

## FURTHER INVESTIGATIONS ON FULVIC ACID-Cu<sup>2+</sup>-MONTMORILLONITE INTERACTIONS\*

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(Received 28 August 1973)

**Abstract**—The major mechanism by which fulvic acid removed Cu<sup>2+</sup> from Cu<sup>2+</sup>-montmorillonite was complexation, most likely chelation. This was confirmed by the use of a specific cupric ion electrode which showed that whereas the total Cu<sup>2+</sup> concentration in the supernatant solutions increased with rise in pH, about 7 per cent of the total Cu<sup>2+</sup> solubilized by fulvic acid occurred in the 'free' or 'uncomplexed' form at pH 2.5, only 0.6 per cent was similarly distributed at pH 4.5 and 0.0009 per cent at pH 6.5. External surface area measurements by a dynamic BET method showed the following surface areas: 2.5 m<sup>2</sup> g<sup>-1</sup> for the fulvic acid, 8.0 m<sup>2</sup> g<sup>-1</sup> for the Cu<sup>2+</sup>-montmorillonite but 16.1 m<sup>2</sup> g<sup>-1</sup> for the FA-Cu<sup>2+</sup>-montmorillonite complex. Electron micrographs of the FA-clay complex confirmed that fulvic acid was adsorbed in interlamellar spaces and on external surfaces of the Cu<sup>2+</sup>-montmorillonite.

### INTRODUCTION

A previous communication from this laboratory (Schnitzer and Kodama, 1972), reported reactions of fulvic acid (FA), a water-soluble humic fraction, with Cu<sup>2+</sup>-montmorillonite. The adsorption of FA by the clay was characterized by an increase in interlamellar spacing, the extent of which decreased with increases in the pH of the medium. Differential thermal and thermogravimetric analyses showed that in addition to interlayer adsorption, FA was also retained on external clay surfaces. I.R. spectra indicated that  $\beta$ -diketone groups in FA reacted with Cu<sup>2+</sup> in or on the clay to form acetylacetonate-type chelates. This paper provides additional information on the nature of the reaction between Cu<sup>2+</sup>-montmorillonite and FA and on the clay-FA complexes that are so formed. In our earlier publication (Schnitzer and Kodama, 1972) we estimated the amounts of Cu<sup>2+</sup> complexed by the FA by subtracting  $\mu$ g of Cu<sup>2+</sup> solubilized by distilled H<sub>2</sub>O from those brought into solution by FA. This approach entailed considerable uncertainty, which we have now overcome by the use of a specific Cu<sup>2+</sup>-ion electrode, which enabled us to measure 'free' or 'uncomplexed' Cu<sup>2+</sup> aside from 'total' Cu<sup>2+</sup>, which we determined as reported previously. Thus, the difference between 'total' and 'free' Cu<sup>2+</sup> gave the proportions of "complexed" Cu<sup>2+</sup> with a high degree of accuracy. We also set out to obtain more detailed information on the physical characteristics of the clay-FA complex by making surface area measurements and studies on the

electron microscope. The results of these investigations are reported herein.

### MATERIALS AND METHODS

#### *FA and Cu<sup>2+</sup>-montmorillonite*

The FA and Cu<sup>2+</sup>-montmorillonite samples were the same as those described previously (Schnitzer and Kodama, 1972). A FA stock solution was prepared by dissolving 2.0 g of FA in 1 l. of distilled H<sub>2</sub>O. The pH of the latter solution was 2.5.

#### *Preparation of FA-Cu<sup>2+</sup>-montmorillonite complex*

Twenty mg of clay were weighed into a 35 ml graduated ground-glass stoppered centrifuge tube and suspended in 20 ml of FA stock solution. When required, the pH was adjusted to the desired value by the addition of 0.2 N NaOH solution, and the final volume was made to 25 ml with distilled water. The tube plus contents were agitated on a reciprocating shaker at room temperature for 18 hr and then centrifuged at 2000 rpm for 1 hr (radius of rotation near top of sediment in centrifuge tube = 19 cm). The supernatant solution was decanted and the residue (=FA-clay complex) dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>.

