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Structure reorganization in montmorillonite gels during drying

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The structure evolution of montmorillonite gels, during drying by evaporation, has been studied by scanning electron microscopy (SEM) after hypercritical drying with liquid CO_2. Fresh Fe^{3+} electrolytes allow clay particles to aggregate to flocs with a structure consistent with diffusion-limited aggregation. Compression under the capillary stresses, during evaporation, leads to gelation. During further drying by evaporation, the Fe bonding is strong and prevents the complete collapse of the gel into a parallel stacking of clay plates. On the contrary, such a collapse occurs more easily when fresh Fe electrolyte has not been added.

1. Introduction

In a recent publication [1], two of us (Zou and Pierre) reported on the direct observation of montmorillonite aerogel networks. This clay was composed of plate-like particles large enough to be observed under a scanning electron microscope, with a plate-extent dimension of the order of 2 μm and an estimated plate thickness of the order of 10 nm. We found that the gel network had an aspect consistent with diffusion-limited aggregation [2] by edge-to-edge linkage of the platelets. Here, we report on the gel structure evolution during drying by evaporation.

2. Experimental procedure

The gels investigated were made from montmorillonite aqueous suspensions. Their initial pH, immediately after dispersion and before the addition of electrolyte, was 9.4. The suspensions were stirred for 30 min with a magnetic stirrer at room temperature ($23\,^{\circ} \pm 1\,^{\circ}C$) just prior to their use. The clay was a sodium montmorillonite obtained from the Clay Minerals Society's Repository at the University of Missouri (reference SWy-1), for which most characteristics have been published [3]. Its specific surface area in the as-received state, according to our measurements by Brunaver–Emmett–Teller (BET) porosimetry, was $25 \pm 4 \times 10^3\ m^2\ kg^{-1}$. The electrolytes were either $FeCl_3$ or $Fe_2(SO_4)_3$, which both give very similar results depending on the iron concentration [Fe]. Only fresh aqueous solutions of these electrolytes were always added to the clay suspensions.

A first group of experiments was conducted with 0.5% (by mass) montmorillonite suspensions. The clay suspensions were contained in graduated cylinders with an inside diameter of 28 mm and an appropriate amount of the electrolyte was added. Samples with [Fe] ranging from 0 to 50 mM have been studied, though most of the results presented here concern [Fe] = 0 and 5 mM. Just after preparation, the cylinders were covered with a parafilm to prevent water evaporation. Then, these cylinders were hand-shaken forcefully to distribute the components uniformly inside the suspensions. The initial suspension volume for all samples was 100 mL. The cylinder diameter was sufficiently large to neglect the wall effect, according to a previous study by Michaels and Bolger [4]. Evaporation drying was performed in the laboratory and the data on mass versus time were recorded.

While this first series of drying experiments was appropriate for studying the gelation itself, it left a very thin, solid, dry sediment. Other series of experiments were therefore conducted with suspensions containing 5% clay (by mass). The second series was carried out in Pyrex crystallizing dishes with an inside diameter of 119 mm and a height of 65 mm. A third series was carried out in crystallizing dishes with an inside diameter of 64 mm and a height of 50 mm. Each dish contained 0.1 kg of suspension, and the [Fe] concentration varied in the same range as in the first series of experiments. The evolution of sample mass with time was recorded.

Besides samples used to measure the drying kinetics, other identical samples were used for the SEM observation at three main stages: (i) before gelation, (ii) immediately after gelation, and (iii) in the dry state. In each stage, evaporation was stopped in some samples which were dried hypercritically, after exchange of water for liquid CO_2. Hypercritical drying is a technique which allows the production of, for instance, extremely tenuous silica aerogels [5]. Liquid CO_2 is transformed to CO_2 gas by turning around its critical point, without ever creating a liquid–gas meniscus. Finally, the gas is evacuated. This technique has the advantage of minimizing the shrinkage occurring when drying by evaporation. The dry samples were coated with gold and examined by SEM.

