

## EFFECTS OF HUMIC ACID ON THE CRYSTALLIZATION OF ALUMINUM HYDROXIDES<sup>1</sup>

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**Abstract**—The effects of humic acid (HA) on the crystallization of precipitation products of Al under mildly acidic to alkaline conditions were investigated. The extent of Al precipitation substantially decreased with increasing HA concentration (0 to 75  $\mu\text{g}/\text{ml}$ ) in the pH range 6 to 10 during the 80-day aging period. The X-ray powder diffraction (XRD) data show that, at pH 6.0, the amount of pseudoboehmite formed in the systems decreased with the increasing concentration of HA present. The proportion of Al hydroxide polymorphs (gibbsite and bayerite) was greatly influenced by the amounts of HA present in the systems. At pH 6.0 and HA concentration of 37.5  $\mu\text{g}/\text{ml}$ , all the precipitation products of Al were noncrystalline. At pH 8.0 and a HA concentration of 12.5  $\mu\text{g}/\text{ml}$ , the formation of gibbsite and bayerite was completely inhibited and only pseudoboehmite was evident in the XRD patterns. Further increase in HA concentration (25–75  $\mu\text{g}/\text{ml}$  HA) at pH 8.0 resulted in no precipitation of Al, and only a broad peak at  $\sim 3.3$  Å, characteristic of HA, was observed. The XRD patterns of the precipitates of Al formed in the absence of HA at pH 10.0 showed the characteristic peaks of bayerite. At pH 10.0, the precipitation products of Al formed even at the HA concentration of 2.5  $\mu\text{g}/\text{ml}$  yielded no XRD peaks. Infrared absorption spectra and transmission electron micrographs of the precipitation products of Al formed in the systems studied substantiate the findings obtained by XRD. The data obtained in this study indicate that HA affects the formation of Al hydroxide polymorphs, pseudoboehmites and short-range ordered mineral colloids.

**Key Words**—Aluminum hydroxide, Bayerite, Boehmite, Crystallization, Gibbsite, Humic acid, X-ray powder diffraction.

### INTRODUCTION

Aluminum in soil solutions and natural waters undergoes hydrolysis and may precipitate as various crystalline Al hydroxides (Hsu, 1977). The crystallization of Al hydroxides is, however, influenced by low molecular weight organic acids (Kwong and Huang, 1975, 1977, 1979a, 1979b, 1981; Huang and Violante, 1986). The occupation of the coordination sites of Al by organic ligands apparently disrupts the hydroxyl bridging mechanism, which is indispensable for the polymerization of Al ions. The effect of the organic ligands on the formation of Al hydroxides, oxyhydroxides, and noncrystalline products has been found to vary with the affinity of organic ligands toward Al and the ligand/Al molar ratios (Kwong and Huang, 1981; Violante and Huang, 1985).

Although low molecular weight organic acids are constantly introduced to soil through vegetation, the major components of organic materials are humic acid (HA), fulvic acid (FA), and humin. The inhibitory effect on Al crystallization is not only limited to low molecular weight organic acids; Kwong and Huang

(1981) found that tannic acid promotes the formation of noncrystalline to poorly crystalline precipitation products of Al. Furthermore, Kodama and Schnitzer (1980) reported that the addition of increasing amounts of FA first delays and then inhibits the crystallization of Al hydroxides.

HA, which differs from FA in molecular complexity, functional group concentration, and total acidity, is the major component of the humic matter in soils and sediments (Stevenson, 1985; Schnitzer, 1986). Therefore, the effect of HA on the nature of the crystallization products of Al is important in a wide range of soils and sediments. The objective of the present study was to examine the effect of HA on the crystallization of Al hydroxides under slightly acidic to alkaline conditions.

### MATERIALS AND METHODS

#### *Humic acid*

HA was extracted from an Udic Haploboroll (Orthic Black Chernozemic soil) from Saskatchewan according to the procedure recommended by the International Humic Substances Society (Aiken, 1985; Hayes, 1985; Leenheer, 1985; Swift, 1985). The HA contained 1.29% ash, 54.1% C, 32.7% O, 4.6% H, 4.23% N, and 0.75% S. The  $E_4/E_6$  extinction coefficient ratio was 4.2. The freeze-dried HA was added to deionized distilled water to prepare a Na-humate solution (400  $\mu\text{g}/\text{ml}$  HA) by slow additions of 0.1 M NaOH to pH 6.0.

