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ELECTRON MICROSCOPE OBSERVATIONS OF CHROMIUM HYDROXIDE-INDUCED MONTMORILLONITE MICROCLUSTERS

Key Words—Chromium, Microcluster, Montmorillonite, SEM, TEM.

The adsorption of hydroxy-Cr polymers by smectites has received considerable attention in recent years. Most work has focussed on the intercalation of smectites with hydroxy polymers of Cr alone (Pinnavaia *et al* 1985) or of Cr along with Al (Carrado *et al* 1986, Skoularikis *et al* 1988). These clays are then heated to produce fixed oxide pillars which give the clay catalytic properties. Other workers have intercalated smectite simply to elucidate the structure of the unheated hydroxy-Cr polymers (Carr 1985, Drljaca *et al* 1992, Dubbin *et al* 1994). Despite advances in understanding the nature of these hydroxy-Cr polymers, little is known of their effect on the arrangement of individual smectite tactoids. Variations in this arrangement could greatly influence access to the interlayer region by reactant molecules.

Tactoid thickness is known to be a function of the type of adsorbed cation (Schramm and Kwak 1982). Multivalent cations increase tactoid thickness due largely to greater electrostatic forces. The adsorption of hydroxy-metal polymers further increases tactoid thickness (Barnhisel and Bertsch 1989). The effectiveness of a hydroxide as a cementing agent increases with decreasing crystallinity (Hsu 1989). Iron hydroxides have been shown to be less effective cementing agents than Al hydroxides, due to greater crystallinity of the former (Frenkel and Shainburg 1980). Chromium hydroxides, as they are less crystalline than either Al or Fe hydroxides, would be expected to be the most effective cementing agents. The superior cementing ability of hydroxy-Cr polymers would reveal itself not only in the presence of thicker tactoids, but likely also in the formation of unique structures. Within this note is reported, for the first time, the formation of microclusters of montmorillonite tactoids induced by adsorbed hydroxy-Cr polymers.

EXPERIMENTAL

Prior to fractionation, the montmorillonite (SWy-1, Crook County, Wyoming) was Na-saturated by washing five times with 1 *N* NaCl then washed free of Cl^- as determined by the $AgNO_3$ test. Five grams of the <2 μm fraction were suspended in 2 liters deionized water. Aluminum chloride and $CrCl_3$ were added to separate clay suspensions to give each suspension a total trivalent cation (M^{3+}) concentration of 400 cmol(M^{3+})/kg clay. The two clay-cation suspensions were stirred vigorously and titrated at 1 mL/min with 0.1 *N* NaOH until a final NaOH/M^{3+} molar ratio of 2.5 was reached (Dubbin *et al* 1994). A third clay suspension containing 5 g of the <2 μm fraction, which did not have any Al, Cr, or NaOH added, served as the control. All three suspensions were brought to final volumes of 3 liters and then transferred to capped bottles. The suspensions were aged at 23 ± 0.5°C for 30 days and were agitated daily. After aging, the solid phase was isolated by ultrafiltration through a Millipore filter of 0.025 μm pore size and then washed free of Cl^- as determined by the $AgNO_3$ test. Aluminum and Cr in the supernatant were quantified with atomic absorption spectroscopy. All clays were allowed to dry by evaporation under ambient conditions.

In preparation for scanning electron microscopy (SEM), the gently-powdered clay samples were mounted on aluminum stubs with carbon paint then sputter-coated with gold in a vacuum evaporator. The SEM images were obtained with a Cambridge Stereoscan 120 microscope operating at 20 kV. Image enhancement and storage was carried out with an IBAS 20 image analyser. Samples for transmission electron microscopy (TEM) were prepared by evaporating a dilute clay suspension onto carbon-coated Formvar films supported by copper grids. Analysis was conducted with a Philips EM 420 microscope operating at 100 kV.

RESULTS AND DISCUSSION

The pH of the Cr-clay suspension decreased from 5.7 to 4.2 during the aging period. This decrease indicated that the Cr had undergone hydrolysis and polymerization. Of the 400 cmol Cr/kg clay added to the suspension, only 66 cmol Cr/kg clay remained in the supernatant after 30 days. Therefore, most of the hydroxy-Cr polymers were sorbed to the montmorillonite surface at the end of the aging period. Previous analyses with X-ray photoelectron spectroscopy found all the Cr in these sorbed hydroxy polymers to be Cr(III) (Dubbin *et al* 1994).