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3. Experimental results

3.1. Sedimentation behaviour

As reported previously by Zou and Pierre [6], the behaviour of montmorillonite suspensions depends on the electrolyte concentration whose most important features can be summarized as follows.

When no $FeCl_3$ was added, the individual clay particles (or, most probably, initial aggregates) did not aggregate in bigger flocs. They fell slowly under gravity; the heaviest ones fell first. A sediment slowly accumulated at the bottom of the dish. At an intermediate stage three layers could be observed from the bottom to the top of the test cylinders: (1a) the sediment; (2a) a diffuse layer where the smallest clay initial aggregates were still dispersed; (3a) 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 volume and did not flow when the test cylinder was tilted, it is designated here as the solid-like sediment (Fig. 1a).

With 5 mM fresh Fe, the initial clay aggregates themselves aggregated in bigger flocs, each floc being the beginning of a gel network. However, the building of a single, large gel monolith did not occur, because each floc slowly fell under gravity. In the test tubes two layers could be observed from the bottom to the top: (1b) the sediment layer; (2b) the supernatant liquid layer (Fig. 1b); the transition between the two layers was sharp. The sediment volume was much higher than without Fe, and it could flow when the cylinder was tilted. It is designated here as a liquid-like sediment. Its solid content could be as low as 1%, depending on the electrolyte conditions.

3.2. Drying Kinetics

The data on 0.5% (by mass) montmorillonite suspensions are given in Fig. 2. In the samples with [Fe] = 5 mM, the supernatant layer evaporated first, while the liquid-like sediment undertook an extremely slow syneresis (shrinkage) inside its mother liquid. However, the drying front of the supernatant liquid caught up with the upper surface of the liquid-like sediment at a time labelled S in Fig. 2. During further evaporation, this liquid-like sediment was the only layer remaining and it dried up directly. As can be seen in Fig. 2, this did not modify the drying kinetics at all – a phenomenon which is well known [7]. This sediment remained liquid-like down to some point designated here as the gel point GP. After that moment, the test cylinder could be turned upside down with no flow occurring. However, drying and shrinkage continued with the same drying rate. This constant drying rate was maintained to point L, which has been designated as the "leatherhard point" or the "critical point" in previous literature [7, 8]. It is designated here as the "leatherhard point", to distinguish it from the thermodynamical critical point at the end of the liquid–gas phase transition of CO_2. After this point L, shrinkage stopped and the drying rate fell drastically; it appears as a horizontal line in the drying data of Fig. 2.

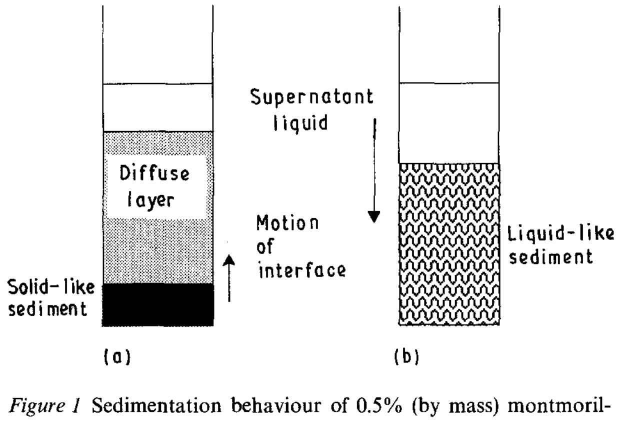

Figure 1 Sedimentation behaviour of 0.5% (by mass) montmorillonite suspensions: (a) without $FeCl_3$, (b) with 5 mM $FeCl_3$.

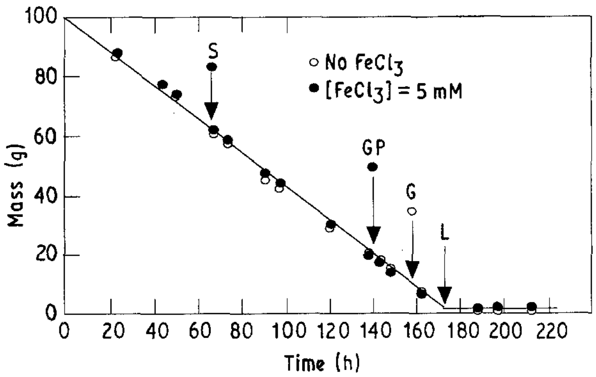

Figure 2 Drying kinetics of 0.5% SWy-1 montmorillonite suspensions without and with 5 mM $FeCl_3$.