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### Al hydroxide-humic acid system

An aliquot of 450 ml of a  $2 \times 10^{-3}$  M  $\text{AlCl}_3$  solution was titrated dropwise to pH 4.8 with 0.1 M NaOH; the solution was vigorously stirred during the titration. The solution was then mixed with 0 to 150 ml of the Na-humate solution. Each of these solutions was then slowly titrated with 0.1 M NaOH to pHs of 6.0, 8.0, or 10.0. After the titration, the final volume of each solution was made up to 800 ml with deionized distilled water; the concentrations of HA ranged from 0 to 75  $\mu\text{g}/\text{ml}$ . The solutions were aged for 80 days at room temperature ( $\sim 25^\circ\text{C}$ ) with occasional shaking and pH adjustments to maintain the initial values.

After aging, precipitates were separated by filtration through Millipore filters (0.01- $\mu\text{m}$  pore diameter) and then freeze-dried. Precipitates were mounted on glass slides and examined by XRD on a Philips diffractometer using Ni-filtered  $\text{CuK}\alpha$  radiation. Infrared spectra of the precipitates were recorded from KBr disks containing freeze-dried samples on a Perkin-Elmer 983 instrument. For transmission electron microscope (TEM) examination, a drop of dilute suspensions was deposited on a grid covered with a carbon-coated Formvar film. TEMs were taken at 60 kV with a Philips EM 400 instrument.

Al in solution was determined by atomic absorption (flame) on a PYE Unicam SP atomic absorption spectrophotometer. Organic carbon in the precipitates was determined by an improved method of dry combustion (Tiessen *et al.*, 1981).

## RESULTS

### Precipitation of HA and Al from solution

Table 1 shows the removal of HA and Al from solution as a result of precipitate formation and aging for 80 days. At pH 6.0 all HA was removed from solution in the entire concentration range of HA studied. Likewise, all Al precipitated from solution at all HA levels. In the systems prepared at pH 8.0 and the HA concentration range of 0–12.5  $\mu\text{g}/\text{ml}$ , all HA and Al precipitated from solution. At higher HA concentrations, about 11–15% of the added HA remained in solution, and the precipitation of Al was not observed. At pH 10.0, the precipitation of HA gradually decreased as the HA concentration exceeded 12.5  $\mu\text{g}/\text{ml}$ . At the HA concentration of 75  $\mu\text{g}/\text{ml}$ , all HA remained in solution. At pH 10.0, the fraction of Al precipitated decreased drastically, as the HA concentration increased from 5.0 to 12.5  $\mu\text{g}/\text{ml}$ . At pHs of 8.0 and 10.0 and a HA concentration  $> 12.5$   $\mu\text{g}/\text{ml}$ , the precipitation of hydrolytic products of Al was prevented.

### X-ray powder diffraction data

In the absence of HA, the precipitate consisted of pseudoboehmite (6.3 and 3.10  $\text{\AA}$ ) and gibbsite (4.83, 4.36, 3.30, 2.45, 2.39, and 2.36  $\text{\AA}$ ). At HA concentra-

Table 1. Precipitation of humic acid (HA) and aluminum as influenced by pH and humic acid concentration after aging for 80 days at room temperature.

pH	Initial HA concentration ( $\mu\text{g}/\text{ml}$ )						
	0	2.5	5.0	12.5	25.0	37.5	75.0
% Fraction of HA precipitated							
6.0	—	100	100	100	100	100	100
8.0	—	100	100	100	85	89	85
10.0	—	100	100	52	40	14	0
% Fraction of Al precipitated <sup>1</sup>							
6.0	100	100	100	100	100	100	100
8.0	100	100	100	100	tr	0	0
10.0	100	100	100	12	0	0	0

<sup>1</sup> The initial concentration of Al was 30.4  $\mu\text{g}/\text{ml}$  Al.

