

SEDIMENTATION BEHAVIOR OF A FINE KAOLINITE IN THE PRESENCE OF FRESH Fe ELECTROLYTE

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Abstract—The sedimentation behavior of a fine kaolinite, comprising a substantial proportion of colloidal particles as well as non-colloidal ones, has been studied when fresh FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$ electrolytes are added. The sedimentation behavior depends on the pH and the nature of electrolytes and can be explained qualitatively, in our study, by the theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO theory). Fe helps also to aggregate the kaolinite particles in flocs. Two extreme kinds of qualitative sedimentation have been observed: flocculation-sedimentation and accumulation-sedimentation. However, the transition between the two kinds of sedimentation is quite progressive. The present results are discussed in reference to the DLVO theory and the hydrolysis behavior of Fe electrolytes.

Key Words—Colloid, Flocculation, Iron, Kaolinite, Sedimentation.

INTRODUCTION

The behavior of raw materials in aqueous media plays an important role in ceramic processing. It influences the formation of crack-free wet parts from the powder, as well as the sintering and the quality of a final product. Because it is a major raw material for ceramics, the flocculation and dispersion behavior of kaolinite in aqueous media has been studied extensively.

When an electrolyte is added, the flocculation of a kaolinite suspension depends on the valence and the nature of the ions, ionic strength, and pH (Hiemenz, 1977; van Olphen, 1977; Rand *et al.*, 1977; Bolland *et al.*, 1976; Arora *et al.*, 1979; Swartzen-Allen *et al.*, 1976; Goldberg *et al.*, 1987). The stability of a colloidal system can often be explained by the DLVO theory (Hiemenz, 1977). When the electrical repulsion of identically charged double layers around particles is strong enough, the colloidal system remains dispersed (Swartzen-Allen *et al.*, 1974). Flocculation is brought about by the decrease of this repulsion. However, in clay suspensions the situation is complicated by different charges on the edges and faces of platelike particles (Swartzen-Allen *et al.*, 1974; van Olphen, 1977; Worrall, 1986). For kaolinite, the reported values for the point of zero charge (z.p.c.) are between pH 5.5 and 6.7, depending on the conditions (Young *et al.*, 1987). Below the z.p.c, the edges of kaolinite particles are considered to be charged positively and the faces are charged negatively. Above the z.p.c, the edges also become negatively charged, and thereby increase the stability of the clay dispersion (Goldberg *et al.*, 1987; Swartzen-Allen *et al.*, 1976; Bolland *et al.*, 1976). Consequently, for kaolinite, a number of interaction modes has been proposed which call for face-to-face (FF), edge-

to-face (EF) or edge-to-edge (EE) particle associations (van Olphen, 1977; Rand *et al.*, 1977; Flegmann *et al.*, 1969).

It is desirable to elucidate the actual structure of clay aggregates. For this purpose, a technique was successfully applied by Zou and Pierre to montmorillonite (1992). Relatively strong montmorillonite flocs, with respect to mechanical compaction, were made with fresh Fe^{3+} electrolyte and the flocs were dried by the supercritical method. Fe^{3+} is known to play a triple role on the flocculation-dispersion behavior of clay suspensions: (1) as a counterion; (2) as an exchange cation anchoring Fe hydrolysis complexes to the surface of clay; (3) as a bonding agent between clay particles by the intermediate of the Fe hydrolysis complexes (Greenland, 1975; Young *et al.*, 1987; Rengasamy *et al.*, 1977; Goldberg *et al.*, 1987).

In a preliminary step, it is necessary to determine the pH and Fe electrolyte concentration levels where flocculation occurs with kaolinite. This was the purpose of the present work. Aqueous kaolinite suspensions with a particle size ranging from colloidal to non-colloidal, according to the supplier, have been studied. Their sedimentation kinetics in the presence of Fe electrolytes are reported and discussed. The macroscopic aspects of the sediments, with respect to thickness and qualitative fluidity are described.

EXPERIMENTAL PROCEDURE

The kaolinite studied was Hydrite UF from the Georgia Kaolin Company, Inc. The median particle size was $0.20 \mu\text{m}$ and the mass proportion of colloidal particles with size $\leq 0.20 \mu\text{m}$ was about 55%, according to the supplier (Georgia Kaolin Company, 1990). The specific area determined by the BET was $20.1 \text{ m}^2/\text{g}$,

which is consistent with the value provided by the supplier.