In samples without Fe, the supernatant layer, the diffuse liquid layer, and the solid-like layer dried successively. However, this did not show up in the drying data. The letter G, in Fig. 2, designates a state where only the solid-like sediment remains. This solid-like sediment kept drying for some time with the same drying rate, until it reached the leatherhard point, like the samples with Fe. The mass at the gel point increased with [Fe] as indicated in Fig. 3.

The samples with 5% (by mass) montmorillonite examined in more detail the phenomenon near the leatherhard point, since they gave a thicker sediment. It must be pointed out that the initial suspensions could already be called gels, since they no longer flowed after a short time at rest. The drying data from the second sample series (dish with a 119 mm inside diameter) still show a constant drying rate, with a sharp transition at the leatherhard point (Fig. 4). During this drying process, warping and then cracking occurred before the end of the constant drying rate. However, this did not show up in the data.

With the third sample series, the dishes had an even smaller inside diameter (64 mm) hence a greater sediment thickness. When the drying time reached 48 h, a crack occurred in samples containing no $FeCl_3$, and warping was extensive. As a result, the transition at the leatherhard point appears as more progressive in Fig. 5. In samples with 5 mM $FeCl_3$, a crack occurred after 90 h only, and warping was not so extensive. Consequently the leatherhard transition appears as sharp again in Fig. 5. Other samples with 10 mM $FeCl_3$ remained monolithic until the end of drying.

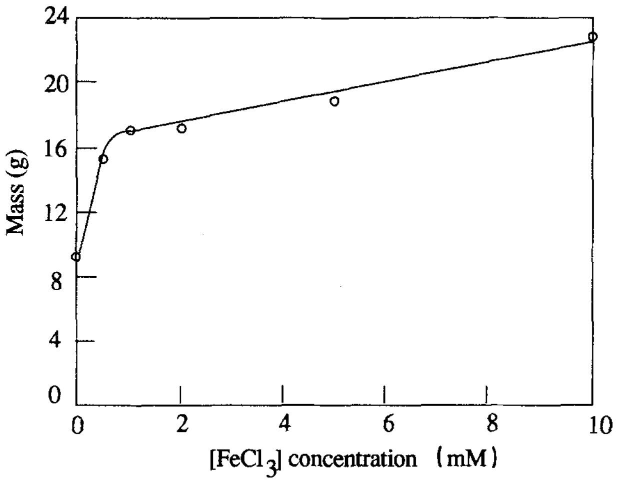

Figure 3 Mass at gel point of 0.5% montmorillonite suspensions as a function of $FeCl_3$ concentration.

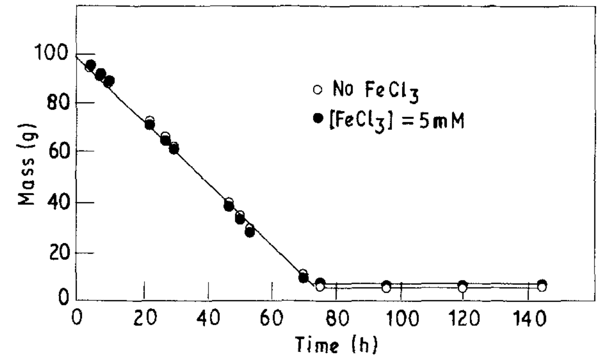

Figure 4 Drying kinetics of 5% SWy-1 montmorillonite gel without and with 5 mM $FeCl_3$ in 119 mm diameter dishes.

