Clays and Clay Minerals, Vol. 47, No. 4, 522–526, 1999.

NOTE

CLAY SEDIMENT-STRUCTURE FORMATION IN AQUEOUS KAOLINITE SUSPENSIONS

KUNSONG MA AND ALAIN C. PIERRE
University of Alberta, Edmonton, Canada

Key Words—Bingham Yield Stress, Colloid, Flocculation, Fractal, Iron, Kaolinite, Scanning Electron Microscopy (SEM), Sediment, Suspension, Zeta Potential.

INTRODUCTION

Plate-like kaolinite particles have different crystal structures on edges and faces (van Olphen, 1977), thus the electric property of the edges is different from that of the faces. After treatment by the Schofield and Samson method (1954), kaolinite particles are converted to the Na form and carry negative electric charges on their faces and positive charges on their edges. In aqueous kaolinite suspensions, clay particles can interact in the edge to edge (EE), edge to face (EF), and face to face (FF) modes (van Ophen, 1977). They constitute different types of flocs or aggregates in suspensions (Michaels and Bolger, 1962) and can form sediments with different structures such as cardhouse, bookhouse, dispersed, stair-step structures, etc. (van Olphen, 1977; Bennett and Hulbert, 1986). The interaction of clay particles and structure formation of flocs or aggregates in aqueous media were studied systematically by sedimentation, rheology, and electrophoresis by Rand and Melton (1977), Melton and Rand (1977a, 1977b), and Michaels and Bolger (1962).

In the present study, clay-sediment samples, prepared by supercritical drying, were observed under a scanning electron microscope (SEM). Since supercritical drying eliminates the capillary force on a sediment sample, this technique can relate sediment structures to their sedimentation behaviors. The process of microstructure formation in aqueous kaolinite suspensions is discussed by comparing the results obtained here with previous work (Rand and Melton, 1977; Melton and Rand 1977a, 1977b; Michaels and Bolger, 1962).

EXPERIMENTAL PROCEDURE

Kaolinite ("Hydrite UF," Georgia Kaolin Company, 1990) with a median size of 0.20 μm equivalent spherical diameter, was provided by the Georgia Kaolin Company Inc. The kaolinite was converted to the Na form by the Schofield and Samson treatment (1954). After this treatment, the pH value of this kaolinite suspension was 6.9 and the solid concentration was 5% by mass. Suspensions of 10 mL (0.5 g kaolinite) were transferred to 100 mL graduated cylinders for sedimentation test. Then, 40 mL of distilled water were added to the cylinder. The pH value of the suspension was adjusted with dilute HCl or NaOH to 2.0, 4.0, 6.0, and 9.5.

Two groups of sedimentation tests were performed. The first group was without $FeCl_3$. For this group, more distilled water was added to obtain a suspension volume of 100 mL. The second group involved using $FeCl_3$ solution prepared with distilled water just prior to use. To be in accordance with Ma and Pierre (1997), this solution is referred to as "unaged" $FeCl_3$ solution. 50 mL of 1.34 mM $FeCl_3$ solution was added to the kaolinite suspension. Thus, the quantity of the suspension was 100 mL, and the concentration of $FeCl_3$ was 0.67 mM.

The sedimentation tests were performed at room temperature. The final sediment thickness was defined as the thickness obtained after sedimentation of 360 h. A height of 1 cm corresponded to a volume of 6.16 mL in a graduated cylinder.

To observe the sediment structure, some kaolinite suspensions were directly prepared in dialysis tubes. After sedimentation, ethanol was used to replace water in the kaolinite sediments of the tubes. These tubes were placed in a supercritical point dryer (BIO-RAD E3000 Series), and then the ethanol was exchanged by liquid CO_2. The sediment samples were supercritical-dried by bringing temperature and pressure of CO_2 over the critical point. The supercritical-dried samples were examined in a Hitachi S-2700 SEM.

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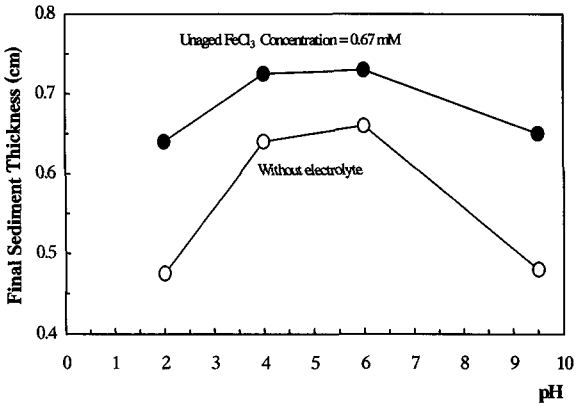


Figure 1. Final thickness of the sediments made from 0.5% Na-kaolinite suspensions as a function of pH.