tion of 2.5  $\mu\text{g}/\text{ml}$  and pH 6.0, the intensity of these gibbsite reflections decreased, whereas the pseudoboehmite reflection essentially was unchanged (Figure 1b). At a HA concentration of 5.0  $\mu\text{g}/\text{ml}$ , the major pseudoboehmite reflection was weaker and broader and shifted to a higher d-value (6.5  $\text{\AA}$ ) (Figure 1c), indicating the formation of smaller crystallites of the synthetic Al oxyhydroxide (Tettenhorst and Hofmann, 1980; Violante and Huang, 1984). The reflections associated with the crystalline Al hydroxides, on the other hand, were stronger and sharper. A decrease in the 4.83/4.36  $\text{\AA}$  intensity ratio as well as a very weak shoulder at 4.70  $\text{\AA}$  suggested the incipient formation of bayerite. At the HA concentration of 12.5  $\mu\text{g}/\text{ml}$ , the pseudoboehmite was not evident and the diagnostic peaks (4.70 and 2.21  $\text{\AA}$ ) for bayerite were very pronounced (Figure 1d). At the HA concentration of 25.0  $\mu\text{g}/\text{ml}$ , all reflections indicative of crystalline Al hydroxides had decreased in size; but among these, those of bayerite were the most prominent (Figure 1e). If the HA concentration was further increased to 37.5  $\mu\text{g}/\text{ml}$ , all reflections indicative of crystalline Al hydroxides and oxyhydroxides disappeared, leaving only broad bands characteristic of HA (Figure 1f).

XRD tracings obtained at pH 8.0 in the absence of HA (Figure 2a) showed the presence of pseudoboehmite (6.5 and 3.16  $\text{\AA}$ ), gibbsite (4.83, 4.36, 2.45, and 2.37  $\text{\AA}$ ), and bayerite (4.70 and 2.21  $\text{\AA}$ ). The 020 spacing (6.5  $\text{\AA}$ ) (Figure 2a) was larger than that for the precipitate at pH 6.0 (Figure 1a), suggesting a smaller crystallite size of pseudoboehmite (Tettenhorst and Hofmann, 1980; Violante and Huang, 1984). At as low a concentration of HA as 5.0  $\mu\text{g}/\text{ml}$ , the intensity of the reflections from crystalline Al hydroxide polymorphs decreased; however, the reflections of pseudoboehmite were still pronounced (Figure 2b). At a HA concentration of 12.5  $\mu\text{g}/\text{ml}$ , only the reflections of pseudoboehmite were present (Figure 2c). At a HA concentration of 37.5  $\mu\text{g}/\text{ml}$ , only a broad reflection at  $\sim 3.3$   $\text{\AA}$ , characteristic of humic acid, was evident (Fig-