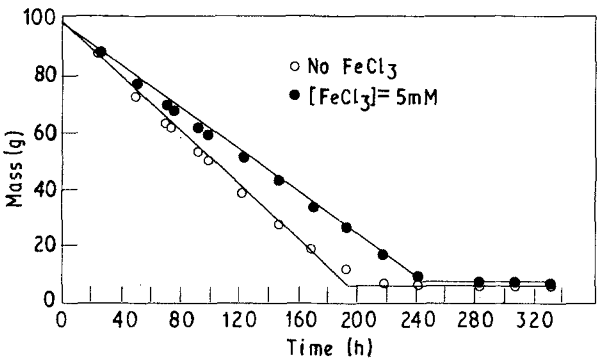

Figure 5 Drying kinetics of 5% SWy-1 montmorillonite gel without and with 5 mM $FeCl_3$ in 64 mm diameter dishes.

The data in Fig. 5 seem to show a different constant drying rate between the samples without Fe and the samples with [Fe] = 5 mM. However, we checked, with pure distilled water dishes, that this is only due to a different, local convection effect. We found that, to get a consistently reproducible drying rate, the samples had to be placed in exactly the same place in the laboratory, and inside identical dishes. The moisture content, after the leatherhard point, increases with [Fe] as indicated in Fig. 6.

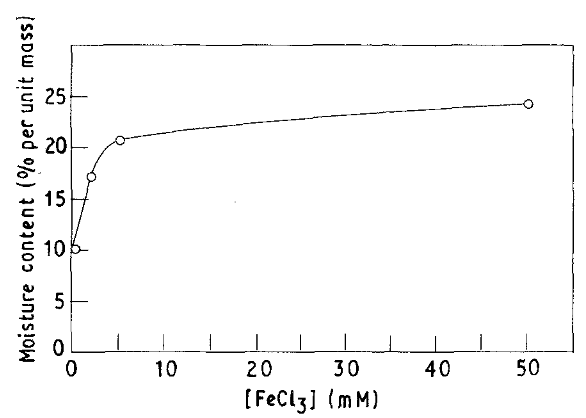

Figure 6 Moisture content of 5% (by mass) SWy-1 montmorillonite gels at leatherhard point as a function of $FeCl_3$ concentration.

3.3. SEM observations

Hypercritical drying allowed the transformation of the montmorillonite liquid-like sediment, obtained with 5 mM $FeCl_3$, to a dry aerogel with a high specific surface (4.00×10^5 m^2 kg^{-1}). Its structure was fractal, as is well illustrated in Fig. 7b. The overall picture is roughly consistent with the model known as hierarchical (diffusion-limited aggregation DLA) [2] and explains the high gel volume. In the solid-like sediment obtained without $FeCl_3$, the particles were packed more uniformly (Fig. 7a). In both cases, the clay particles are linked to each other in an edge-to-edge fashion [1].

After the gel point, the hypercritically dried structures of samples with and without 5 mM $FeCl_3$, observed by SEM after the hypercritical drying, are shown in Figs 8 and 9. In both cases (on the smaller scale (10 μm)) clay platelets are still linked in the same edge-to-edge fashion as they were initially (Fig. 8). The main differences can be seen in Fig. 9 (on the larger scale (100 μm)). The gels were not very strong from the solid-like sediments without Fe. They easily broke into large, roughly spherical agglomerates. Inside each agglomerate, the packing structure is very uniform. With 5 mM $FeCl_3$, the gels immediately after gel point were able to withstand handling more readily, indicating that strong links had established between the flocs. The initially very open fractal network of the liquid-like sediment can still be identified in Fig. 9b. However, this network has undergone considerably compaction, with fractal organization characterized by shorter and thicker branches than initially.

After complete drying by evaporation, the structures of samples observed by SEM show that the packing patterns of the clay platelets also depend on the presence of Fe electrolyte. The overall organization is characterized by a very laminar structure, with marked preferred orientation, in the samples without Fe electrolyte (Fig. 10a). The preferred orientation is less prominent in montmorillonite samples with [Fe] = 4 mM (Fig. 10b).