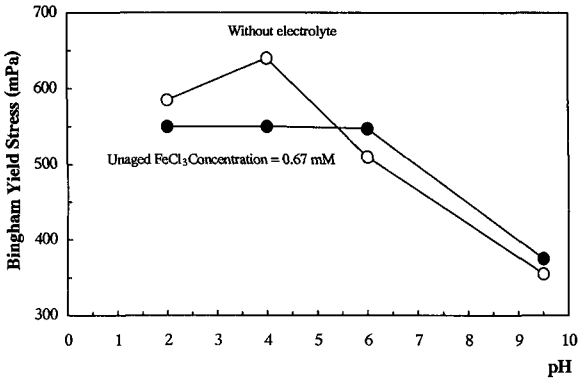


Figure 2. Bingham yield stress of 10% (by mass) kaolinite suspensions as a function of pH.

The electrophoretic measurement and zeta potential calculation followed the same procedure as that of Ma and Pierre (1997). The rheological properties of the suspensions were determined with a cylindrical rotor viscometer, of the type CONTRAVE RHEOMAT 115. Flow curves were first recorded by increasing, then by decreasing the shear rate, and waiting for equilibrium at each shear rate in suspensions with a kaolinite content adjusted to 10% by mass. The Bingham yield stress was determined from the increasing shear rate data.

RESULT AND DISCUSSION

Each sedimentation test for the two groups of kaolinite suspensions was completed in about one hour. In most cases, clay-particle flocs were formed hourly after homogenizing the clay suspensions. These flocs then coalesced to form an apparently uniform sediment, separated by a sharp interface from the clear supernatant liquid. The interface settled continuously until equilibrium was established. The final thickness of the kaolinite sediments at the equilibrium is shown in Figure 1. The maximum final sediment thickness occurred between pH = 4–6 for both groups with and without $FeCl_3$. The final thickness of the kaolinite sediments made without $FeCl_3$ electrolyte was lower than that of the kaolinite sediments made with $FeCl_3$ at the same pH value.

The Bingham yield stresses of the kaolinite suspensions as a function of the pH are reported in Figure 2. At pH values below 6, the suspensions without Fe additive had a higher Bingham yield stress than the suspensions containing unaged $FeCl_3$. The latter suspensions had a constant Bingham yield stress below pH of 6. The Bingham yield stress of both suspensions decreased with increasing pH, starting at pH = 6. The two curves of the Bingham yield stress intercepted at a pH near 5.5.

The zeta potentials of kaolinite particles are shown in Figure 3. The zeta potential decreased from positive to negative values as the pH increased. The zeta potentials in suspensions with $FeCl_3$ are greater than that without $FeCl_3$, except at pH of 2. The isoelectric point was at pH = 3.7 without $FeCl_3$, whereas it was at a pH of 7.2 with 0.67 mM $FeCl_3$.

The present results of the final sediment volume and Bingham yield stress were similar to Rand and Melton (1977), and Melton and Rand (1977a, 1977b). Rand and Melton suggested that clay particles were associated in EF mode when the pH was close to the edge isoelectrical point of kaolinite particles. According to their method (Rand and Melton, 1977), the edge isoelectrical point was the pH value where the Bingham yields stress curves intercepted. In our case, this was at near pH of 5.5. Increasing the pH value above the isoelectrical point made the kaolinite particles connect in the EE mode. The addition of any Fe electrolyte compressed the electric double layers around kaolinite particles and promoted the FF clay-particle aggregation (Ma and Pierre, 1977).

