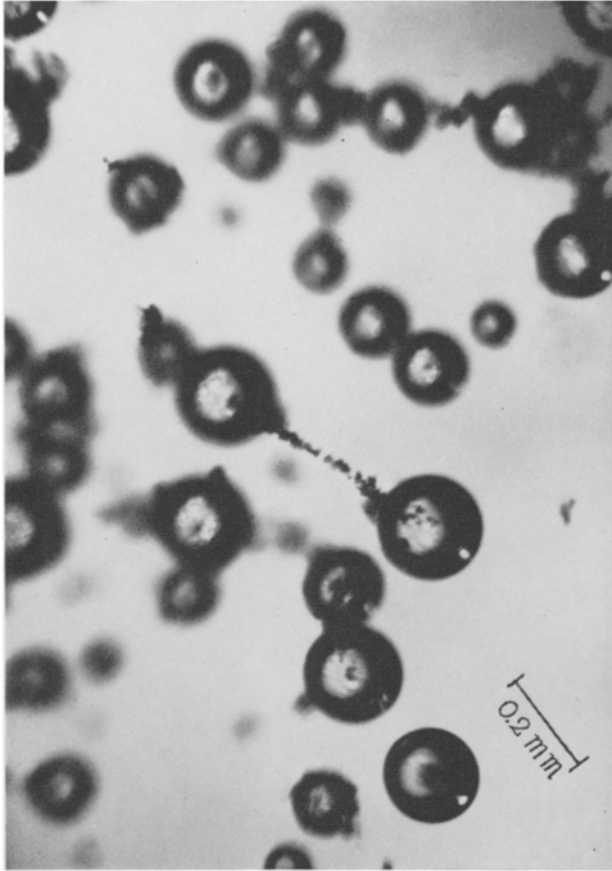


PLATE 3.—H,Al-kaolinite ( $-325$  mesh) at pH 6.5. Adlineated floccule stretched between two bubbles.

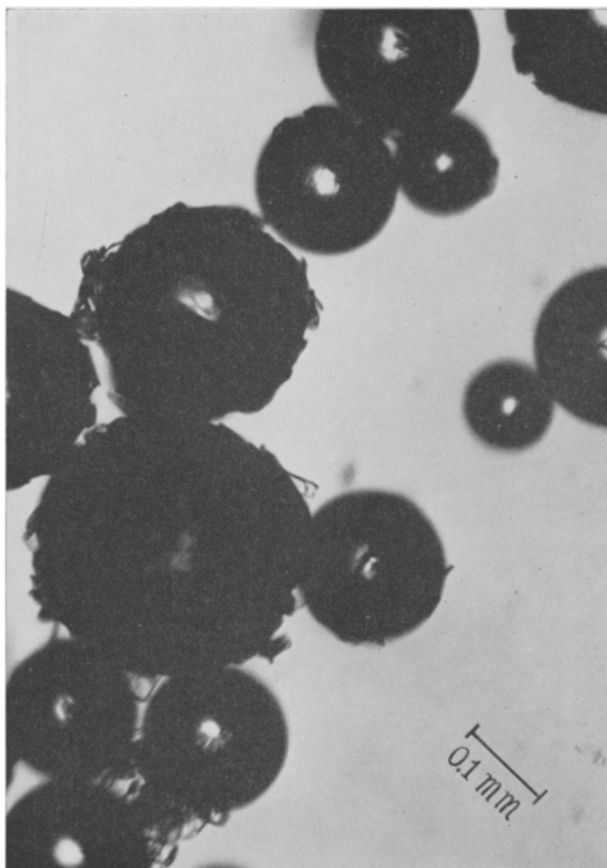


PLATE 4.—Ca-dickite (+325 mesh) at pH 6.7. Basal surfaces of particles, showing face-to-face flocculation, are in contact with bubbles.

remained undisturbed for five minutes. The suspension was then evacuated to 520 mm Hg by a pump attached to the open end of the tube.

The type of flocculation, and the mode of particle-attachment to the bubbles, were observed, while the stability of the bubbles, the quantity of particles attached to them, and the strength of the attachment, were assessed qualitatively. For example, the behavior of the suspension on shaking indicated the stability of the bubbles and the strength of the attractive force between them and their adherent crystals.

The sign and approximate magnitude of the electrical charge on the bubbles, in solutions of varying pH containing no suspended clay, were assessed by noting the direction and velocity of electro-phoretic migration, in the axial region of a rotating cylindrical horizontal glass tube having electrodes near its end (McTaggart, 1914).

## RESULTS

### *Formation and Subsequent History of Bubbles*

Evacuation caused bubbles to form on or between the crystals, presumably where gas-nuclei had been present on surfaces or in cleavage-cracks or other cavities. The bubbles were fully developed after 10–15 min. They began to rise, transporting adherent clay, after attaining *ca.* 0.1 mm dia. The behavior of the bubbles was observed intermittently for periods up to 48 hr.