Upon mixing 5% (by mass) of montmorillonite in water, with or without Fe electrolyte, we had mentioned that the suspensions solidified to gels when at rest. However, the structure of these gels is quite

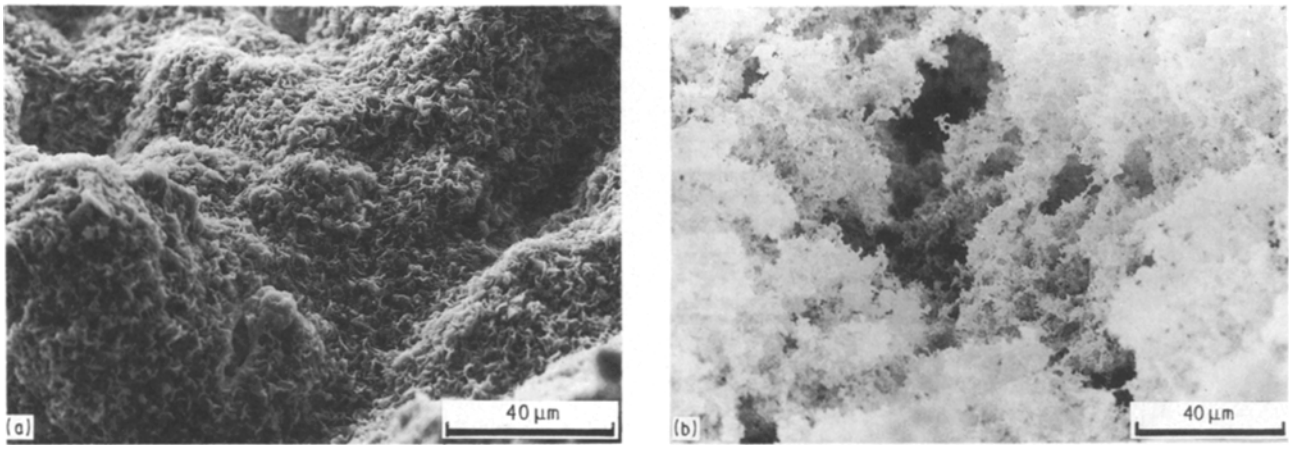

Figure 7 View under the SEM of sediments obtained from 0.5% (mass) aqueous montmorillonites suspensions, after hypercritical drying with liquid CO_2: (a) without $FeCl_3$, (b) with 5 mM $FeCl_3$.

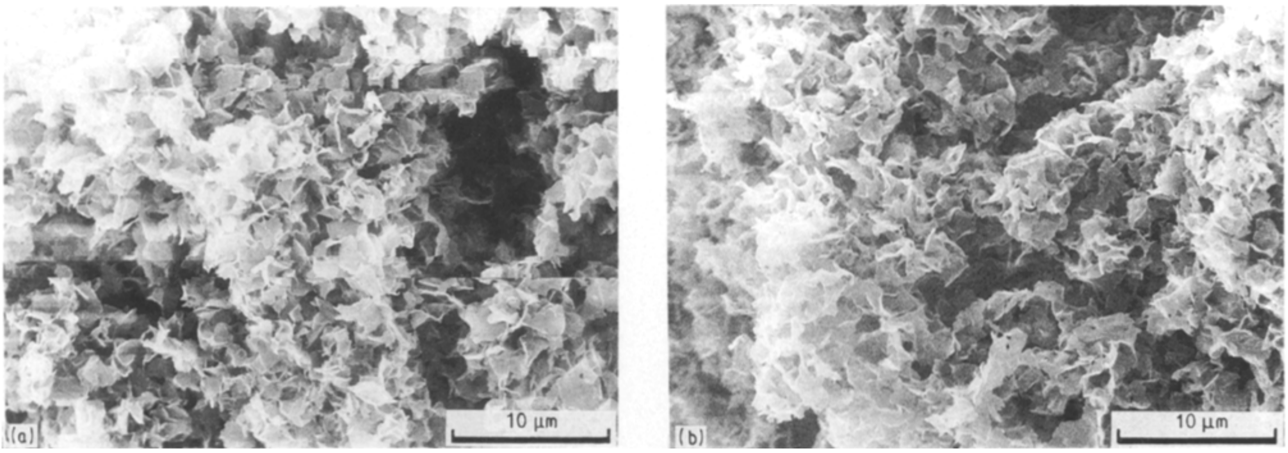

Figure 8 SEM structure after hypercritical drying of 0.5% SWy-1 montmorillonite suspensions at gel point: (a) without $FeCl_3$, (b) with $[FeCl_3] = 5$ mM.