#### *Cu<sup>2+</sup>-determinations*

'Free' or 'uncomplexed' Cu<sup>2+</sup> (Cu<sub>f</sub>) was determined on clear supernatant solutions, made 0.1 N in KNO<sub>3</sub>, with the aid of an Orion cupric ion activity electrode (model 94-92). The reference electrode was a single-junction (Orion, model 90-01) electrode, filled

\* Contribution No. 467. Dedicated to the memory of Dr. W. F. Bradley.

with 4 N KCl solution saturated with AgCl. The electrodes were connected to an Accumet model 320 expanded scale research pH meter. The electrodes were calibrated with standard  $\text{Cu}(\text{NO}_3)_2$  solution (Orion, cat. no. 94-92-06) and the calibration curve, plotted on semi-log paper, covered a range of  $10^{-1}$ – $10^{-8}$  moles  $\text{Cu}^{2+}/\text{l}$ . Without the addition of  $\text{KNO}_3$  solution to the supernatant solutions containing FA, periods of 3–4 hr were required to attain a constant electrode response. When  $\text{KNO}_3$  solution was added, however, constant readings were obtained after only 5–10 min.

Total  $\text{Cu}^{2+}$  ( $\text{Cu}_t$ ) was measured by atomic absorption on a Techtron spectrophotometer. Since preliminary experiments had shown that the FA did not interfere with  $\text{Cu}^{2+}$  determinations by atomic absorption, analyses were done directly on solutions still containing the FA.

#### Surface area measurements

External surface areas of freeze-dried FA,  $\text{Cu}^{2+}$ –montmorillonite and the FA– $\text{Cu}^{2+}$ –montmorillonite complex were measured by a dynamic BET method, (Winer, 1968) using a mixture of nitrogen and helium gases after degassing at  $70^\circ\text{C}$  overnight under a continuous flow of helium.

#### Investigations by electron microscopy

Specimens were prepared by spotting 0.01 per cent (w/w) suspensions onto copper grids coated with thin films of carbon, and allowing them to dry at room temperature. Dilutions of the FA and  $\text{Cu}^{2+}$ –montmorillonite were made with distilled water. The FA– $\text{Cu}^{2+}$ –montmorillonite was suspended in distilled water adjusted with dilute HCl to pH 2.5, in order to prevent desorption of complexed FA from the interlayer spaces. The prepared specimens were stored in a vacuum desiccator over  $\text{P}_2\text{O}_5$  at room temperature. The electron microscope was a Philips EM 300 instrument operated at 80 kV.

## RESULTS AND DISCUSSION

#### The nature of the FA– $\text{Cu}^{2+}$ –montmorillonite interaction

Deviating from the earlier investigation (Schnitzer and Kodama, 1972), we halved the concentrations of the FA solutions and also the weights of the clay in order to minimize interferences in the  $\text{Cu}^{2+}$  measurement by the specific ion electrode. As shown in Table 1, amounts of 'free'  $\text{Cu}^{2+}$  ( $\text{Cu}_f$ ) in the supernatant solutions decreased significantly as the pH increased, although the total Cu-content ( $\text{Cu}_t$ ) increased. Above pH 3.5, close to 100 per cent of the  $\text{Cu}^{2+}$  was complexed, attesting to the relatively high complexing

Table 1. Amounts of  $\text{Cu}^{2+}$  solubilized by shaking for 18 hr 20 mg of  $\text{Cu}^{2+}$ –montmorillonite with 25 ml (= 50.0 mg) of FA solution

pH	$\mu\text{g Cu}^{2+}$ -solubilized		$\text{Cu}_f/\text{Cu}_t \times 100$ (= %)
	$\text{Cu}_t$	$\text{Cu}_f$	
2.5	125.8	7.8	6.8
3.5	193.0	4.8	2.5
4.5	233.8	1.3	0.6
5.5	249.8	0.2	0.07
6.5	257.8	0.001	0.0009