Arrows indicate nearly spherical montmorillonite clusters, approximately 1 μm in diameter, on the surface of a large montmorillonite aggregate (Figure 1). As these microclusters were not present in either the untreated clay or the Al-clay, the adsorbed hydroxy-Cr polymers were shown to be a requirement for cluster formation. At a higher magnification, a single microcluster can be seen resting on a base of flat montmo-

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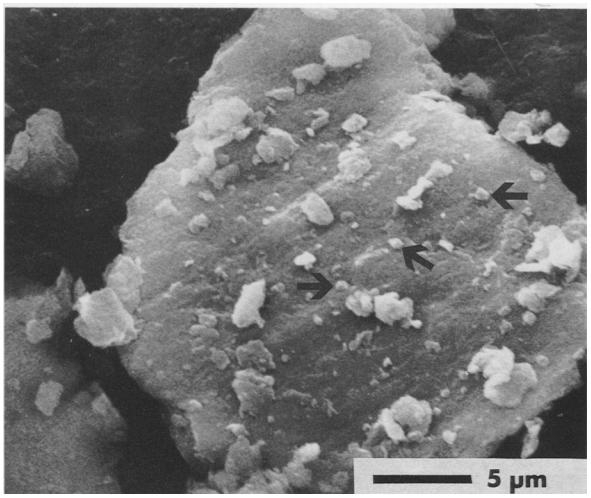


Figure 1. SEM image of a large montmorillonite aggregate. Arrows indicate microclusters (approximately 1 μm in diameter) resting on the surface.

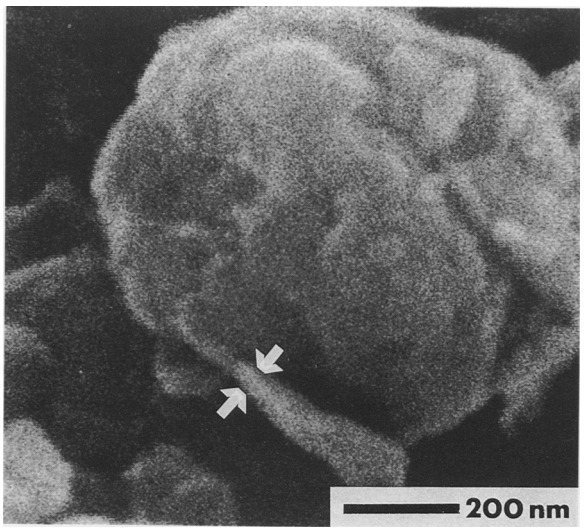


Figure 3. High magnification (approximately 75,000 times) SEM image of the microcluster in Figure 2. Individual tactoids, 20 to 30 lamellae thick, are visible (arrows).

rillonite flakes (Figure 2). The outer shell of the cluster appears to be composed of several montmorillonite flakes enveloping a central core. Magnification of the microcluster approximately 75,000 times allowed for a rare, direct observation of individual montmorillonite tactoids (Figure 3). By assigning a basal spacing of 18 Å for this interlayered clay (W. E. Dubbin, unpublished data), each tactoid is shown to consist of 20 to 30 lamellae. This increased tactoid thickness is consistent with the expected cementing properties of Cr hydroxide. At this higher magnification, one can also see that several tactoids are not adhering fully to the cluster. These tactoids may be recent additions which have not yet fully complexed with the central core of the cluster.

Transmission electron microscopy revealed the presence of Cr hydroxide polymers, 5 to 10 nm in diameter, sorbed to the external surface of the montmorillonite (Figure 4). The strong contrast between these polymers

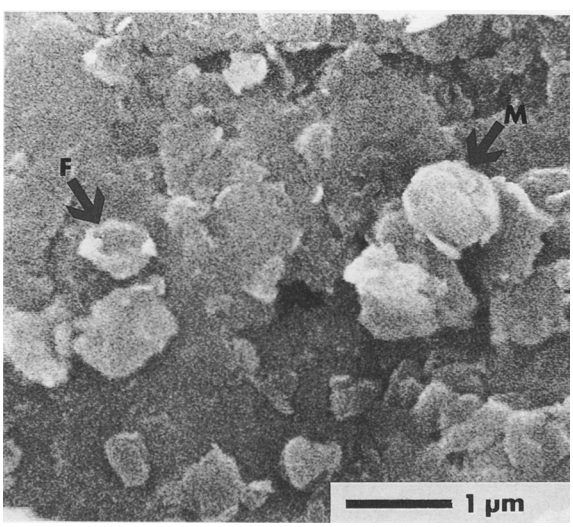


Figure 2. SEM image showing a single microcluster (M) at right. A curled montmorillonite flake (F) is visible at left. Several other flakes display raised edges.