However, in the present study, the EF and EE particle association modes seem to be rare at all pH values and all unaged $FeCl_3$ concentrations, according to

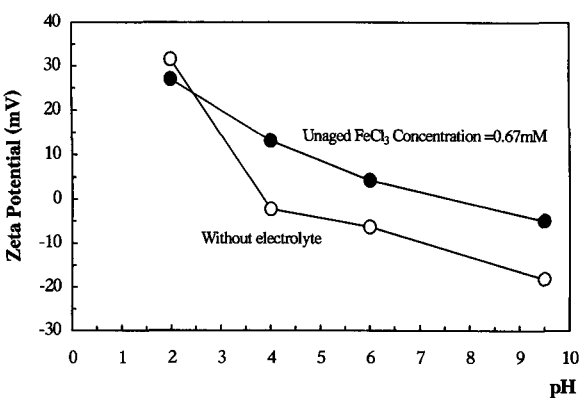


Figure 3. Zeta potentials of kaolinite particles as a function of pH.

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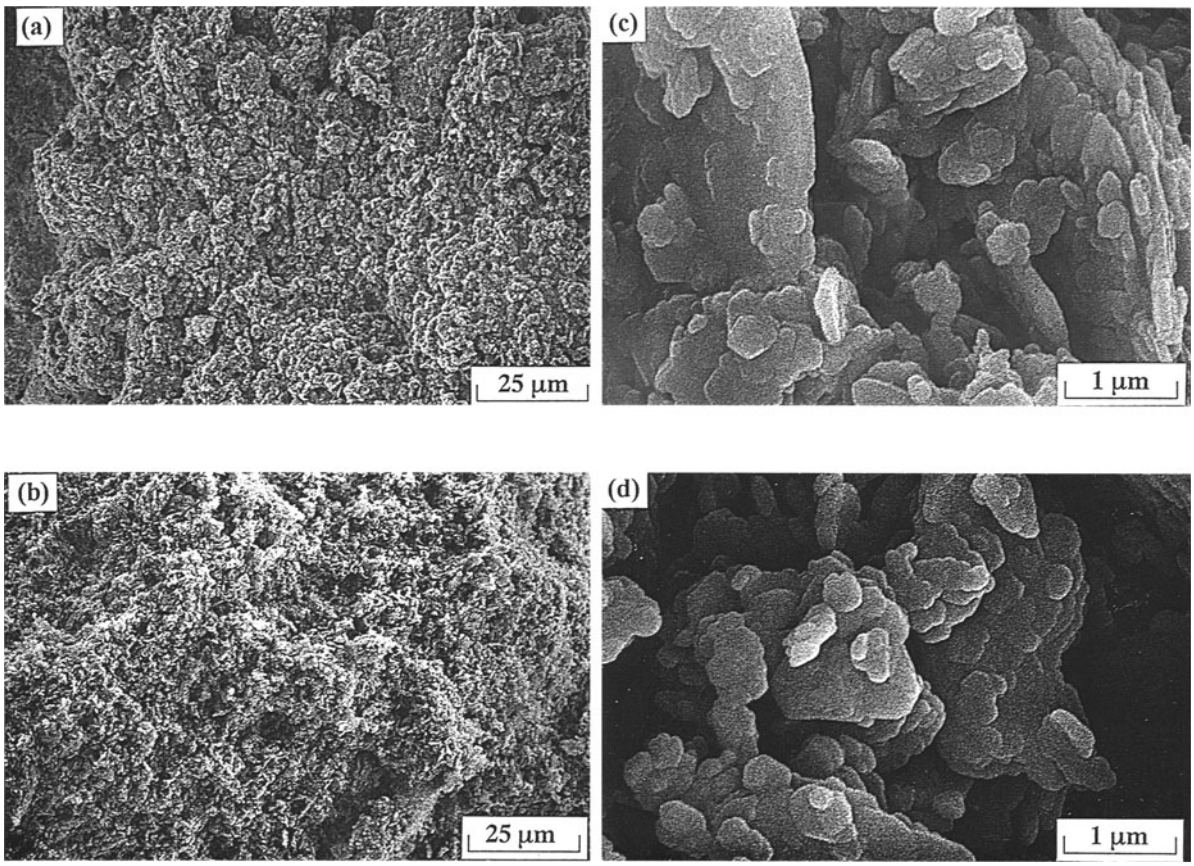


Figure 4. SEM micrographs of kaolinite sediments made from 0.5% (by mass) kaolinite suspensions at pH = 2.0: (a) and (b) without unaged $FeCl_3$; (c) and (d) with 0.67 mM unaged $FeCl_3$, at increasing magnification.