This kaolinite was treated according to the method of Schofield and Samson (1954) with 1M NaCl solution adjusted at pH 3 with HCl to convert the kaolinite to the sodium form. The treated kaolinite was washed with distilled water until there was no evidence of Cl^- in the supernatant liquid tested by AgNO_3 . Treated kaolinite (0.5 g) was mixed with 50 g distilled water, then 1 ml of 0.5 N $\text{Na}_4\text{P}_2\text{O}_7$ solution was added to disperse the kaolinite. The kaolinite suspension pH was 9.30 ± 0.05 . This process insured that the clay particles carry only negative charges both on edges and faces, as the phosphate anions are not easily desorbed. This should permit the comparison of the results with the predictions from the DLVO for platelike particles (Pierre, 1992), after a further structure study by supercritical drying is achieved.

In the present study, the colloidal interactions were modified by changing the pH, and/or adding a fresh Fe^{3+} electrolyte. The electrolytes we studied most extensively were fresh FeCl_3 and fresh $\text{Fe}_2(\text{SO}_4)_3$.

In order to avoid interaction between different anions, the pH values of the kaolinite suspensions were adjusted with NaOH to 10.0 and 11.0, and with HCl or H_2SO_4 to 8.0, 6.0, 4.0, and 2.0, depending on the anion in the electrolyte. For example, HCl was used if the effect of FeCl_3 was investigated, while H_2SO_4 was used with $\text{Fe}_2(\text{SO}_4)_3$. At each pH, six different FeCl_3 or $\text{Fe}_2(\text{SO}_4)_3$ concentrations were examined: 0.0, 0.5, 1.0, 2.0, 5.0, and 10.0 mN (meq/liter). Fresh FeCl_3 , or $\text{Fe}_2(\text{SO}_4)_3$, was always prepared just prior to an experiment.

Each suspension was prepared in a graduated cylinder with an inside diameter of 28 mm, which was large enough to neglect the wall effect (Michaels *et al.*, 1962). Then, distilled water and a proper amount of fresh 20 mN electrolyte solution were added to get an initial suspension volume of 100 ml. The cylinders were turned upside down 20 times to uniformly distribute the components inside the suspensions. All experiments were performed at room temperature and the cylinders were covered with a piece of parafilm to prevent water evaporation.

To investigate the role of different cations and anions on the sedimentation behavior, supplementary experiments were carried out with the electrolytes FeSO_4 , NaCl and Na_2SO_4 at concentrations of 0.5, 1, 2, 5, and 10 mN at pH 2.

In all sedimentation experiments where a clear interface occurred, the position of this interface was read every 5 or 10 minutes during the first hour, then every hour for the following two hours, and finally every 24 hours until 360 hours. The rate at which this interface moved was used to measure the accumulation rate, or the settling rate (depending on sample behavior), in cm/hour.

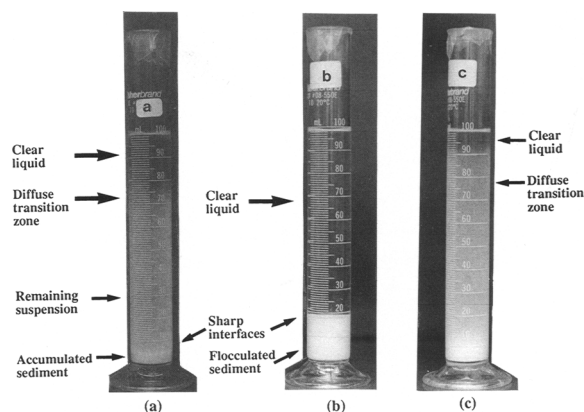


Figure 1. Sedimentation of 0.5% Na-kaolinite suspensions at pH = 4.0 after 3 day settling: (a) accumulation-sedimentation with $\text{FeCl}_3 = 10$ mN; (b) flocculation-sedimentation with $\text{FeCl}_3 = 1.0$ mN; (c) mixed accumulation-flocculation sedimentation with $\text{FeCl}_3 = 5.0$ mN.

