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Structure of kaolinite flocs formed in an aqueous medium

A. C. PIERRE, K. MA, C. BARKER
Department of Mining, Metallurgical and Petroleum Engineering, The University of Alberta, Edmonton, Alberta, Canada T6G 2G6

The structure evolution of kaolinite flocs during their formation in aqueous medium was studied under a scanning electron microscope by hypercritical drying with liquid CO_2, as a function of Fe electrolyte content. Without any Fe electrolyte, a sediment with uniform porosity formed by accumulation of particles under gravity. Fresh Fe electrolytes made it possible to aggregate the kaolinite particles to flocs with an architecture consistent with diffusion limited aggregation (DLA). With 0.67 mM Fe, a single shrinking DLA flocs layer formed. With 3.33 mM Fe, extensive face to face aggregation of the clay particles occurred and a sediment with preferred horizontal orientation accumulated. With 0.17 mM Fe a shrinking DLA floc layer and a uniformly porous accumulated sediment formed concurrently, while with 1.67 mM Fe a shrinking DLA flocs layer and an accumulated sediment with preferred orientation formed concurrently.

1. Introduction

In a recent publication [1], we reported on the direct observation of diffusion limited montmorillonite aggregates and their evolution during drying. Clays are usually comprised of big enough platelike particles to be observed under a scanning electron microscope. Presently, we report on the long-range structure of kaolinite aggregates made in aqueous media with fresh Fe electrolytes, while a first publication was devoted to the kinetics of formation of these sediments in a range of electrolyte conditions [2].

2. Experimental procedure

The flocs investigated were made from kaolinite aqueous suspensions. The clay was "Hydrite UF" from the Georgia Kaolin Company. Its specific surface area in the as-received state, according to our measurements by BET porosimetry, was $21 \pm 4\,m^2\,g^{-1}$. This kaolinite was treated according to a standard procedure [3] to convert it to the sodium form. The Fe electrolyte was $FeCl_3$ and only fresh solutions, that is aqueous solutions of this electrolyte prepared just prior to use, were always added to the clay suspensions.

Kaolinite suspensions were first prepared in graduated cylinders with an inside diameter of 28 mm. The kaolinite content was 0.5% (by mass). Dispersion was achieved with 1 ml of 4.5% $Na_4P_2O_7$ for 100 ml of total suspension volume, which is known to provide negative charges both to the faces and edges of the kaolinite particles [4]. The initial pH just after dispersion and before addition of Fe electrolyte was adjusted to 4.0 with HCl because Fe electrolytes are known to make gels in these conditions [5]. Then, the appropriate amount of the Fe electrolyte was added and mixed. The selected Fe electrolyte concentrations were 0 mM, 0.17 mM, 0.67 mM, 1.67 mM and 3.33 mM. The suspension cylinders were hand-shaken forcefully to distribute the components uniformly inside the suspensions. The initial suspension volume for all samples was 100 ml.

Some samples were kept in graduated cylinders and covered with a parafilm to prevent water evaporation. They were used to record the shrinkage or the accumulation kinetics of sediments. Other identical samples were then transferred to dialysis tubes with an inside diameter of 28.6 mm, provided by the Spectrum company and sedimentation was allowed to proceed. These samples were aimed at performing hypercritical drying, in order to observe their structure under SEM. For each observation, a dialysis tube containing a sample was submitted to a slow liquid exchange for alcohol, then for liquid CO_2 in a critical point dryer from the Biorad company. Only samples aged for several hours were submitted to these liquid exchanges, that is to say after the Fe electrolyte was known to terminate its hydrolysis and building of clay aggregates [6]. This made it possible to avoid any noticeable volume change in the samples. Hypercritical drying is a technique which allows production of, for instance, extremely tenuous silica aerogels [7]. Liquid CO_2 is transformed to CO_2 gas by turning around its critical point, without ever creating a liquid-gas meniscus. The gas is finally evacuated. This technique gives the advantage of minimizing the shrinkage occurring when drying by evaporation. The dry samples were coated with gold and examined under SEM.