SEM micrographs (Figures 4 and 5). Instead, kaolinite particles are more frequently associated in the FF mode, as shown in Figure 4b and 4d, and Figure 5b and 5d. Thus, the clay particles constitute FF domains, and these domains are plate-like in shape. Domains are randomly connected in suspensions with and without $FeCl_3$ at low pH (pH = 2.0) as shown in Figure 4b and 4d. When the pH value is increased to 6, the FF domains are packed in a bookhouse structure (Figure 5b and 5d), as Sloan and Kell (1966) suggested.

Figure 4a and 4c shows the sediment characteristics of kaolinite with and without $FeCl_3$ at pH of 2.0, respectively. The kaolinite sediments are relatively uniform and compact structures, which correspond to their low final-sediment volumes. In contrast, the kaolinite sediments prepared at pH of 6.0 without $FeCl_3$ and with unaged $FeCl_3$, were porous and not homogenous (Figure 5a and 5c). Furthermore, both figures show that the sediments have a fractal-like structure. The mass M of a fractal structure inside a sphere of radius R varies as:

$$M = R^f \quad (1)$$

where f is the fractal dimension. The fractal dimension could not be obtained from the SEM micrographs or by other available methods. However, the appearance of the sediment structures is similar to the diffusion-limited aggregation (DLA) structure proposed by Witten and Meakin (1983). This structure was simulated numerically and in three-dimensional Euclidean space, f was equal to 2.5 (Meakin, 1983).

In the present study, we verified that kaolinite particles treated by the method of Schofield and Samson have negative charges on faces and positive charges on edges in aqueous media (Ma, 1995). The clay particles were always associated with each other in FF mode at all pH values. Actually, calculations (Flegmann, 1969) showed that EF and FF associations could concurrently occur for the clay particles with faces and edges having electric charges of opposite sign. The clay-particle association not only depends on the interaction energy between particles, but also on the collision frequency. In the present study, the collision frequency for the FF configuration was probably much higher than for the EF or EE configurations, hence a plate-like domain formed by FF particle relationships.

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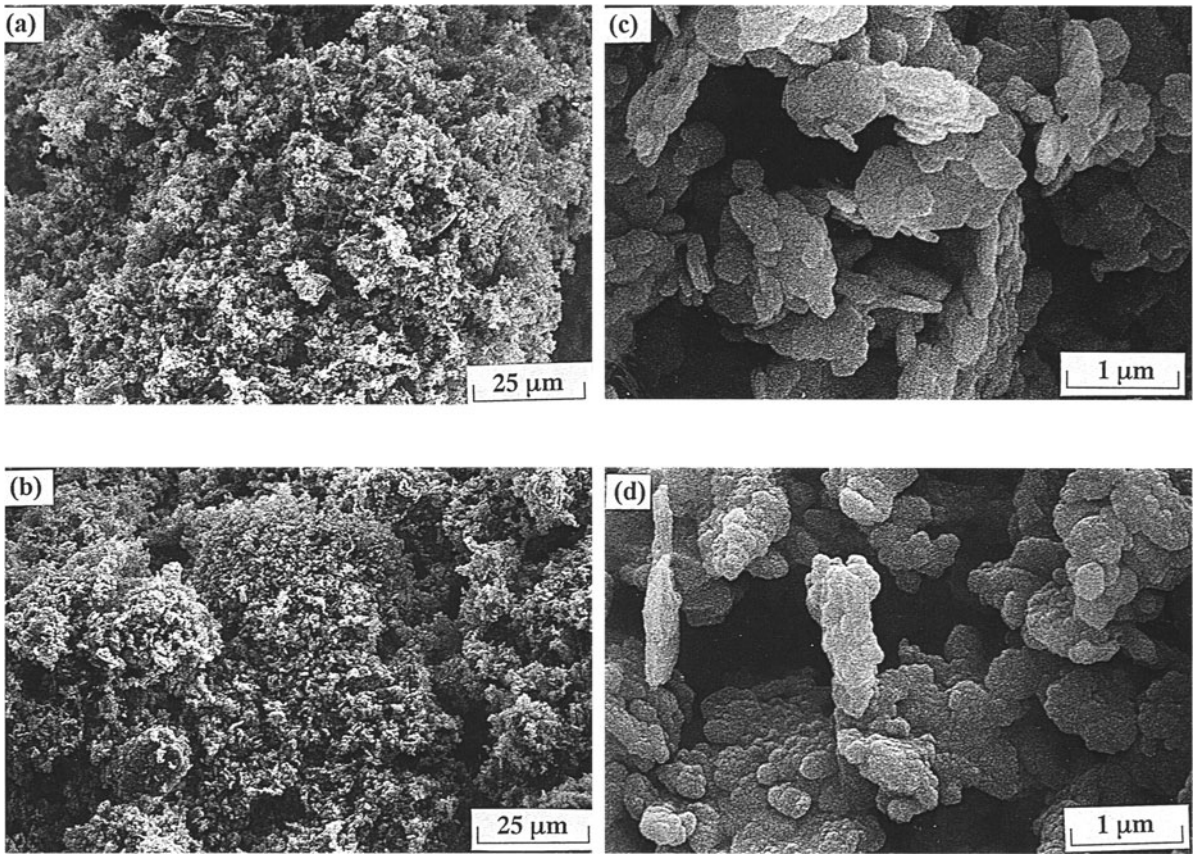