### *H, Al- and Na-Clays*

The maximum number of crystals was retained by bubbles in suspensions of pH *ca.* 5 and here the plates or booklets had their edge-faces predominantly in contact with the bubbles, simultaneously showing edge-to-face flocculation. Some flocs or single particles linked one bubble to another. The adhesion between crystals and bubbles was relatively strong (Plates 1 and 2).

The addition of small amounts of Na-montmorillonite to the suspensions tended to inhibit the formation of flocs, and the basal surfaces rather than the edges of the crystals were presented to the bubbles, which retained relatively few particles.

Most adventitious mica-flakes had their basal surfaces against the bubbles (Plate 2).

Shaking the suspensions of pH 4–7 showed that the attraction between the crystal-edges and the bubbles was still considerable.

Suspensions of –325 mesh clays at pH *ca.* 6.5 developed yarn-like floccules 1–5 mm long when gently shaken. These floccules depended from or linked bubbles (Plate 3), and resembled the adlineated floccules postu-

lated by Street (1956). Elongated floccules developed also when the movement of a bubble along the wall of the glass tube stretched a floccule partly anchored to this wall or to another bubble. The particles in the elongated floccules were too minute for their mutual arrangement to be clearly observed.

At  $\text{pH} < 3$  the crystals were feebly attracted to the bubbles by their edges and basal surfaces and there was a marked diminution in the number of particles retained.

In basic suspensions, which showed deflocculation, the tendency to bubble-formation, and the numbers of particles retained, decreased drastically with increasing pH. The particles were very weakly retained via their basal surfaces or edges (Fig. 1).

### *Stability of Bubbles*

Bubbles were regarded as relatively stable when they did not readily coalesce, even when brought into closer proximity by gentle agitation. A broad and strongly held mantle of crystals made coalescence more difficult.

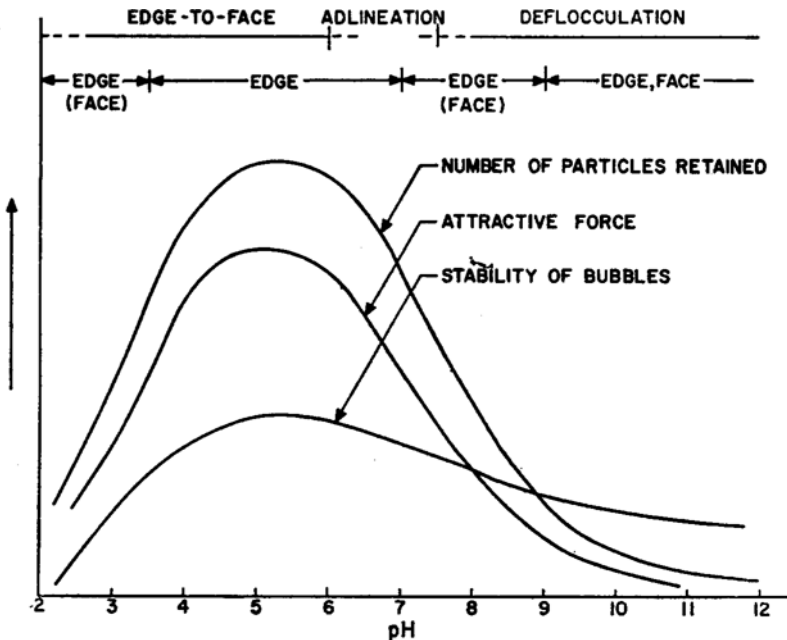


FIGURE 1.—Schematic representation of the variation in the number of particles retained, the attractive force between the bubbles and the particles, and the stability of the bubbles in kaolinite or dickite suspensions of changing pH. Regions of deflocculation, and of different types of flocculation, are indicated, together with the mode of attachment to the bubbles.



However, the diameters of bubbles changed with time, as the greater internal pressure of the smaller bubbles favored the passage of dissolved air from these to their larger neighbors. The resulting changes in bubble-size were slower, however, where the interposition of adherent particles and flocs increased the length of the diffusion path. In general, strongly held flocs of particles, in edge-to-face array, tended to increase the stability of the bubbles, both by offering mechanical resistance to close approach, and because their open texture caused the bubbles to be relatively far apart. Contiguous bubbles, without interposed clay-particles, were relatively unstable and coalesced instantly when the larger had grown at the expense of the smaller bubble, until the ratio of their diameters was very approximately 10 : 1. The relations between bubble stability and some other properties of the suspensions are summarized in Fig. 1.