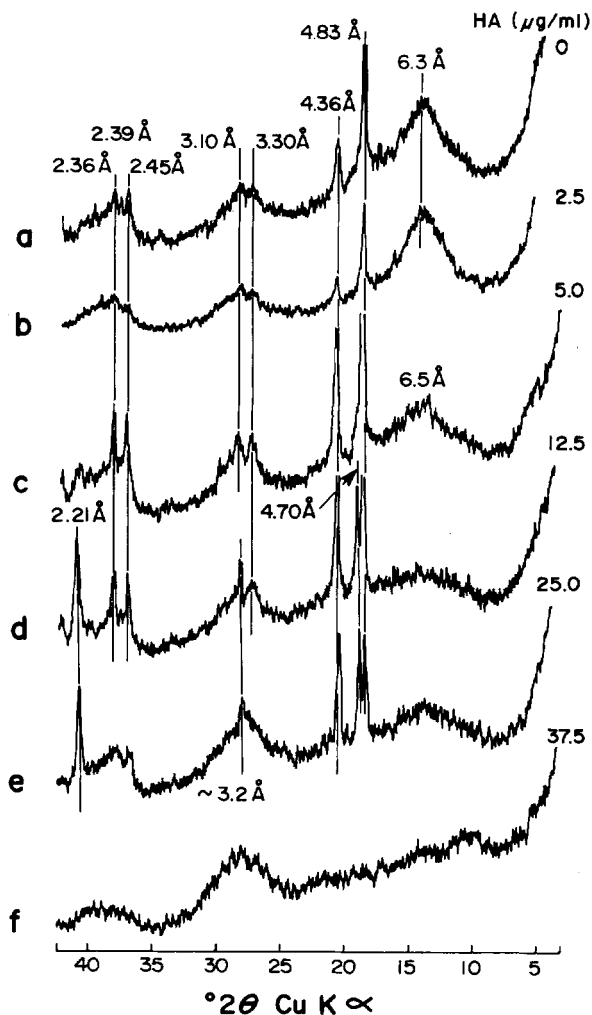


Figure 1. X-ray powder diffractograms of precipitation products of Al formed at pH 6.0 and different concentrations of humic acid after aging for 80 days.

ure 2d), indicating that at this HA concentration Al phases did not precipitate (Table 1).

The XRD patterns of the precipitates formed at pH 10 in the absence of HA (Figure 2e) showed that bayerite (4.70, 4.34, 3.19, and 2.21 Å) was the dominant crystalline precipitation product of Al. At the HA concentration of 2.5 µg/ml, crystalline compounds were not evident (Figure 2f).

#### Infrared absorption data

At pH 6.0 and in the absence of HA, only weak absorption bands at 3620, 3520, and 3445  $\text{cm}^{-1}$ , diagnostic for gibbsite, and at 3120  $\text{cm}^{-1}$ , indicative of pseudoboehmite (Violante and Huang, 1985; Kodama and Schnitzer, 1980), were observed (Figure 3a). At greater concentrations of HA, an absorption band at 3457–3459  $\text{cm}^{-1}$ , characteristic of bayerite (Violante and Huang, 1985), became pronounced (Figures 3d

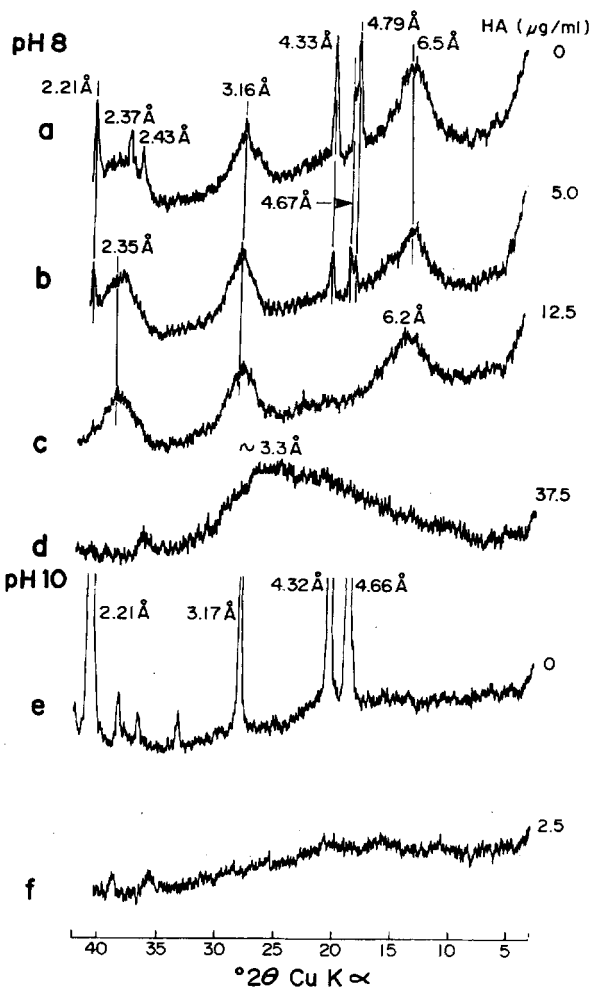


Figure 2. X-ray powder diffractograms of precipitation products of Al formed at pHs of 8.0 and 10.0 and at different concentrations of humic acid after aging for 80 days.