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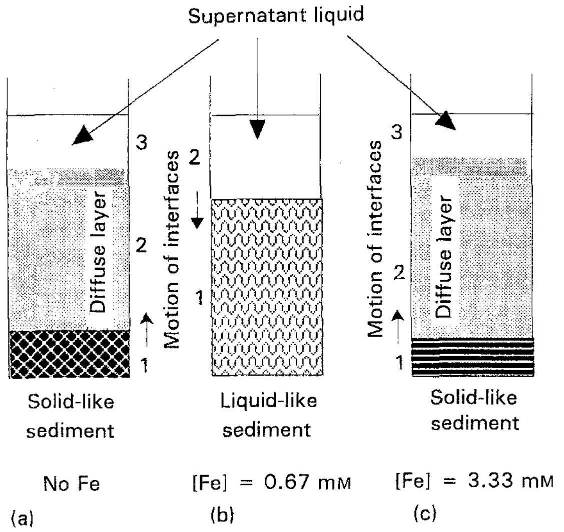

Figure 1 Sedimentation behaviour of 0.5% (by mass) kaolinite suspensions: (a) without Fe; (b) with 0.67 mM Fe; (c) with 3.33 mM Fe.

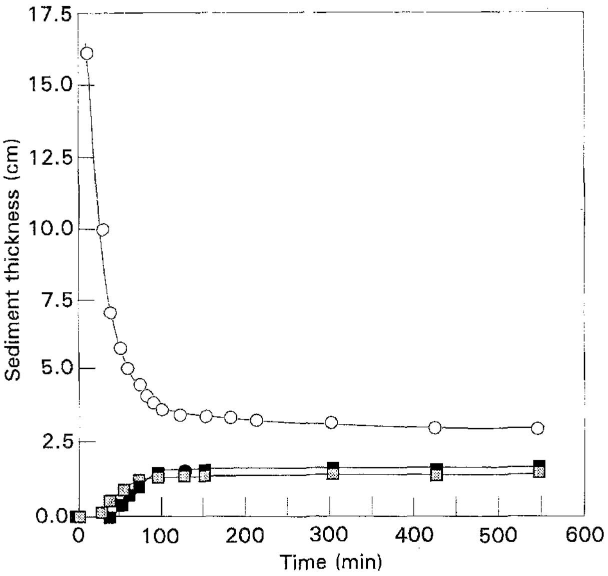

Figure 2 Sedimentation kinetics of 0.5% kaolinite suspensions without and with 0.67 and 3.33 mM Fe. (■) Solid-like sediment, 3.33 mM; (□) solid-like sediment, 0 mM; (○) liquid-like sediment, 0.67 mM.

3. Experimental results

3.1. Sedimentation behaviour

When no Fe electrolyte was added, the individual clay particles (or most probably initial aggregates) did not aggregate in bigger flocs. They slowly fell under gravity, the heaviest ones first. A sediment slowly accumulated at the bottom of the dish (Fig. 1a). At an intermediate stage one could observe three layers from the bottom to the top of test cylinders: (1) the sediment; (2) a diffuse layer where the smallest clay initial aggregates were still dispersed; (3) a supernatant liquid layer apparently containing no particles. With the clay being used, the diffuse layer slowly disappeared while the sediment thickness increased. This sediment had a low final volume and did not flow when tilting the test cylinder; it is designated here as the solid-like sediment (Fig. 1a). Its interface with the diffuse layer was sharp.

With 0.67 mM Fe, the initial clay aggregates themselves aggregated in bigger flocs, each floc being the beginning of a gel network. In the test-tubes one could observe two layers from the bottom to the top (Fig. 1b): (1) the apparently uniformly dense sediment layer; (2) the supernatant liquid layer. The transition between the two layers was sharp. The sediment volume was much greater than without Fe (Fig. 1a). However, it could flow when tilting the cylinder, hence the building of a single big gel monolith did not occur. It is designated here as a liquid-like sediment. With 3.33 mM Fe, the initial clay aggregates themselves assembled in bigger dense aggregates which fell under gravity and built a solid-like sediment by accumulation (Fig. 1c), as without Fe (Fig. 1a). However the present SEM observations showed later on that these two solid-like sediments, without and with 3.33 mM Fe, had a different long-range aggregation architecture. With 0.17 mM Fe, the behaviour was intermediate between 0 and 0.67 mM Fe. A solid-like sediment started to accumulate as in Fig. 1a. However, after some time, the remaining diffuse layer formed a liquid-like sediment as in Fig. 1b. At last, with 1.67 mM Fe, the behaviour was intermediate between 0.67 and 3.33 mM. A solid-like sediment similar to the sediment with 3.33 mM (Fig. 1c) started to accumulate. However a liquid-like flocculated layer later on formed on top of the solid-like sediment, as in Fig. 1b.