power of FA for  $\text{Cu}^{2+}$  (Schnitzer and Hansen, 1970). Increases in  $\text{Cu}^{2+}$  complexing as the pH rises were most probably due to increases in ionization of oxygen-containing functional groups in the FA. The data in Table 1 indicate that the mechanism by which FA removed  $\text{Cu}^{2+}$  from the clay was almost exclusively complexation, most likely chelation. Since 20 mg of clay contained 540.0  $\mu\text{g}$  of  $\text{Cu}^{2+}$ , the proportions of  $\text{Cu}_t^{2+}$  removed by the FA ranged from 23.3 (at pH 2.5) to 48.7 per cent (at pH 6.5) of those in the initial clay samples. Thus, at pH 6.5, one treatment with dilute aqueous FA solution (containing 50 mg of FA) sufficed to remove one half of the  $\text{Cu}_t^{2+}$  in and on 20 mg of  $\text{Cu}^{2+}$ -saturated montmorillonite. This result demonstrates the disruptive action that FA solutions can exert on naturally occurring minerals, especially at pH above 3.5.

#### Surface area measurements

The data in Table 2 show that the external surface area of the FA–clay complex was considerably greater than those of the untreated FA and the  $\text{Cu}^{2+}$ –montmorillonite separately. While the FA–clay complex exhibited a greater  $d_{001}$  spacing (15.1 Å) than the Cu–clay (10.0 Å), it is unlikely that the increased spacing contributed significantly to the substantial increase in external surface shown by the FA–clay complex. Carbon analysis of the latter indicated that it consisted of 30% FA and 70% clay. Assuming that about 1/2 of the total FA was adsorbed in interlayer spaces and the remaining 1/2 on external clay surfaces (Kodama and Schnitzer, 1969), and that no interaction occurred between the two components, then the FA would be expected to contribute  $0.15 \times 2.5 = 0.4 \text{ m}^2 \text{ g}^{-1}$  and

Table 2. Surface area measurements

Material	Surface area ( $\text{m}^2 \text{ g}^{-1}$ )
FA	2.5
$\text{Cu}^{2+}$ –montmorillonite	8.0
FA– $\text{Cu}^{2+}$ –montmorillonite complex prepared at pH 2.5	16.1