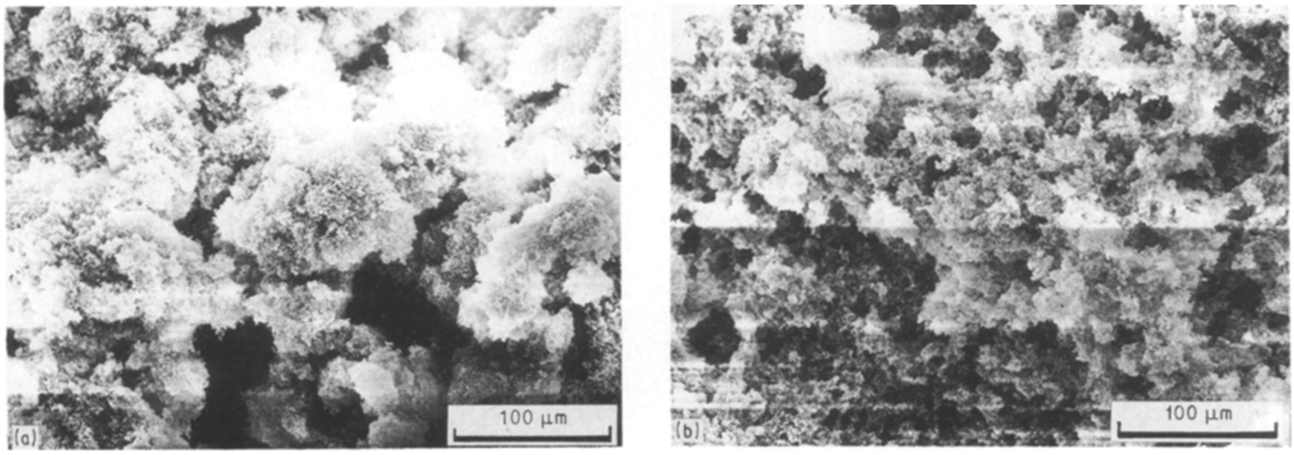

Figure 9 SEM structure after hypercritical drying of 0.5% SWy-1 montmorillonite suspensions at gel point: (a) without $FeCl_3$, (b) with $[FeCl_3] = 5$ mM.

different from those obtained from 0.5% (by mass) montmorillonite suspensions, where fractal flocs had time to form before sedimentation and compaction of the sediment under capillary forces. This is well illustrated in Fig. 11, where the structures of 5% suspensions, observed by SEM after hypercritical drying, show rather compact uniform grids in both cases. However, it seems that with a concentration of [Fe] = 5 mM spherical domains can be observed (Fig. 11b).

4. Discussion

Clay particles, especially montmorillonite, are well known to make big flocs and gels [7]. The SEM