3.2. Sedimentation kinetics

The data on sedimentation kinetics with Fe concentrations of 0, 0.67 and 3.33 mM are reported in Fig. 2. In the samples without Fe, the only sharp interface was between the solid-like sediment and the diffuse suspension at the beginning, or the supernatant liquid at the end. The solid-like sediment thickness increased with time and its evolution is reported. The same is true in the samples with 3.33 mM Fe. In the samples with 0.67 mM Fe, the only sharp interface was between the liquid-like sediment and the supernatant liquid. This liquid-like sediment underwent a slow syneresis (shrinkage), inside its mother liquid. Consequently its thickness decreased with time and the evolution is reported in Fig. 2.

In the sample with 0.17 mM Fe, a sharp interface between the solid-like sediment and the remaining diffused suspension was observed in a first stage. The thickness of this sediment increased with time, as in the sample without Fe. However, in a second stage, the remaining diffuse suspension transformed to a liquid-like sediment, so that a sharp interface between this liquid-like sediment and the supernatant liquid could be observed. Actually, this liquid-like layer on top of the solid-like sediment was very thin. The overall sediment thickness decreased with time as with 0.67 mM Fe. During this second stage, the sharp interface between the solid-like sediment at the bottom of the tube and the liquid-like sediment above, progressively became impossible to observe because of a progressive loss of contrast between the two sediment layers. The data are reported in Fig. 3 and they are compared with the sedimentation kinetics with

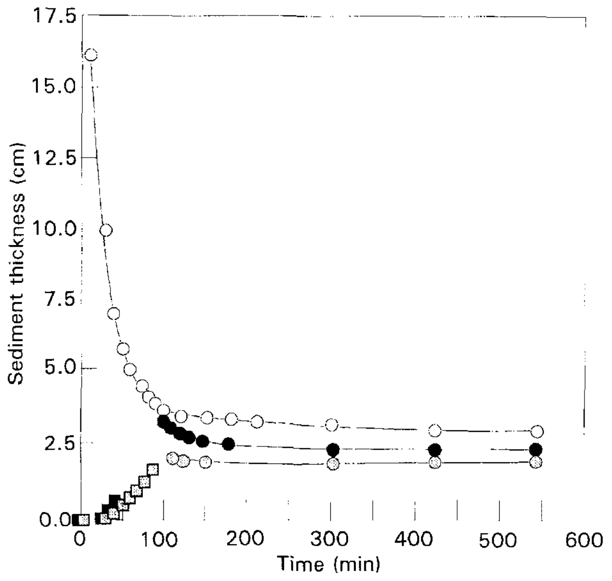

Figure 3 Sedimentation kinetics of 0.5% kaolinite suspensions with 0.17, 0.67 and 1.67 mM Fe. (■) Solid-like sediment, 1.67 mM; (□) solid-like sediment, 0.17 mM; (●) liquid-like sediment, 1.67 mM. (○) liquid-like sediment, 0.67 mM; (○) liquid-like sediment, 0.17 mM.

0.67 mM Fe. With 1.67 mM Fe, the same types of interfaces were observed as with 0.17 mM Fe, that is to say a sharp interface between a solid-like sediment and the diffuse suspension at the beginning, and a sharp interface between the liquid-like sediment and the supernatant liquid at the end. The data are also reported in Fig. 3.

3.3. SEM observations

The aggregate architecture depended largely on the Fe concentration. Fig. 4a, with a 25 μm scale bar, shows a piece cut from a solid-like sediment without Fe. At this scale, the individual particles cannot really be seen and this solid-like sediment appears quite compact. However, in Fig. 4b, with a 7.5 μm scale bar, the individual clay particles can be observed. It shows that the solid-like sediment without Fe was packed with a rather uniform pore size. A liquid-like sediment piece made with 0.67 mM Fe can be seen to be comprised of interconnected flocs in the enlarged Fig. 5 with 25 μm scale bar. Three such interconnected flocs can be observed in Fig. 6; one floc centre was labeled C. In the enlarged Fig. 6 with 7.5 μm scale bar, on the same sample with 0.67 mM Fe as in Fig. 5, the floc structure can be seen to be very open and its packing density is on average decreasing when going from C to B (Fig. 6). However, at this scale, the complete long-range aggregate architecture, visible in Fig. 5, is lost.

