

EFFECT OF TANNATE, pH, SAMPLE PREPARATION, AGEING AND TEMPERATURE ON THE FORMATION AND NATURE OF Al OXYHYDROXIDES

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Abstract—The aim of this work was to study the influence of tannate concentration (tannic acid/Al molar ratio $[R]$ of 0.01–0.1), pH (5.0 and 8.0), order of aluminum, hydroxyl, and tannate addition, and prolonged ageing at different temperatures (10 months at 50°C and 5 y at room temperature and further ageing for 3–15 days at 140°C) on the nature and crystallinity of synthetic boehmite. Tannate facilitated the formation of boehmite relative to Al(OH)₃ polymorphs when coprecipitated with Al and also when added to Al(OH)_x phases already formed at pH 4.5 or 8.0. However, the organic ligand was more effective in preventing or perturbing the growth of the crystals of boehmite when coprecipitated with Al than when added to soluble Al(OH)_x species or preformed Al precipitates. Boehmite aged at temperatures $\leq 50^\circ\text{C}$ typically showed a fibrous morphology. Crystals with a rhombic habit were observed in some treatments after ageing at 140°C. Significant amounts (15–30% C) of tannate were present in the precipitates after prolonged ageing. This tannate was only partly ($<50\%$) oxidized by repeated treatments with H₂O₂. With further ageing at 140°C, the crystallite size of selected samples increased only slightly, suggesting that much of the remaining tannate was present in the internal structure of these samples and not simply adsorbed to their surfaces. Atomic force microscopy observation showed the presence of globular nanoparticles (probably Al tannate precipitates) attached to the elongated crystals of boehmite. Taken together, our results demonstrate that the crystalline phases that formed under mild conditions in the presence of low concentrations ($R = 0.01$) of foreign ligands have the same structure as boehmite, but with a poorly ordered and defective ion arrangement. At higher ligand concentrations ($R \geq 0.05$), mixtures of materials are formed having varying degrees of order, particle size and morphology.

Key Words—Atomic Force Microscopy, Boehmite, Crystallite Size, Poorly Ordered Material, Tannic Acid.

INTRODUCTION

Boehmite obtained at low temperatures (20–100°C) and pressures shows broad X-ray diffraction (XRD) peaks (the strongest found at 0.640–0.680 nm), contains more water and has a greater specific surface area than boehmite synthesized at high temperatures and pressures (Calvet *et al.*, 1953; Papee *et al.*, 1958; Yoldas, 1973; Violante and Violante, 1980; Violante and Huang, 1984, 1985, 1993; Hsu, 1989). Boehmite formed at low temperatures and pressures in the absence of foreign anions is particularly unstable and converts easily to Al(OH)₃ polymorphs (Souza Santos *et al.*, 1953; Papee *et al.*, 1958; Bye and Robinson, 1964; Aldcroft *et al.*, 1969; Yoldas, 1973). However, many studies have ascertained that at certain pH (from 5.0 to 11.0) and critical ranges of ligand/Al molar ratio (R), inorganic and low-molecular-mass organic ligands (Violante and Jackson, 1981; Violante and Huang, 1984; 1985; Huang

and Violante, 1986; Hsu, 1989; Violante *et al.*, 1993) as well as fulvic (Kodama and Schnitzer, 1980), tannic (Kwong *et al.* 1981; Violante and Huang, 1984) and humic acid (Singer and Huang, 1980) facilitated the formation of boehmite which remained stable for years (up to 10 y according to Violante *et al.*, 1993). In an extensive investigation of the effect of foreign ligands on Al solid-phase formation, Violante and Huang (1985) found that various anions promote and stabilize the formation of boehmite over well crystallized polymorphs according to the following sequence:

chloride < sulfate < succinate = phthalate < glutamate < silicate < aspartate < phosphate < salicylate = malate < tannate < citrate < tartrate. Humic and fulvic acids showed behavior similar to that of tannate.

Polydentate and large ligands (tannate, fulvate, humate) are usually more influential in facilitating the formation of boehmite than ligands with few functional groups and small size (Violante and Huang, 1985; Singer and Huang, 1990). Aluminum-organic interactions are of paramount importance in natural environments (Vance *et al.*, 1996).