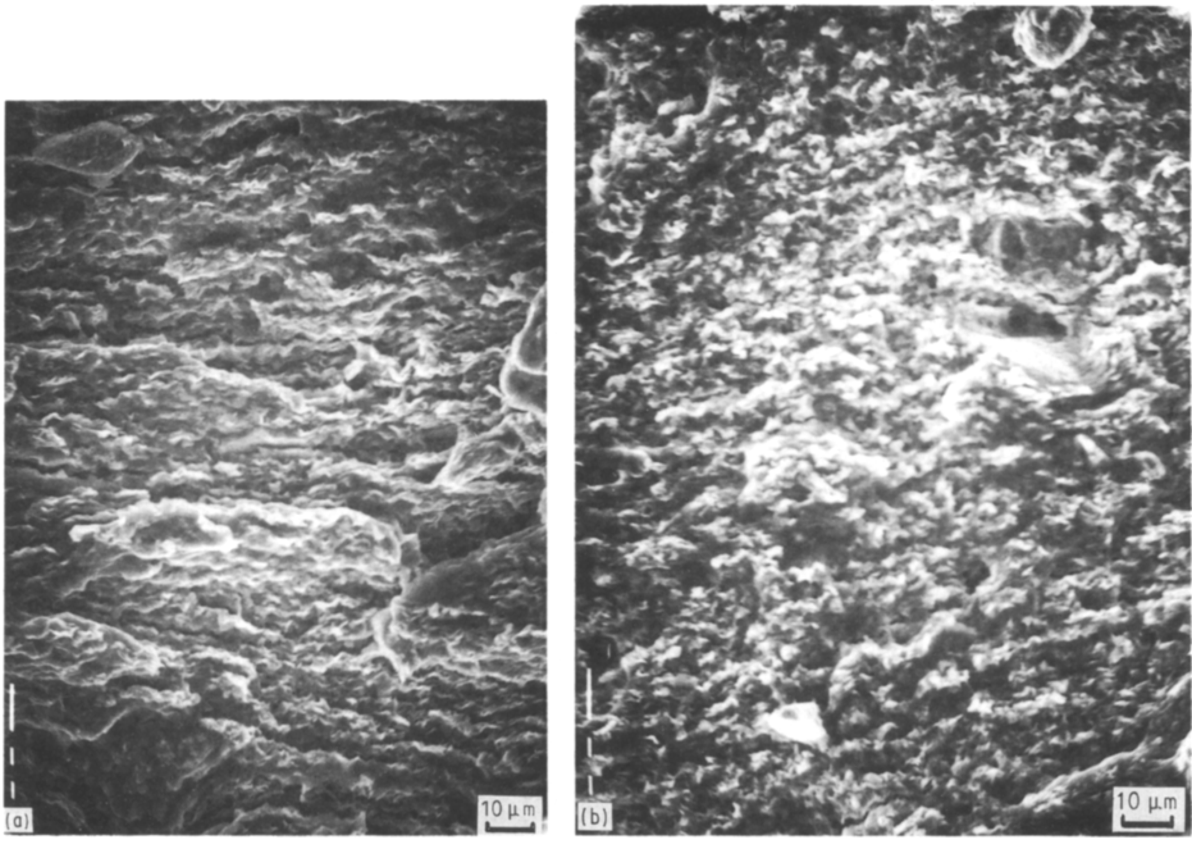

Figure 10 SEM structure of conventionally dried sediments of 5% SWy-1 montmorillonite gel: (a) without any Fe, (b) with [Fe] = 4 mM, from $Fe_2(SO_4)_3$.

observations of the structure of these flocs and gels, after hypercritical drying by liquid CO_2, show that particle linkage is mostly by edge-to-edge sharing. This is consistent with the Derjaguin–Landau–Verwey–Overbeek (or DLVO) theory of gelation, since it is well known that the electric double layer is less thick near the edges of plates than near the faces and hence favours linear aggregation [9]. Also, the overall architecture of the flocs is roughly consistent with the theoretical DLA model [2], which is known to prevail in the gelation behaviour of most colloidal ceramic systems [10]. According to this model, clay platelet particles diffuse by Brownian motion inside the mother liquid and, whenever the electrostatic and Van der Waals interactions allow it, they can link to each other during collisions. Fractal flocs build up slowly.

If the particles were really of colloidal size, as frequently occurs with silica gels for instance, the Brownian diffusion forces of these flocs would have remained stronger than gravitational forces. Hence the flocs would have kept growing, by linking to each other, and 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, for instance in zero gravity in space.