The liquid-like sediment in Fig. 5 and Fig. 6 has a 3-dimensional network and it is not possible to focus simultaneously on all the particles. Consequently, some areas appear as being too bright while others are too dark, both being out of focus. However, the overall floc architecture is well illustrated. Its structure is qualitatively typical of aggregates known as "DLA aggregates" according to computer simulations by Witten *et al.* [6]. These aggregates have a fractal structure, that is the mass M of aggregate inside a sphere of radius R and centre C (Figs 5 and 6) increases as:

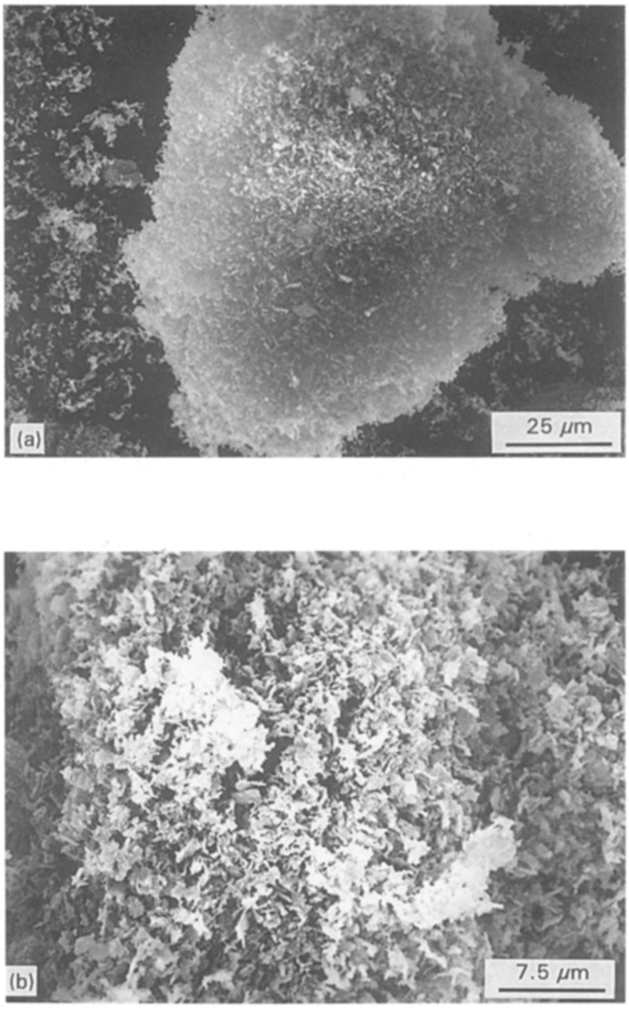

Figure 4 Microstructure, in a horizontal section, of the kaolinite sediment without Fe concentration with a scale bar of: (a) 25 μm; (b) 7.5 μm.

$$M = R^f$$

where f is known as the fractal dimension. For a uniformly porous aggregate such as in Fig. 4, $f = 3$. For three-dimensional DLA aggregates according to computer simulations $f = 2.5$ [9]. In our case the micrographs do not make it possible to estimate f. However they allow us to compare the aggregate aspect, with those from computer simulations.

It must be stressed that observations at higher magnifications, as in Fig. 7 with a scale bar of 1 μm, more clearly show the individual clay particles. However, they are unable to show the long-range architecture of the aggregates, precisely as DLA computer simulations with twenty particles would nor really show the DLA fractal structure. Hardly any difference between the solid-like sediment without Fe (Fig. 7a), and the liquid-like sediment with 0.67 mM Fe (Fig. 7b), can be observed. Also, these observations are very difficult to comment on with respect to near neighbour particle association. Fig. 7a seems to show complete face to face (FF) overlap (arrow A), slight FF overlap (arrow B), edge to edge (EE) (arrow C) and maybe some EF