RESULTS

The sedimentation behavior of kaolinite suspensions depended largely on the electrolyte concentration, the cation and the anion in the electrolyte, and the pH. Three types of sedimentation behavior were observed. Two of these, called flocculation-sedimentation and accumulation-sedimentation, were observed earlier for montmorillonite (Zou and Pierre, 1992). However, they were called, respectively, two-layer and three-layer behavior in the previous publication. The third sedimentation behavior is called mixed flocculation-accumulation here. The three sedimentation behaviors can be described as follows.

Figure 1a shows accumulation-sedimentation. From the bottom to the top of the test cylinder one sees successively: (1) the accumulated sediment; (2) the remaining diffuse suspension of particles; (3) the clear supernatant liquid. A sharp interface separates the accumulated sediment and the remaining suspension. This interface kept moving up with time from the beginning to the end of the experiment. That is to say, the accumulated sediment thickness increased with time. Also this accumulated sediment did not flow easily when tilting the cylinder. In contrast, the transition zone between the remaining suspension and the supernatant liquid is not sharp. With a spectrophotometer, it should be possible to define arbitrarily an interface corresponding to a given turbidity of the liquid, but we did not have the instrumentation to do so. However, qualitatively, the remaining suspension kept settling down by feeding the accumulated sediment, until it disappeared completely.

Figure 1b shows flocculation-sedimentation. A single sediment layer is separated by a sharp interface with the clear supernatant liquid. This interface kept moving down from the beginning to the end of sedimentation. That is to say the sediment kept shrinking until

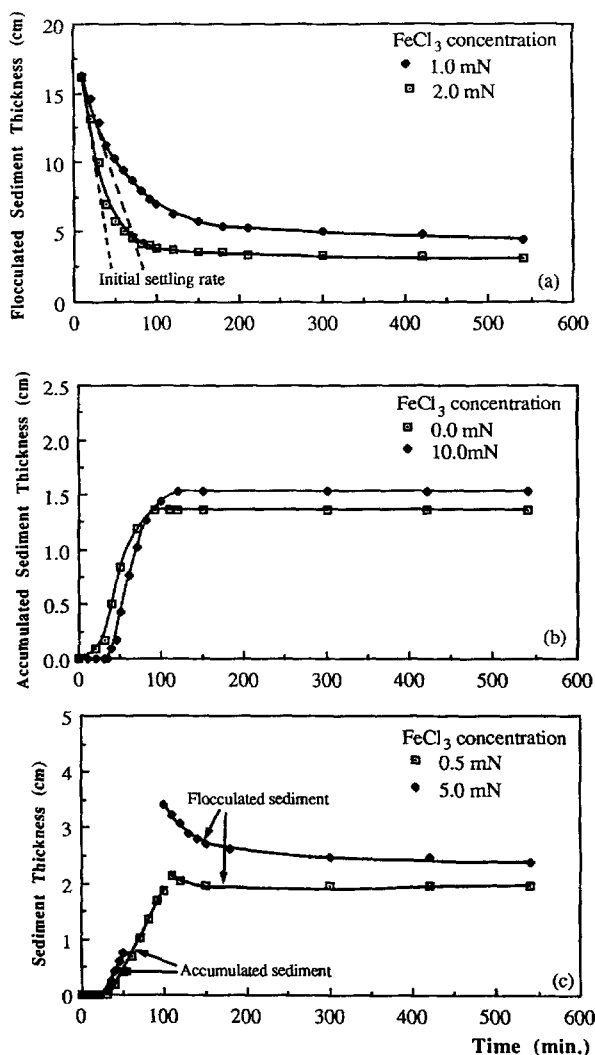


Figure 2. Displacement rate of sharp interfaces in 0.5% Na-kaolinite suspensions at pH = 4.0: (a) flocculate-supernatant liquid interface with FeCl₃ concentrations 1.0 and 2.0 mN; (b) accumulated sediment-remaining suspension interface with 0.0 and 10.0 mN of FeCl₃; (c) flocculate-supernatant liquid and accumulated sediment-remaining suspension with 0.5 and 5.0 mN of FeCl₃.

it reached a final volume. Also, this sediment would flow easily when tilting the cylinder.