In the laboratory conditions, these flocs settled at the bottom of test cylinders and dishes, forming a liquid-like sediment. These sediments should not be called gels as long as they can flow. According to the definition by Flory [11], a gel is formed only after the

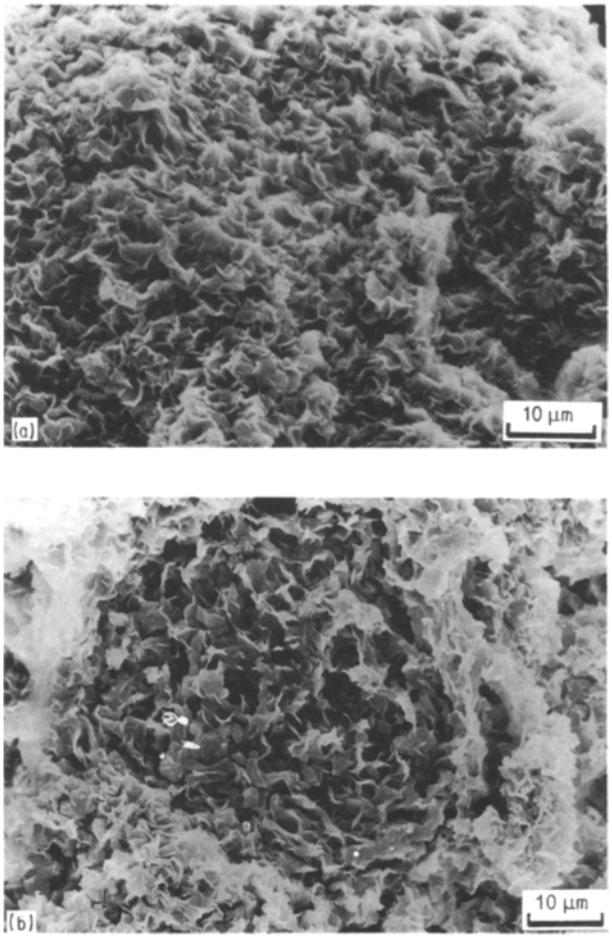

Figure 11 SEM structure of 5% SWy-1 montmorillonite gel: (a) without $FeCl_3$, (b) with $[FeCl_3]$ = 2 mM.

gel point, where for the first time a single elastic network is limited in extent only by the size of the sample.

True gels, in Flory's sense, form during drying by evaporation. Under capillary forces, the flocs are compressed. The SEM pictures show that their fractal structure is deformed and that they are forced to interpenetrate. The fact that, at some time, the liquid-like sediments transform into solids which no longer flow, also proves that the compressive capillary stresses have induced a real linkage between the flocs. This is a behaviour akin to sintering.

The effect of fresh Fe^{3+} cations is well known [12]. First, they act as counter-ions favouring an edge-to-edge approach of negatively charged clay plates. Secondly, they start to exchange with the other cations in the clay, such as Na^+ in our case. Lastly, provided this is a fresh Fe^{3+} solution which has not yet completed its hydrolysis, the solution continues its own hydrolysis in the presence of the clay particles, which end up being linked by rather strong Fe polymeric chemical complexes. The effect of Fe in making strong bonds shows up on the mass at gel point, on the moisture content at the leatherhard point and on the clay-particle-packing in the final dry state. While the capillary forces could force the clay particles to stack parallel to each other (face-to-face final configuration) in the sediment without Fe, they were not able to achieve the same result in the gel with Fe due to the stronger edge-to-edge bonds. Simultaneously, the mass at gel point and the moisture content at the leatherhard point is higher in gels containing Fe.

Without fresh Fe electrolyte, the electrical double layer around each particle, according to the DLVO theory, is too thick and forbids any new linkage. Certainly, the initial clay suspensions are not composed of single individual platelet particles, but of small aggregates forming themselves by edge-to-edge particle linkage; and these small aggregates slowly sediment individually, without having the opportunity to associate in larger fractal flocs.

5. Conclusion

The gelation of montmorillonite clay particles, in the presence of fresh Fe^{3+} electrolytes, occurs in agreement with the DLVO theory and the DLA theory. The first theory is a good explanation of how linkage proceeds between a particle and the neighbouring particle. The second theory explains the overall network structure well. With clay particles having sizes outside the colloidal range, and thicknesses of colloidal dimensions, sedimentation occurs before complete gelation can be achieved. Nonetheless a true gel can be made under compression by the capillary forces during drying by evaporation.

Acknowledgements

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