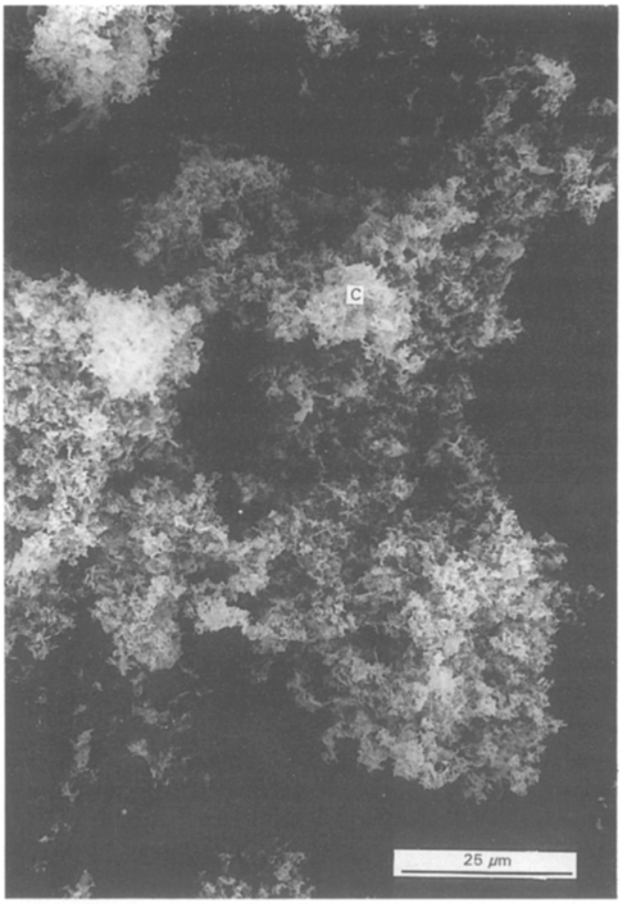

Figure 5 Enlarged microstructure, in a horizontal section, of the kaolinite sediment with 0.67 mM Fe concentration and with a 25 μm scale bar.

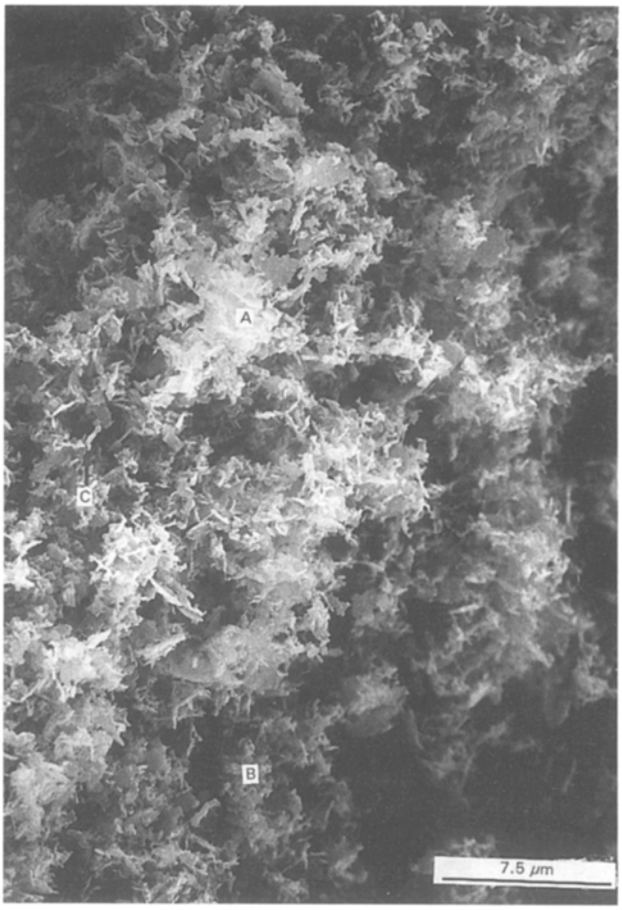

Figure 6 Enlarged microstructure, in a horizontal section, of the kaolinite sediment with 0.67 mM Fe concentration and with a 7.5 μm scale bar.

association (arrow D). Only at longer range as in Fig. 6, it seems that FF overlap is more scarce in the liquid-like sediment. For instance, the particles which are perpendicular to the plane of the picture just above A, in Fig. 6, are very thin and they do not show any FF stacking.