Mixed sedimentation behavior begins as an accumulation-sedimentation in Figure 1a, with a sharp interface between the accumulated sediment and the remaining suspension. This sharp interface moves up. With time, however, the diffuse suspension slowly flocculates. In spite of the fact that its interface with the bottom sediment remained sharp (well-defined line), the contrast in turbidity between each side of the interface slowly decreased. After some time, depending on the visual acuteness of the experimentalist, it was no longer possible to observe this sharp interface. Fig-

ure 1c shows the stage where this sharp interface is no longer visible. Only one sediment layer is visible and its transition-zone with the clear supernatant liquid is diffuse. However, after a longer time, this transition-zone transformed from a diffuse-zone to a sharp interface. The end of the sedimentation experiment looked like flocculation-sedimentation as in Figure 1b, with apparently one single sediment separated from the top supernatant liquid by a sharp interface. This sharp interface kept moving down.

Flocculation-sedimentation kinetics are reported for FeCl₃ concentrations of 1.0 and 2.0 mN at pH 4.0 in Figure 2a. It was characterized, at the beginning, by an initial period when no obvious settling occurred, on the order of 10 minutes. During this induction period, flocs were being formed. At some moment, these flocs joined to each other and created an apparently uniform sediment, separated by a sharp interface from the clear supernatant liquid. Settling of the flocculated sediment started at a relatively fast initial settling rate. Later, the settling rate began to slow down progressively, until it reached an aging stage when the sediment thickness decreased very slowly, a process known as syneresis in sol-gel science.

The sedimentation data with FeCl₃ concentrations 0.0 and 10.0 mN at pH 4.0 are reported in Figure 2b. They are of the accumulation-sedimentation type. This bottom accumulated sediment was formed by the fastest-settling clay particles, the largest and heaviest clay particles. Its initial volume was zero and it increased slowly by accumulation of new particles. On top of the accumulated layer, the remaining suspension was comprised of smaller, slower-settling clay particles. They constituted a colloidal sol, showing that no extensive flocculation had occurred. In agreement with the information by the supplier, that the particles were not of uniform size, the interface between this colloidal sol and the supernatant liquid was not sharp, but diffuse. The final sediment volume in accumulation-sedimentation was much lower than that in flocculation-sedimentation. Therefore, the accumulated sediment was more densely packed than the flocculated sediment. Also, no syneresis occurred.

In this study, the mixed flocculation-accumulation sedimentation behavior occurred in conditions intermediate between those for flocculation- and accumulation-sedimentation. The evolution of the sediment volumes is reported in Figure 2c for FeCl₃ concentrations of 0.5 mN and 5.0 mN. The data show initially the accumulation rate of the bottom sediment as long as it could be followed. They also show, in the end, the settling-rate of the flocculated-sediment on top of the accumulated sediment, starting from the moment when a sharp interface with the supernatant liquid could be observed. For 5 mN FeCl₃, the data points for these 2 periods form a single curve with a maximum in the sediment volume after approximately 100 min. How-