As the stability of the bubbles tended to increase with the number of particles retained, it was especially marked at pH *ca.* 5, but it was pronounced throughout the pH range 4-7, because the mantle of adherent particles was not readily displaced to allow coalescence.

At pH < 3 few particles were attracted to the bubbles and the attraction was relatively feeble. Coalescence of bubbles was easy.

In basic suspensions the bubbles were rather stable, although only a few particles adhered to them, and these were but weakly attracted.

#### *Behavior of Ca- and Pb-Clays*

In approximately neutral suspensions the crystals showed face-to-face flocculation (cf. Schofield and Samson, 1954, p.143). Their basal surfaces were predominantly in contact with the bubbles (Plate 4). The bubbles retained many flocs and held them rather strongly. The flocs of Pb-clay retained were more numerous and denser than those of Ca-clay.

#### *Behavior of Muscovite*

The behavior of muscovite (sample D, Table 1) is shown schematically in Fig. 2. Only adhesion of the basal surfaces was generally observed, but some adhesion of the edges was noticed around pH 5. This was accompanied by a tendency to edge-to-face flocculation.

## DISCUSSION

Detailed discussion of the possible origins of the electrical charges on air-bubbles in water are beyond the scope of this communication. The orientation and distortion of the water molecules at the air-water interface (Fletcher, 1962), and the ions present in this vicinity (McTaggart, 1914), may be involved in the formation, sign, and magnitude of these charges.

McTaggart (*op. cit.*) observed that air-bubbles were negatively charged in dilute HCl and the charge decreased to nearly zero as the concentration of the acid increased. The excessive formation of gas at the electrodes prevented observation of the possible change to a positive charge when the concentration of acid was sufficient. The present electrophoretic studies gave results similar to those of McTaggart. Thus the negative charge on a bubble in a clay-suspension may be expected to diminish as the pH is decreased. An acidic pH, however, favors the development of positive edge charges on kaolinite (Schofield and Samson, 1954), but an alkaline pH may cause the edge surfaces to develop negative charges, which supplement those persisting on the basal surfaces despite pH changes (Schofield and Samson, 1953, p.46; Street and Buchanan, 1956). The present studies showed that dickite behaved similarly to kaolinite.

A disposition of the kaolinite crystals with their edges to the bubbles indicated significant positive edge-charges. Although these charges developed in acid suspensions, the negative charges on the bubbles were reduced as the acidity increased. Thus the maximum retention of particles at a particular acid pH, here *ca.* 5, was explicable.

The marked decrease in particle-retention by the bubbles, following the addition of Na-montmorillonite to acid suspensions, was in excellent

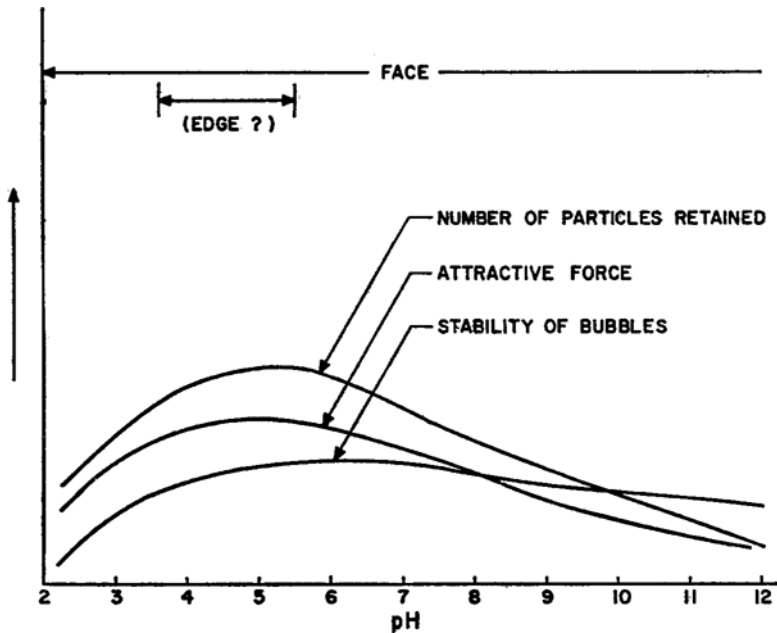


FIGURE 2.—Schematic representation for mica (cf. Fig. 1). A probable, but unconfirmed, region of edge-attachment to bubbles is indicated.

accord with the observations of Schofield and Samson (1954) who showed that such addition was antagonistic to edge-to-face flocculation, presumably because the montmorillonite platelets lay with their basal planes on the edge-surfaces of the kaolinite crystals and thus screened the positive charges (cf. West *et al.*, 1960, Fig. 12).