In the solid-like sediment with 3.33 mM Fe, Fig. 8a in a horizontal cross-section and Fig. 8b in a vertical cross-section show a very dense packing with preferred horizontal orientation of the clay particles. We mentioned that the sediments with 1.67 mM Fe were comprised of a solid-like sediment at the bottom, and a liquid-like sediment on top of the solid-like one. These top and bottom sediments are respectively shown in Fig. 9a and b. The top sediment is consistent with the 0.67 mM Fe liquid-like structure, as in Fig. 6, while the bottom sediment has a remarkable horizontal layer structure as in Fig. 8. Finally, the sediment with 0.17 mM Fe was mostly comprised of a solid-like layer of the same type as in Fig. 4 and of a thin liquid-like layer as in Fig. 6, on top of the solid-like layer.

4. Discussion

The manner in which fresh Fe electrolyte solutions help to link clay particles by the intermediary of Fe gels to make relatively strong flocs is known [10] and it was commented on in a previous publication [1]. appropri(The aim of the present investigation was to focus on the long-range architecture of kaolinite aggregates and flocs, as a function of the amount of Fe electrolyte and to relate it to the sedimentation behaviour of kaolinite suspensions.

In the conditions where the suspensions are prepared, the kaolinite particles are known to carry a negative charge both on edges and on faces [4]. Since the various hydroxo-complexes of the Fe electrolyte undertaking hydrolysis were polycations [5], they also were counterions for the kaolinite particles, according to the theory by Derjaguin, Landau, Verwey and Overbeek on coagulation (DLVO theory) [11]. Of course, this theory cannot be quantitatively applied here because: (1) these counterions were changing in nature with time during the first hour; (2) they adsorbed on the clay particles; (3) the kaolinite particles were only colloidal in their thickness, not in the plate extent. However, qualitatively, we could expect that an increasing concentration of Fe complex counterions would progressively reduce the electric double layer thickness. Hence coagulation was not expected to occur without Fe, while it was expected to occur with higher Fe concentrations, which we did observe.

While the negative charge on the edges of the plates may be lower than on the faces, the double layer thickness was a function of the bulk iron concentration which was the same for both the edges and the

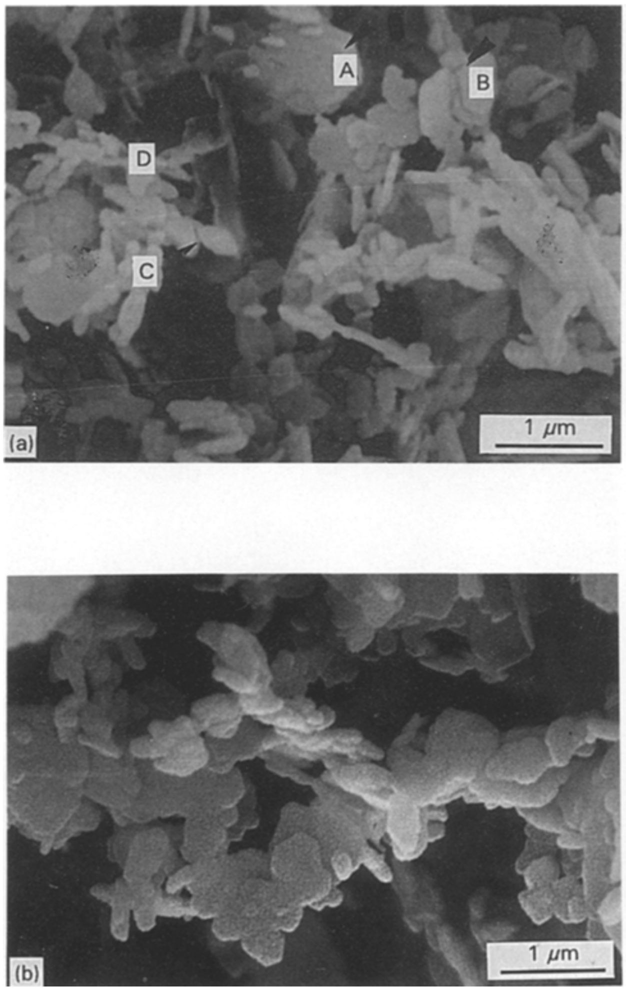

Figure 7 Microstructure, in a horizontal section, of the kaolinite sediments with a 1 μm scale bar made: (a) without Fe; (b) with 0.67 mM Fe.