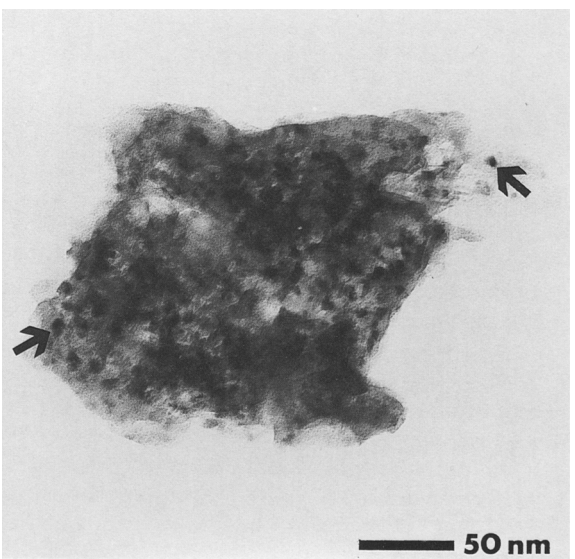


Figure 4. TEM image with arrows showing hydroxy-Cr polymers (5 to 10 nm in diameter) distributed on the external surface of a montmorillonite flake.

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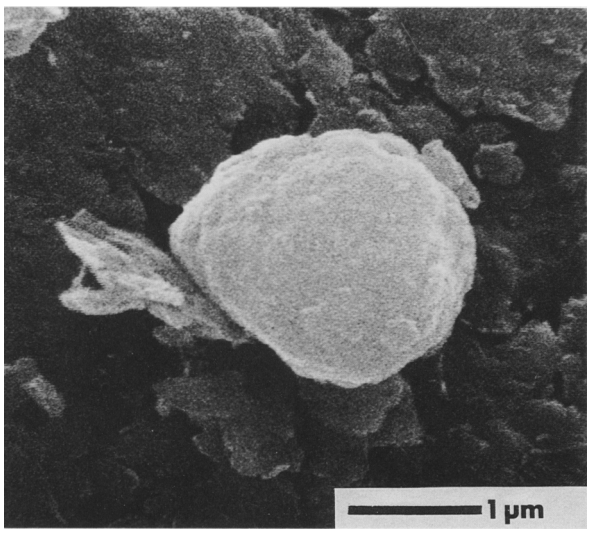


Figure 5. SEM image revealing mode of cluster growth. A single montmorillonite flake is enveloping the central core from left to right.

and the montmorillonite grain indicated that the polymers had a substantial thickness along the c-axis. Residual positive charge on these polymers would provide an effective means for binding adjacent tactoids.

Microcluster formation is believed to involve several steps. First, evaporative drying causes the montmorillonite flakes at the surface to curl. A single montmorillonite grain in this first stage of cluster formation is visible in Figure 2. Several other grains in this image display raised edges. As adjacent flakes encounter each other they would adopt a quasi-spherical arrangement which, for curled particles, would be the most stable conformation. As much of the water from the clay surface has been lost due to drying, the tactoids are able to come into intimate contact with each other. This close contact allows adjacent tactoids to be bridged through the hydroxy-Cr polymers. The resultant microclusters would be highly resistant to mechanical disruption because the Cr likely forms stable inner-sphere complexes with the oxygen of the siloxane surface (Drljaca *et al* 1992). Chemical destruction, however, would be easily achieved through either proton dissolution of the polymers or oxidation of the Cr(III). As Figure 5 reveals, microcluster growth occurs simply through the incorporation of additional montmorillonite flakes. Growth would continue as long as dried montmorillonite flakes of appropriate size are available.

Only a small portion of the total montmorillonite was present as clusters. Evaporative drying, which was used in this study, does not favor the formation of these spherical aggregates (Xiang *et al* 1992). However, the population of clusters would be greatly increased through the use of a spray-drying technique similar to that employed by Tsvetkov *et al* (1990). The cluster population, therefore, may be altered to suit the intended use of the clay. If one wishes to increase the accessibility of the interlayer region, then the cluster population should be reduced or eliminated. This reduction can be achieved either by modifying the method of drying or by decreasing the number of hydroxy-Cr polymers on the external surface of the clay. If, however, the clusters are shown to have some application, their numbers could be deliberately increased.

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