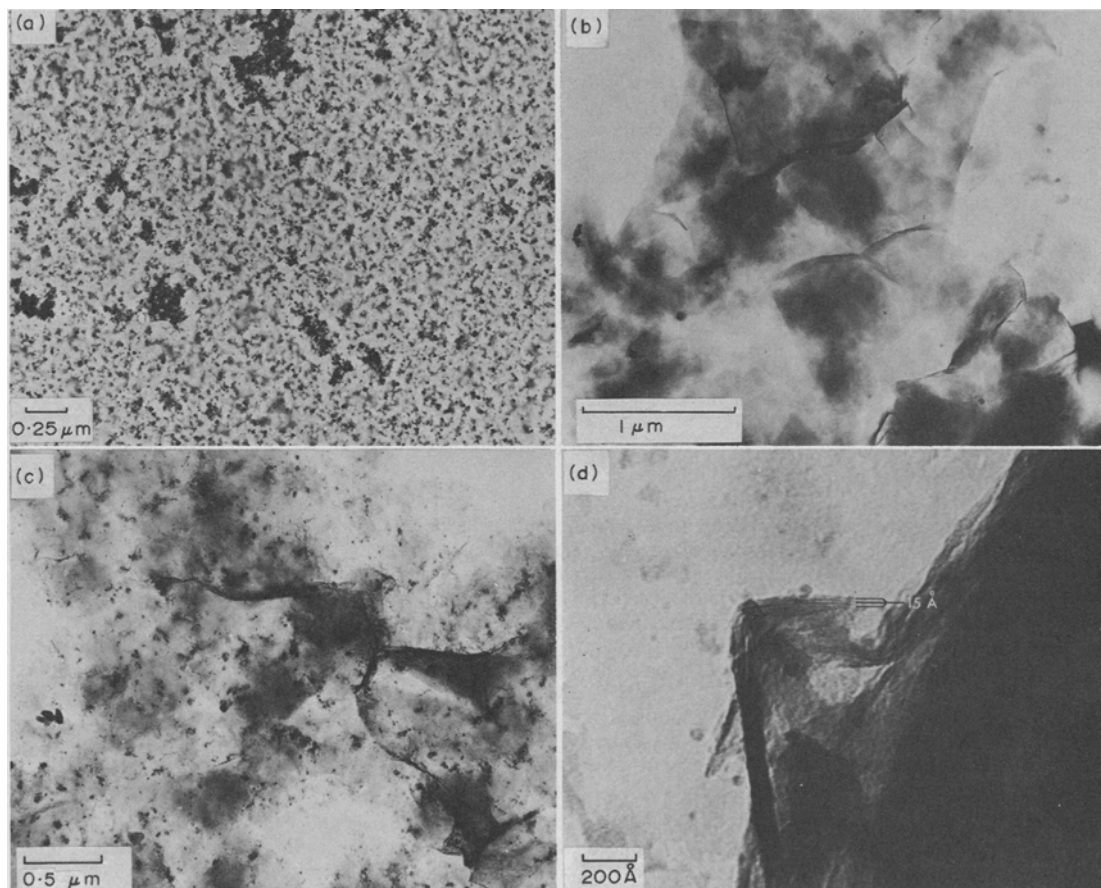


Fig. 1. Electron micrographs of: (a) FA; (b) Cu<sup>2+</sup>-montmorillonite; (c) FA-Cu<sup>2+</sup>-montmorillonite complex prepared at pH 2.5; (d) enlargement taken from edges of FA-clay complex shown in (c).

the clay  $0.85 \times 8.0 = 6.8 \text{ m}^2 \text{ g}^{-1}$ , for a total surface area of  $7.2 \text{ m}^2 \text{ g}^{-1}$ . Since experimentally the surface area of the FA-clay complex was found to be more than twice this value (see Table 2), it is likely that the adsorption of FA on the external clay surfaces was associated with changes in the conformation of the FA which resulted in an expansion of the FA surface, a phenomenon that we are unable to explain at this time.

#### Electron microscopic investigations

As illustrated in Fig. 1(a), the electron micrograph of the FA shows two types of particles: relatively uniform discs and a transparent, shapeless material. Figure 1(b), which is the electron micrograph of Cu<sup>2+</sup>-montmorillonite, exhibits the presence of thin, flaky, tissue paper-like material, typical of montmorillonite. The electron micrograph of the FA-Cu<sup>2+</sup>-montmorillonite complex (Fig. 1c) shows preservation of the major montmorillonite features. In general, outlines in Fig. 1(c) show more contrast than those in Fig. 1(b), due, most

likely, to interlamellar adsorption of FA. Figure 1(c) also shows adsorption of FA on external clay surfaces. Figure 1(d) is an enlarged electron micrograph which is a lattice image taken from the edges of a FA-Cu<sup>2+</sup>-montmorillonite complex. The observed periodicity of the lattice image ranges from  $\sim 13$  to  $\sim 18 \text{ \AA}$ , which is well within the range of the  $15 \text{ \AA}$   $d_{001}$  spacing observed by X-ray analysis (Schnitzer and Kodama, 1972).

Thus, the information provided by electron microscopy is in harmony with data obtained by chemical, spectrophotometric, X-ray and thermal methods, all of which show that FA is adsorbed in interlayer spaces as well as on external surfaces of Cu<sup>2+</sup>-montmorillonite, and that the extent of interlamellar adsorption decreases rapidly above pH 3.5.

*Acknowledgements*—We thank G. C. Scott for technical assistance and A. A. Winer, Mineral Processing Division, Mines Branch, Canada Department of Energy, Mines and Resources at Ottawa for surface area measurements.