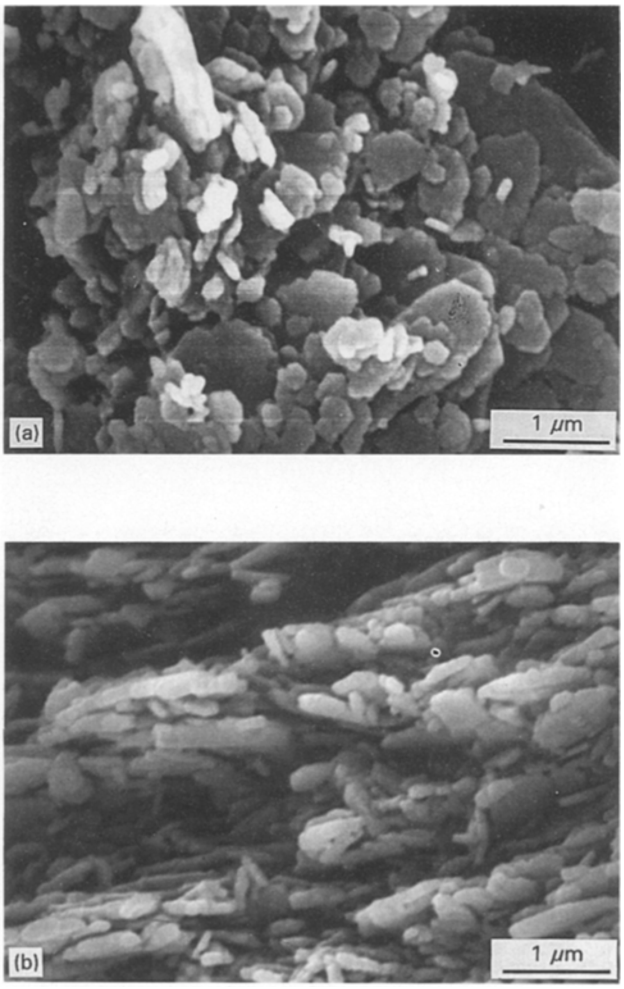

Figure 8 Microstructures of the solid-like sediment with 3.3 mM Fe: (a) in a horizontal section; (b) in a vertical section.

faces. However, even for an identical double layer thickness on the edges and on the faces, the DLVO theory of gelation indicates that when coagulation can begin to operate, that is to say when the double layer is relatively thick, it first favours linear aggregation. This effect is primarily due to the geometrical curvature which attenuates the electric repulsion near the edges, by comparison with the faces [12]. This is consistent with our observations using 0.17 and 0.67 mM Fe. With a higher Fe content, the double layer thickness decreases, the geometrical curvature effect near the edges attenuates and increasingly dense aggregation was expected, which was actually observed for 1.67 and 3.33 mM Fe.

If the kaolinite particles were really of colloidal size, as frequently prevails with silica gels for instance, the Brownian diffusion forces of these flocs would have remained stronger than gravity forces. Hence, the flocs would have kept growing by linking to each other and they would have made a single colloidal gel monolith with elastic properties. It is probable that such an event could be achieved, even with the particle size of the clay used in this experiment, from gravity in the space. In the laboratory conditions, these flocs settled down at the bottom of test cylinders and dialysis tubes, resulting in the formation of sediments. These sediments should not be called gels as long as they can flow. According to the definition by Flory [13], a gel is only formed after the gel point, when for the first time a single elastic network exists which is only limited in extent by the size of the sample. Also, the liquid-like sediment slowly changed by consolidation under gravity. However, this consolidation was asymptotically slow after about 100 minutes (Fig. 2) and the structure modification was very moderate after this time. At shorter times such as a few minutes, when the real structure could not be observed because the dialysis operation takes time, these real transient floc structures are even more open than we observed, since the sediment volume is higher.

On the whole, our microscope observations were fairly representative of the structure in the asymptotic tale of the consolidation curve, when the liquid-like sediment volume only marginally changed (Fig. 2). The structure in this asymptotic consolidation stage consisted in the formation of a layer comprised of interconnected and open flocs. Montmorillonite was known to make big flocs [1]. The SEM observations of kaolinite after hypercritical drying by liquid CO_2 also showed that open flocs can be made with this clay. Qualitatively from their aspect, the flocs looked less open with kaolinite than with montmorillonite