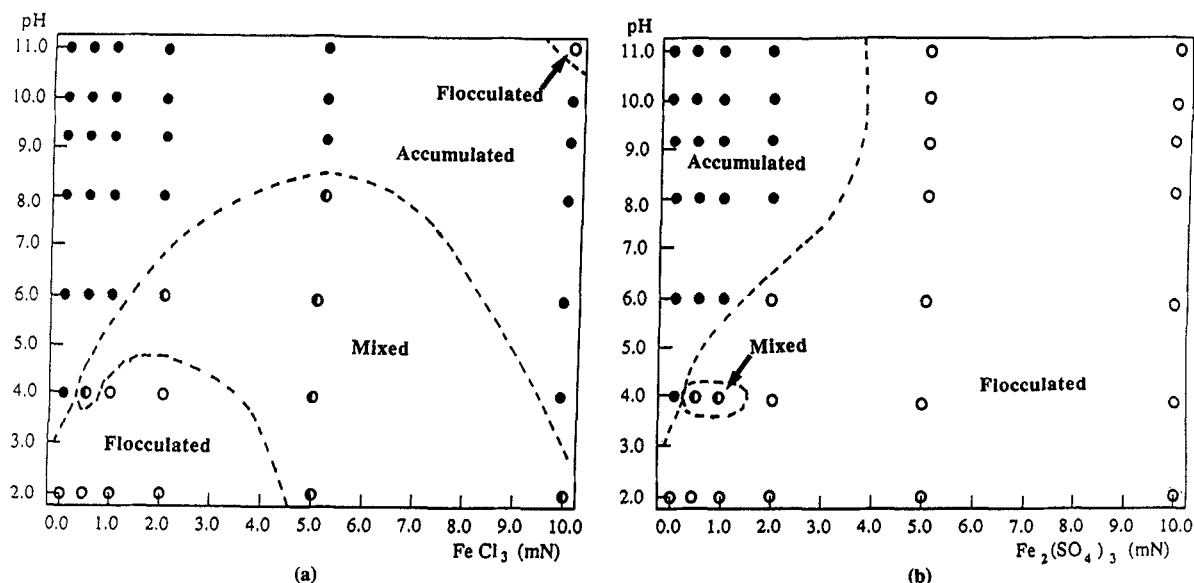


Figure 3. Diagrams of the sedimentation behavior in 0.5% Na-kaolinite suspension with: (a) FeCl_3 ; (b) $\text{Fe}_2(\text{SO}_4)_3$. The black, white, and mixed dots indicate accumulation, flocculation, and mixed behavior, respectively.

ever the points do not concern the same interface. Recent SEM observations show that a thin layer of flocculated sediment is on top of the bottom accumulated sediment (Ma and Pierre, 1992). This is substantiated by the data for 0.5 mN FeCl_3 , where the evolution of the accumulated sediment volume could only be followed for a short time. This interface did not disappear on reaching the top of the remaining suspension. It disappeared by progressive loss of contrast between the accumulated and the flocculated sediment. Actually, this mixed sedimentation behavior occurred when flocculation was slow. The biggest clay particles settled without participating significantly in flocculation, while the smallest particles remained in suspension long enough to achieve substantial flocculation.

Diagrams summarizing the sedimentation behavior of the kaolinite suspensions are shown in Figure 3. The dotted lines have been tentatively drawn to outline the ranges of conditions where each type of sedimentation occurred. The sedimentation behavior not only depended on pH and the Fe^{3+} electrolyte concentration, but also on the nature of anions. With $\text{Fe}_2(\text{SO}_4)_3$, accumulation-sedimentation occurred in a smaller domain of conditions than with FeCl_3 , and the mixed sedimentation regime occurred in only two experiments. By comparison, the range of conditions where flocculation-sedimentation occurred was greatly expanded.

With sedimentation data similar to Figure 2a (which corresponds to what is called flocculation-sedimentation here), previous researchers defined what they called a constant settling rate. This rate describes the beginning of sedimentation when the sediment volume decreases linearly with time (Michaels *et al.*, 1962). This

constant settling rate lasted as long as 30 minutes with kaolinite and is called the initial settling rate in the present study (Figure 2a). We also defined, in the present study, the final sediment volume as the sediment volume after 360 hours' settling. Figure 4 and Figure 5 show the initial settling rate and final sediment volume, respectively, for increasing concentrations of different electrolytes at pH = 2.0. By comparing the data for FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$, it appears that the nature of the anion had a big influence. By comparing the data for NaCl and FeCl_3 , it appears that the cation also had a big influence. Hence, the combination of the anion and cation is important.

The data for initial settling rate and final sedimentation volume are reported in more detail for $\text{Fe}_2(\text{SO}_4)_3$, in Figure 6 and Figure 7, since flocculation-sedimentation occurred in a large range of conditions with this electrolyte, as indicated in Figure 3. In Figure 7, the

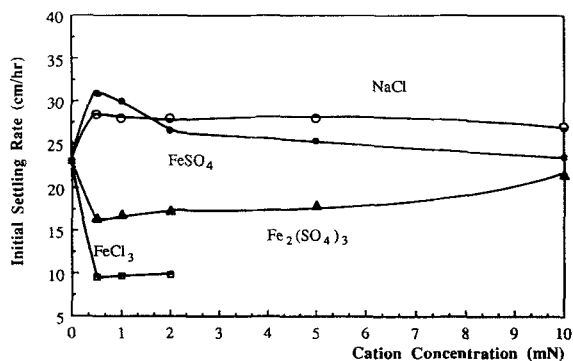


Figure 4. Initial settling rate of 0.5% Na-kaolinite suspension flocculated by different electrolytes at pH 2.0.