and 3e). At the greatest concentration of HA, no absorption bands indicative of crystalline Al hydroxides were present (Figure 3f). The IR spectrum of the precipitate formed at pH 8.0 in the absence of HA showed the presence of bayerite (3652 and 3550  $\text{cm}^{-1}$ ), gibbsite (3620, 3520, and 3440  $\text{cm}^{-1}$ ) and pseudoboehmite (3380 and 3100  $\text{cm}^{-1}$ ). The IR pattern of the precipitate formed in the presence of 5.0 µg/ml HA showed a strong decrease in the absorption bands of gibbsite and only a slight decrease in the intensity of the absorption bands of bayerite; the absorption at 3100  $\text{cm}^{-1}$ , diagnostic of pseudoboehmite, increased slightly in intensity (Figure 3h). At the HA concentration of 12.5 µg/ml, only the absorption at 3100  $\text{cm}^{-1}$  persisted (Figure 3i). These results (Figures 3g and 3h) support the conclusion derived from the XRD data (Figures 2a and 2b), that the addition of HA to the OH/Al system at pH 8.0 suppressed the crystallization of gibbsite more than that of bayerite. Strong absorption bands at 3420,

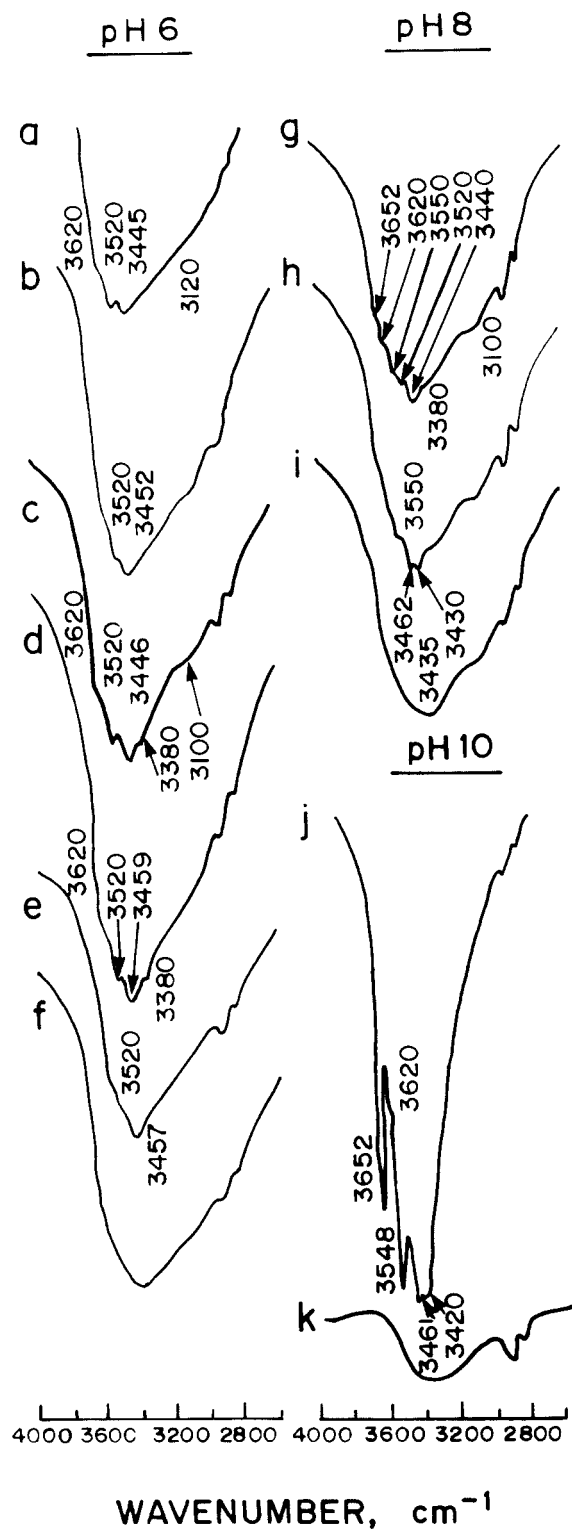


Figure 3. Infrared spectra of precipitation products of Al formed at pHs of 6.0, 8.0 and 10.0 and at different concentrations of humic acid (HA). Systems at pH 6.0: a = 0  $\mu\text{g/ml}$  HA; b = 2.5  $\mu\text{g/ml}$  HA; c = 5.0  $\mu\text{g/ml}$  HA; d = 12.5  $\mu\text{g/ml}$

3461, 3548, and 3652  $\text{cm}^{-1}$  for the precipitate formed at pH 10.0 in the absence of HA (Figure 3j) confirmed the presence of bayerite (Figure 2e). At a HA concentration of 12.5  $\mu\text{g/ml}$ , the weak and broad IR spectrum (Figure 3k) showed that the precipitates were poorly crystalline.