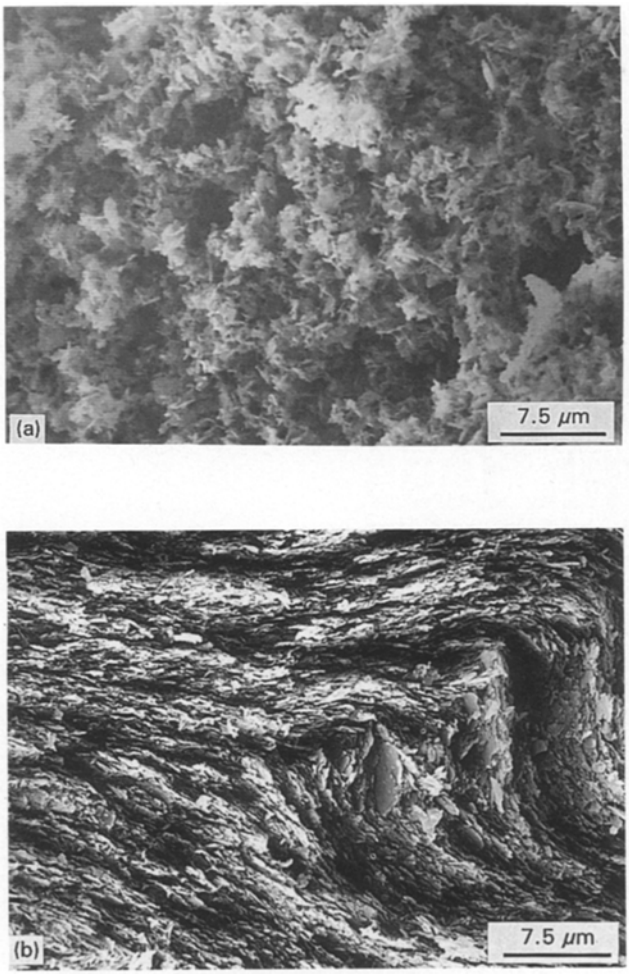

Figure 9 Microstructures, in a vertical section, of the kaolinite sediment with 1.67 mM Fe: (a) liquid-like sediment on top; (b) solid-like sediment with oriented structure at the bottom.

[1]. This is not surprising since these two clays are of a different nature. First, the SEM micrographs showed that the kaolinite particles were thicker than the previous montmorillonite particles, hence the floc structure was more affected by consolidation under gravity. Secondly, building flocs required more Fe electrolyte with kaolinite and hence the kaolinite flocs which could form were expected to be more dense.

In any case, the long-range architecture of these flocs can be explained by a combination of the theoretical diffusion-limited-aggregation model (or DLA) [9], the DLVO theory [12] and the action of gravity. In the asymptotic consolidation stage where the SEM micrographs were made on the liquid-like sediment, these micrographs showed that gravity did not modify in a qualitatively observable fashion the fractal aspect of the flocs, which looked like the expected aspect according to DLA. DLA is known to prevail in the gelation behaviour of most colloidal ceramic systems; it explains how the structure of aggregate is related to the transport of particles by diffusion from far away distances. DLVO gives the probabilities for two particles to remain linked when they collide.

With respect to near-neighbour particles' association in terms of edge to face or edge to edge, the SEM tool used here could not provide a definitive answer. The observations at the highest magnification (scale bar = 1 µm) tended to show that all types of linkage always occurred. At a short range it was difficult to observe marked differences between sediments with 0 to 0.67 mM Fe. This also is consistent with the DLVO theory, since according to this theory only some probabilities of occurrence could be assigned to all the types of linkage. Small differences in the linkage probability of edge to edge versus edge to face would not show up at short range, while it could have a drastic effect at long range. This situation is similar to the structure of glass versus crystalline materials.

5. Conclusion

The long-range architecture of kaolinite particle flocs, in the presence of fresh Fe electrolyte, is consistent with a combination of the DLVO theory and the DLA theory; slowly distorted by the effect of gravity. The first theory provides a theoretical basis according to which small differences in the linkage probability of edge to edge versus face to edge would lead to different long-range structure. The second theory well explains the long-range floc network structure which is observed in this study, in terms of transport of particles. With clay particles which have a size extent larger than the colloidal range, and a thickness of colloidal dimension, sedimentation occurred before complete gelation could be achieved. However, the long-range architecture of kaolinite flocs and aggregates was well illustrated and related to the sedimentation kinetics.

Acknowledgments

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