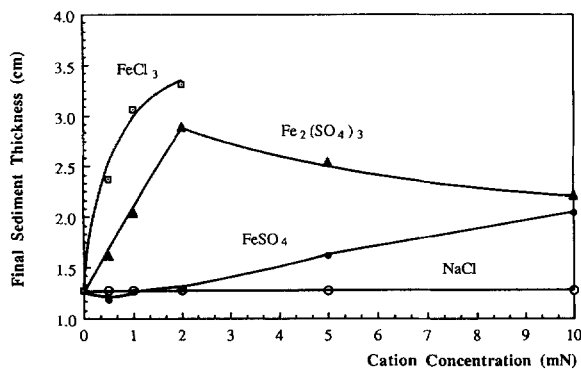


Figure 5. Final sediment thickness, after 360 hours sedimentation, of 0.5% Na-kaolinite suspension flocculated by different electrolytes at pH 2.0.

final sediment volumes when accumulation-sedimentation occurred are also reported. They correspond to the dotted lines. A small initial amount of the electrolyte drastically increased the final sediment volume. However, a further increase in electrolyte concentration slightly decreased the final volume.

By comparing Figure 6 with Figure 7, it appears that the final sediment volume tended to increase when the initial settling rate decreased. A higher $\text{Fe}_2(\text{SO}_4)_3$ concentration resulted in a higher packing efficiency for $\text{pH} > 4.0$. At $\text{pH} \leq 4.0$, the final sediment volume showed a maximum for a $\text{Fe}_2(\text{SO}_4)_3$ concentration near 5 mN.

DISCUSSION

Since the suspensions were prepared with $\text{Na}_4\text{P}_2\text{O}_7$, the kaolinite particles were charged negatively because the phosphate ions do not desorb readily. Hence, the counterions according to DLVO theory are cations. The results of the present study appear to be in qualitative agreement with DLVO theory (Pierre, 1992). The connection with DLVO theory can be summarized as follows.

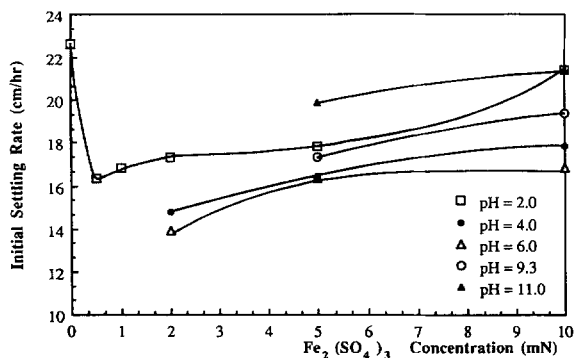


Figure 6. Initial settling rate of 0.5% Na-kaolinite suspensions as a function of $\text{Fe}_2(\text{SO}_4)_3$ concentration, when flocculation occurred.

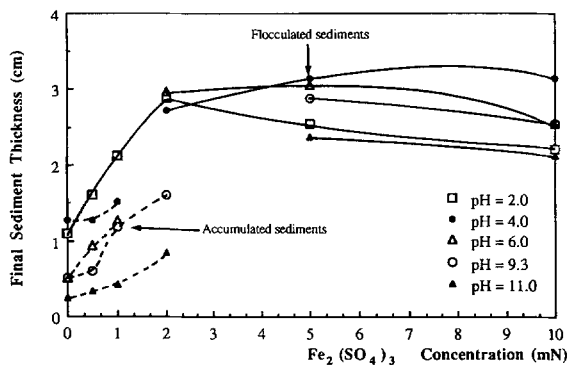


Figure 7. Final sediment thickness, after 360 hours sedimentation, of 0.5% Na-kaolinite suspensions as a function of $\text{Fe}_2(\text{SO}_4)_3$ concentration.

When the Fe^{3+} concentration was low, the electrical double layer around the clay particles was thick and the electrostatic repulsion between clay particles was strong. The heaviest particles settled immediately under gravity and formed the accumulated sediment at the bottom of the cylinders. The colloidal particles remained suspended for a longer period in a sol. Also, because of the size distribution, the population density of particles in this sol decreased progressively with an increasing height in the cylinder. Hence, a diffuse transition-zone with the clear supernatant liquid was observed.