#### Electron microscopic evidence

In the precipitate formed at pH 6.0, the characteristic hexagonal shape of gibbsite was present in the absence of HA (Figure 4a), and only a few hexagonal shaped particles were observed in the presence of 5  $\mu\text{g/ml}$  HA (Figure 4b). Some had the shape of pyramids. Fibrous particles of pseudoboehmite were also present. Other particles were present in shapeless aggregates. At the HA concentration of 12.5  $\mu\text{g/ml}$ , the particles apparently had grown in size through aggregation, and fibrous particles of pseudoboehmite were relatively rare (Figure 4c). At a HA concentration of 37.5  $\mu\text{g/ml}$ , the particles were anhedral and resembled those noted for the noncrystalline products (Figure 4d).

#### DISCUSSION

Organic compounds of higher molecular weight, such as tannic acid (Kwong and Huang, 1981) and fulvic acid (Kodama and Schnitzer, 1980), perturb the crystallization of Al hydroxide polymorphs. The data obtained in the present study show that the addition of HA to the system at pH 6.0 suppressed pseudoboehmite formation. If the HA concentration was increased, the formation of gibbsite was also retarded. Concomitantly, the formation of bayerite was favored. In the presence of HA in the system at pH 4.8, Al was partially complexed with HA. The complexed Al was apparently unavailable for pseudoboehmite formation if the pH was raised to 6.0. Therefore, pseudoboehmite formation was retarded or even inhibited by HA. At low concentrations of HA, the rate of the release of Al from Al-HA complexes appeared to be adequate to form Al hydroxide polymorphs, explaining the increase in the precipitation of crystalline Al hydroxide polymorphs at low concentrations of HA. The formation of bayerite is unusual at pH 6.0; however, its formation was promoted at low concentrations of HA at pH 6.0. Bayerite formation is favored by an increase in alkalinity or an acceleration in precipitation rate (Barnhisel and Rich, 1965; Hsu, 1966). Possibly bayerite formed at pH 6.0 due to an increase in the crystallization rate of Al hydroxide induced by the HA. The influence of organic ligands on retardation or acceleration of the crystallization process of precipitation products of Al is not always related to their chelating power for Al (Violante

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HA; e = 25.0  $\mu\text{g/ml}$  HA; f = 37.5  $\mu\text{g/ml}$  HA. Systems at pH 8.0: g = 0  $\mu\text{g/ml}$  HA; h = 5.0  $\mu\text{g/ml}$  HA; i = 12.5  $\mu\text{g/ml}$  HA. Systems at pH 10.0: j = 0  $\mu\text{g/ml}$  HA; k = 12.5  $\mu\text{g/ml}$  HA.