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**Résumé**—Le mécanisme principal par lequel l'acide fulvique extrait  $\text{Cu}^{2+}$  de la montmorillonite  $\text{Cu}^{2+}$  est la complexation ou plus probablement la chélation. Ceci a été confirmé par l'utilisation d'une électrode spécifique pour l'ion cuivrique; il a été montré que, alors que la concentration totale en  $\text{Cu}^{2+}$  dans les surnageants augmente avec le pH, environ 7 pour cent du  $\text{Cu}^{2+}$  total solubilisé par l'acide fulvique se présente sous forme 'libre' ou 'non complexée' à pH 2,5, 0,6 pour cent seulement à pH 4,5 et 0,0009 pour cent à pH 6,5. La mesure de la surface externe par une méthode BET dynamique donne les surfaces suivantes:  $2,5 \text{ m}^2 \text{ g}^{-1}$  pour l'acide fulvique,  $8,0 \text{ m}^2 \text{ g}^{-1}$  pour la montmorillonite  $\text{Cu}^{2+}$ , mais  $16,1 \text{ m}^2 \text{ g}^{-1}$  pour le complexe montmorillonite  $\text{Cu}^{2+}$ -FA. Les micrographies électroniques du complexe argile-FA confirment que l'acide fulvique est adsorbé dans les espaces interfeuilletés et sur les surfaces externes de la montmorillonite  $\text{Cu}^{2+}$ .

**Kurzreferat**—Als wichtigster Mechanismus, durch den Fulvosäuren  $\text{Cu}^{2+}$  aus  $\text{Cu}^{2+}$ -Montmorillonit verdrängten, erwies sich Komplexbildung, sehr wahrscheinlich in Form der Chelatisierung. Dies wurde durch Verwendung einer spezifischen Kupferionenelektrode bestätigt, die zeigte, daß, während die Gesamt- $\text{Cu}^{2+}$ -Konzentration in der überstehenden Lösung mit Zunahme des pH-Wertes anstieg, etwa 7% des durch Fulvosäure in Lösung gebrachten Gesamt- $\text{Cu}^{2+}$  bei pH 2,5 in 'freier' oder 'nichtkomplexierter' Form auftrat, nur 0,6% in ähnlicher Verteilung bei pH 4,5 und 0,0009% bei pH 6,5 vorlagen. Messungen der äußeren Oberflächen durch eine dynamische BET-Methode ergaben die folgenden Oberflächen:  $2,5 \text{ m}^2 \text{ g}^{-1}$  für die Fulvosäure,  $8,0 \text{ m}^2 \text{ g}^{-1}$  für den  $\text{Cu}^{2+}$ -Montmorillonit, aber  $16,1 \text{ m}^2 \text{ g}^{-1}$  für den Fulvosäure- $\text{Cu}^{2+}$ -Montmorillonitkomplex. Elektronenmikroskopische Aufnahmen des Fulvosäure-Tonkomplexes bestätigten, daß die Fulvosäure in den Zwischenschichten und an den äußeren Oberflächen des  $\text{Cu}^{2+}$ -Montmorillonits adsorbiert wird.

**Резюме** — Главный механизм посредством которого фульвиновая кислота удаляет  $\text{Cu}^{2+}$  из  $\text{Cu}^{2+}$ -монтмориллонита является комплексобразование, повидимому, образование клешневидной формы. Это подтвердили использованием специфического электрода из железа содержащего двухвалентную медь, который показал, что в то время как общая концентрация  $\text{Cu}^{2+}$  во всплывающих растворах поднималась при повышении pH, приблизительно 7% всего  $\text{Cu}^{2+}$ , растворенного фульвиновой кислотой было при pH 2,5 в «свободной» или «некомплексобразовавшейся» форме, при pH 4,5 только 6% было распределено таким же образом, а при pH 6,5 — 0,0009%. Измерения наружных площадей поверхностей динамическим методом BET показало:  $2,5 \text{ м}^2/\text{г}$  для фульвиновой кислоты;  $8,0 \text{ м}^2/\text{г}$  для  $\text{Cu}^{2+}$ -монтмориллонита, но  $16,1 \text{ м}^2/\text{г}$  для комплекса FA- $\text{Cu}^{2+}$ -монтмориллонита. Электронномикроскопические снимки комплексов FA-глины подтвердили, что фульвиновая кислота была адсорбирована в промежуточных пространствах на наружных поверхностях  $\text{Cu}^{2+}$ -монтмориллонита.