The addition of Fe^{3+} electrolytes resulted in a reduction of the electrical double layer thickness. The magnitude of the zeta potential is known to decrease in these conditions (Young *et al.*, 1987). When the reduction in double layer thickness was moderate, linear aggregation of the clay particles was favored and very open flocs formed (Pierre, 1992). These flocs joined to each other and extended from wall to wall in the test tube and formed the flocculated sediment, while the supernatant liquid was free of particles. This flocculated sediment was able to flow. The very open flocs, as proved by the initial thickness of the sediment, are responsible for a slow initial settling rate. However, the fractal arms of the flocs were flexible and could slowly deform during aging in the final sediment. Consequently, its volume decreased slowly with time.

With an increasing Fe^{3+} electrolyte concentration, the electrical double layer was even more compressed. In this case, linear aggregation is known to become progressively less important. Denser aggregation occurred. The flocs were less open, they settled faster, but they were less prone to deformation during aging; hence, a higher final sediment volume.

The mixed flocculation-accumulation behavior occurred when flocculation was very slow and in strong competition with accumulation. Therefore, the final sediment was composed of an accumulated layer and a flocculated layer; the accumulated layer formed first,

and the flocculated layer after. Two sharp interfaces could be followed successively in the same test tube: (1) a sharp interface between the accumulated layer and the remaining suspension, at the beginning; (2) a sharp interface between the flocculated layer and the clear supernatant liquid, at the end.

The effect of anions on the sedimentation behavior in this clay can first be partly explained by the DLVO theory, since the double layer thickness decreases with increasing valence states of both the anions and the cations (Hiemenz, 1977). The fact that the flocculation-sedimentation occurred in a narrower range of conditions with FeCl_3 electrolyte than with $\text{Fe}_2(\text{SO}_4)_3$ is in agreement with the higher valence state of SO_4^{2-} compared to Cl^- (Figure 3). They also had an effect on the hydrolysis of Fe^{3+} .

This study was not a study on the hydrolysis of Fe electrolytes, which was addressed in a large number of previous publications. As mentioned in the introduction, it was known that fresh Fe electrolytes, as well as fresh Al electrolytes, favor the formation of relatively strong clay flocs which do not collapse readily under their own weight (Swartzen-Allen *et al.*, 1974). Our purpose was simply to determine a range of conditions where this happens, for further studies of the flocculate structure, by supercritical drying, as with montmorillonite (Zou and Pierre, 1992). This structure study of kaolinite flocs is underway.

The rather abundant publications on Fe hydrolysis and its action on clay can be summarized as follows (Livage *et al.*, 1988). Fe^{3+} electrolytes experience their own hydrolysis in aqueous media, and form their own gels. When the electrolyte concentration increases, more hydrolysis products are formed. The Fe^{3+} hydrolysis products include α - FeOOH (goethite) at $\text{pH} > 9.0$, α - Fe_2O_3 (haematite) at $\text{pH} < 4.0$, and a mixture of both materials between 4.0–9.0 (Livage *et al.*, 1988). It is also known that the hydrolysis process and the gel formation process depend largely on the anions (NO_3^- , Cl^- , SO_4^{2-}). The hydrolysis of $\text{Fe}_2(\text{SO}_4)_3$ is more complex than that of FeCl_3 . It gives rise to a larger variety of complexes such as $\text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \cdot 2(\text{H}_2\text{O})$, $\text{Fe}_4(\text{SO}_4)(\text{OH})_{10}$ (Matijevic *et al.*, 1975), or the insoluble complex $\text{Na}[\text{Al}_3\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}(\text{SO}_4)_4]$ (Segal, 1984). In the presence of clay, these Fe^{3+} hydrolysis products exchange partly with Na^+ . They are also known to adsorb on the surface of the clay particles, while their hydrolysis proceeds. Hence, they help to increase the strength of clay flocs by the intermediate of an Fe-gel cement. Transmission electron micrographs of the Fe product deposited on the surface of clay particles have been published (Blackmore, 1973; Rengasamy *et al.*, 1977; Greenland *et al.*, 1968; Oades, 1984).

CONCLUSION

The sedimentation behavior of fine kaolinite suspensions in the presence of fresh Fe electrolytes can be

classified into three types: (1) sedimentation by accumulation of individual clay units; (2) sedimentation by settling of a flocculated clay which forms a wall-to-wall network structure in the cylinder; (3) sedimentation by mixed accumulation and settling of a flocculated layer, when flocculation and accumulation are in strong competition. This occurs in conditions intermediate between the 2 other kinds of sedimentations. The observed behavior, where the clay particles are charged negatively, agrees at least qualitatively with the DLVO theory.

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