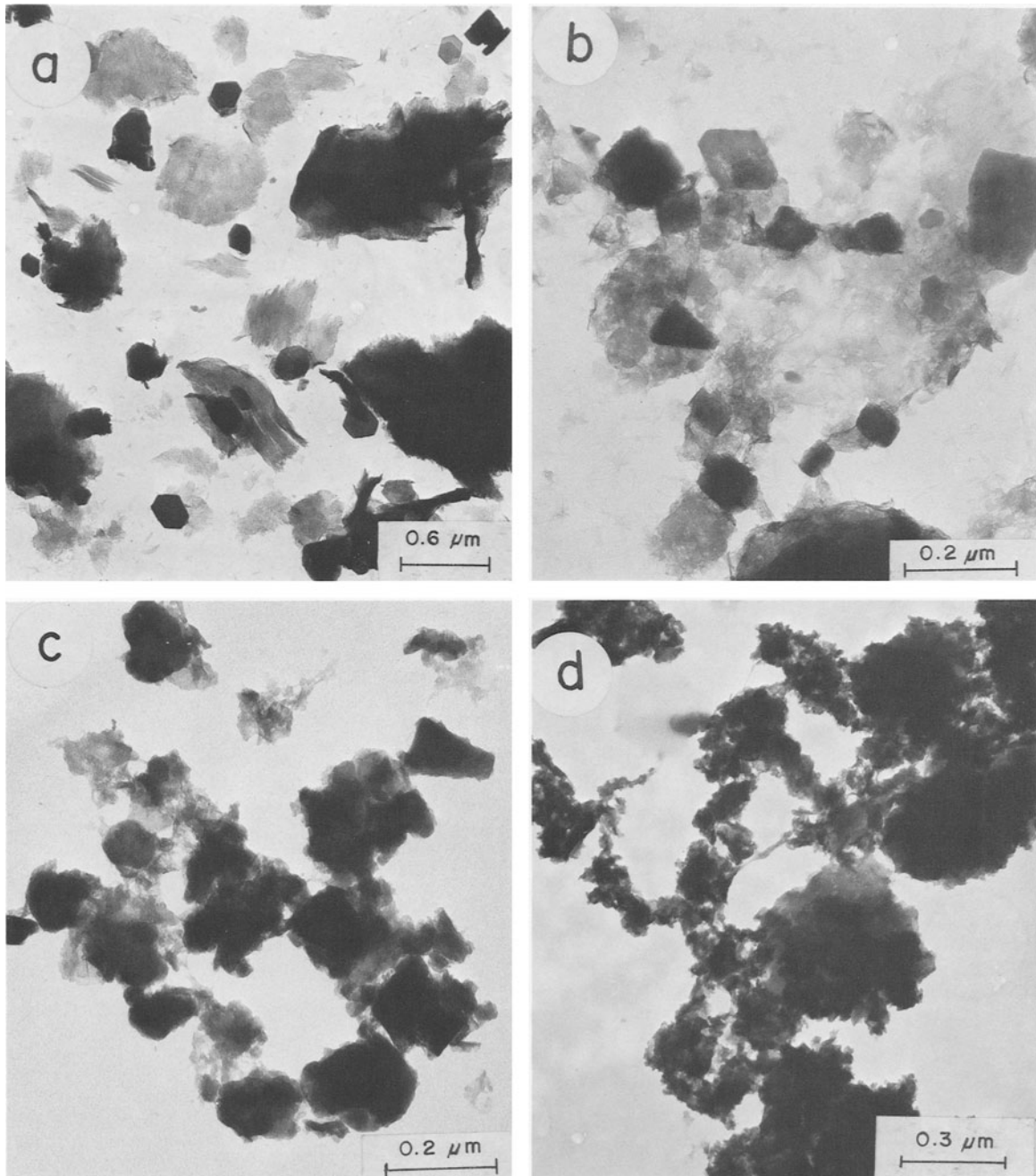


Figure 4. Transmission electron micrographs of precipitation products of Al formed at pH 6.0 and at different concentrations of humic acid (HA). a = 0  $\mu\text{g/ml}$  HA; b = 5.0  $\mu\text{g/ml}$  HA; c = 12.5  $\mu\text{g/ml}$  HA; d = 37.5  $\mu\text{g/ml}$  HA.

and Violante, 1980; Kwong and Huang, 1981; Violante and Huang, 1985). For example, although the Al-tartrate complex is much less stable than the Al-citrate complex, it is more effective in inhibiting the crystallization of Al hydroxide polymorphs (Violante and Huang, 1985). The Al-HA complexes may have been unstable enough to release the Al at a rate appropriate for bayerite precipitation, as observed in the present

study; however, at higher HA concentrations, structural distortions in the precipitates, similar to those produced by tannic acid (Kwong and Huang, 1981) and fulvic acid (Kodama and Schnitzer, 1980), were observed. The extent of the interference of HA on the precipitation of Al hydroxide polymorphs increased with the increasing pH. At pH 8.0, the formation of crystalline Al hydroxide polymorphs was perturbed

even at low HA concentrations. At pH 10.0, the formation of all crystalline Al hydroxide polymorphs was completely prevented, even at very low concentrations of HA.

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