Figure 5. SEM micrographs of kaolinite sediments made from 0.5% (by mass) kaolinite suspensions at pH = 6.0: (a) and (b) without unaged $FeCl_3$; (c) and (d) with 0.67 mM unaged $FeCl_3$, at increasing magnification.

At low pH, protons are adsorbed by clay particles. The electric double layer is quite thick around these clay particles, as indicated by the high zeta-potential values (Figure 3). Consequently, the electric double layer is also relatively extensive around the domains built by the particles. These domains cannot coalesce in the beginning of the sedimentation experiment. Hence, they settle individually by gravity. During the settling process, the kaolinite concentration in the lower portion of the test cylinder increases, so that collisions between domains become more frequent, and flocculation occurs. Then, the sediment becomes flocculated (Ma and Pierre, 1992). However, the sedimentation occurs so rapidly that the domains do not have sufficient time to produce a particular structure. Thus, these domains packed randomly to form a uniform structure.

For pH value near 6, the electric double layer around clay particles becomes very thin. FF domains can form more easily in the sedimentation experiment and these domains associate into larger aggregates. These plate-like domains form a bookhouse structure, which is similar in appearance to the cardhouse structure often proposed for plate-like particles, except that individual particles are replaced by platelike FF domains. Finally, the bookhouse aggregates coalesce to form an extended network in the kaolinite suspension; the clay suspension was completely flocculated.

Michaels and Bolger (1962) suggested that aggregates in suspensions prepared in conditions similar to the present study should be very porous and joined to each other in a network throughout the suspension. The SEM observations are consistent with their suggestion. Furthermore, the aggregate architecture can be described at two different scales. On a small scale, the aggregate showed the bookhouse structure, but on a large scale, the aggregate shows the DLA fractal-type architecture.

Although an FF domain is much larger than clay particles, its size is ~1 μm (Figure 5b and 5d), which is in the size range of colloids. The motion of these domains is therefore controlled by Brownian diffusion and flocs grew up by attaching to other domains, in agreement with the DLA mechanism. Hence, a DLA-type structure can form in suspension. The present fractal-like structures, especially the long "arms", are very fragile. Air-drying or freeze-drying will damage this structure. In the present study, the supercritical-

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drying technique made it possible to observe such morphology.

When the pH value of kaolinite suspensions is increased to basic conditions, the zeta potential of clay particles becomes negative. Thus, similar to sediments at low pH values, the clay sediments become compacted.

As in previous studies (Ma and Pierre, 1992, 1997), when the concentration of an unaged $FeCl_3$ solution was low (<1.67 mM), Fe^{3+} cations and hydrolyzed cations act as counterions to compress the electrical double layer around the clay particles according to DLVO theory (van Olphen, 1977). In our experiment, since the kaolinite particles were charged negatively on faces and positively on edges, the Fe^{3+} cations and hydrolyzed cations compress the electrical double layers at the faces more efficiently than that at the edges. Therefore, the formation of FF association is promoted in the presence of $FeCl_3$. The FF domains produced an open and porous structure in the clay suspension. The other function of Fe^{3+} hydrolysis products is to act as a bonding agent (Ma and Pierre, 1997). They can bond the domains as well as the clay particles. These bonds are strong, therefore, the open and porous structure formed in the suspensions can be maintained better in the resulting sediment (Figure 5).

ACKNOWLEDGMENT

The authors appreciate funding by the NSERC grant (Canada) for the support of this research.

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(Received 19 December 1997; accepted 25 October 1998; Ms. 97-116)

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