The numbers of particles retained by bubbles in acid suspensions of clay-minerals with different prior treatments were: electrolyzed > 0.1 N. HCl-leached > 1.0 N. HCl-leached > (NaCl + HCl)-leached.

If the third is essentially a H-clay, while the first two are H,Al-clays, the greater ability of bubbles to retain these two clays may accord with the suggestion of Cashen (1963) that positive charges may develop near the edges of clay-platelets by the accumulation in this vicinity of an excess of complex aluminum-containing ions in the Stern layer.

The ability of bubbles to resist coalescence may be expected to be influenced by their total charges or, more probably, by their charge densities, by the numbers of particles they can retain and by the strength of the attraction causing this retention. Indeed, these three factors are interdependent.

Bubbles should show maximum instability when their isoelectric point is approached. This, together with the few particles retained, may contribute to the instability of bubbles at  $\text{pH} < 3$ . In alkaline suspensions, however, the bubbles were rather more stable although here, too, they were surrounded by few particles. The greater negative charge density on the bubbles may have contributed predominantly to their stability.

It has been found (Enright *et al.*, 1949) that montmorillonite becomes less wettable when  $\text{Ca}^{2+}$ , and particularly  $\text{Pb}^{2+}$ , are substituted for  $\text{Na}^+$ . The marked adhesion of Ca- and especially of Pb-kaolinite or dickite to bubbles agrees with these observations.

Mica flakes adhered to bubbles by their basal surfaces rather than by their edges, despite change in pH, perhaps because the relative thinness of the flakes increased the probability of contacts between bubbles and surfaces rather than edges. Moreover, disturbance of the system might readily change edge- to surface-contacts. If, however, the surfaces of mica were relatively less wettable than those of H- or H,Al-kaolinite or dickite, this also could be a causal factor. Okuda and Williamson (unpublished observations) noticed similar associations of basal surfaces with bubbles in suspensions of hydrophobic graphite-flakes.

## CONCLUSIONS

Observation of suspensions of coarsely crystallized kaolinite and dickite with the optical microscope confirmed that edge-to-face and adlined flocculation occurred in acid media. The edge-faces were presented to negatively charged bubbles, confirming that they themselves were posi-

tively charged. In alkaline suspensions, the basal surfaces tended to be in contact with the bubbles. Ca- or Pb-saturated crystals, in approximately neutral suspensions, developed face-to-face flocculation.

Mica, and Ca- or Pb-saturated kaolinite or dickite, were attached to the bubbles by their basal surfaces, and the poor wettability of these surfaces is thought to be a causal factor. The large numbers of Pb-saturated crystals retained by air-bubbles suggested that  $\text{Pb}^{2+}$  caused an especially marked diminution in wettability.

The presence of many adherent crystals, particularly when these were strongly held, rendered the coalescence of bubbles difficult. It also retarded the growth of the large, and the diminution of the small, bubbles by lengthening the diffusion path for the dissolved air passing from one bubble to another. The charge density on the bubbles also may have influenced their ability to coalesce.

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#### REFERENCES

- Cashen, G. H. (1963) Electric charges and thixotropy of clays: *Nature*, v.197, pp.349-350.
- Enright, D. P., Sonders, L. R., and Weyl, W. A. (1949) Surface polarization and wettability of inorganic substances by water: *J. Appl. Phys.*, v.20, pp.1011-1012.
- Fletcher, N. H. (1962) Surface structure of water and ice: *Phil. Mag.*, v.7, 8th series, pp.255-269, cf. *idem, ibid.*, v.8, pp.1425-1426.
- Harward, M. E., and Coleman, N. T. (1954) Some properties of H- and Al-clays and exchange resins: *Soil Sci.*, v.78, pp.181-188.
- McTaggart, H. A. (1914) The electrification of liquid-gas surfaces: *Phil. Mag.*, v.27, 6th series, pp.297-314.
- Schofield, R. K., and Samson, H. R. (1953) The deflocculation of kaolinite suspensions and the accompanying change-over from positive to negative chloride adsorption: *Clay Minerals Bull.*, v.2, pp.45-51.
- Schofield, R. K., and Samson, H. R. (1954) Flocculation of kaolinite due to the attraction of oppositely charged crystal faces: *Disc. Faraday Soc.*, No. 18, pp.135-145.
- Street, N., and Buchanan, A. S. (1956) The  $\xi$ -potential of kaolinite particles: *Australian J. Chem.*, v.9, pp.450-466.
- Street, N. (1956) The rheology of kaolinite suspensions: *Australian J. Chem.*, v.9, pp.467-479.
- West, R. R., Gould, R. E., Coffin, L. B., and Lux, J. F. (1960) A method for high-intensity dispersion of clay: *Bull. Am. Ceram. Soc.*, v.39, pp.1-6.