The nature of boehmite formed under mild conditions is not well understood. Papee *et al.* (1958) found that the

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intensities of the XRD reflections of unaged boehmite did not decrease at high angles and that the first reflection corresponding to 020 reflections of boehmite was absent or barely visible from some patterns although the other reflections remained unchanged. Those authors suggested that this Al oxyhydroxide, referred to as “pseudoboehmite” by Calvet *et al.* (1953), is a material with the same structure as well crystallized boehmite, but with a poorly ordered and highly defective arrangement of the elementary units. Violante and Huang (1984, 1985, 1993) also showed that Al oxyhydroxides synthesized under different ionic conditions (pH, nature and concentration of organic and inorganic ligands) were poorly crystalline boehmite. Violante *et al.* (2002) studied, by electron diffraction analysis and transmission electron microscopy (TEM), some Al oxyhydroxides synthesized at pH values ranging from 5.0 to 8.0 in the presence of different concentrations ($R = 0.01$ – 0.03) of selected organic ligands (aspartic, tartaric, citric and tannic acid) and aged for 8 months at room temperature. All the samples showed d spacings characteristic of boehmite, but the relative intensity of the electron diffraction rings was different from one sample to another and some samples showed a complete lack of some diffraction rings. Conversely, Tettenhorst and Hofmann (1980) demonstrated that boehmites synthesized and aged for few days (0–8 days) at temperatures ranging from 20 to 300°C exhibited a continuous gradation in crystallite size. These authors claimed that these Al oxyhydroxides were only finely crystalline boehmite, so the distinction between “pseudoboehmite” and boehmite was arbitrary.

Boehmites have been reported to form under a wide range of pH by coprecipitating Al and organic and inorganic ligands within certain ranges of optimal concentrations and pH (Violante and Huang, 1985; Violante *et al.*, 1993), but the effect of the sequence of addition of components (Al, organic or inorganic ligands and hydroxyls) on the formation, nature and stability of boehmite has not been studied until now.

The aim of this work was to study the effect of: (1) the initial pH (5.0 or 8.0); and (2) the initial tannate/Al molar ratio (0.01, 0.05 and 0.1) on the preparation of Al precipitation products formed by adding Al, tannic acid and OH in different orders; and (3) prolonged ageing at different temperatures (20–140°C) on the possible formation, nature (crystallinity) and stability of Al oxyhydroxides vs. Al(OH)₃ polymorphs.

MATERIALS AND METHODS

Sample preparation

Solutions of AlCl₃ 5×10^{-2} M (200 mL), in the absence or presence of tannic acid (analytical reagent, M.W. 1701), were potentiometrically titrated to pH 5.0 or 8.0 by slowly adding 0.5 M NaOH at a feed rate of 0.5 mL min⁻¹ using an automatic titrator, Metrom

Herisau E 536, in conjunction with an automatic syringe burette 655 Dosimat. During the titrations, the suspensions were stirred thoroughly. The concentration of tannic acid was chosen to produce initial tannic acid/Al molar ratios of 0.01, 0.05 or 0.1. The sequence of addition of tannic acid and NaOH was changed from sample to sample as outlined in Table 1 and summarized below:

(1) tannic acid ($R = 0.01$) and AlCl₃ were neutralized by NaOH up to pH 5.0 (sample A5) or pH 8.0 (sample A8);

(2) stock solutions containing AlCl₃ were neutralized by NaOH up to pH 5.0 or 8.0; after 20 min, tannic acid was added in order to produce $R = 0.01$ (samples B5 and B8), $R = 0.05$ (samples D5 and D8), or $R = 0.1$ (samples F5 and F8). The final pH of the suspensions was adjusted to 5.0 or 8.0;

(3) stock solutions containing AlCl₃ were neutralized with NaOH up to pH 4.5; after 15 days, tannic acid was added in order to produce $R = 0.01$, 0.05 or 0.1. The final pH of the suspension was adjusted to 5.0 or 8.0. Samples C5 and C8 had $R = 0.01$ and final pH 5.0 and 8.0, respectively; samples E5 and E8 had $R = 0.05$ and pH 5.0 and 8.0, respectively; and, finally, samples G5 and G8 had $R = 0.1$ and pH 5.0 and 8.0, respectively.

For all the samples the final volume was adjusted to 1 L and the concentration of total Al was 10^{-2} M. The suspensions, held in polypropylene containers, were kept for 1 week at 20°C keeping the pH constant, then were aged for 10 months at 50°C and, finally, for 5 y at room temperature without pH control. Selected suspensions were aged for a further 3–15 days at 140°C in hydrothermal-pressure Teflon vessels without further pH control.

After ageing, aliquots of the suspensions were dialyzed (M.W. cutoff = 15,000) in deionized water until Cl⁻-free and analyzed by scanning and transmission electron microscopy (SEM and TEM) and atomic force microscopy (AFM). The samples, freeze dried and lightly ground to pass through a 100-mesh sieve, were stored for 24 h at 20°C in a desiccator containing CaCl₂ and analyzed by XRD.

The organic C was determined by dry combustion, using a Hewlett-Packard Model 185 R-1 Analyzer (Violante and Huang, 1989).

X-ray diffraction

Powder XRD patterns of random specimens were obtained using a Rigaku Geigerflex D/Max III C X-ray diffractometer equipped with Fe-filtered CoK α radiation generated at 40 kV and 30 mA, at a continuous scan speed of $0.5^\circ 2\theta \text{ min}^{-1}$ with $0.05^\circ 2\theta$ average count interval, a $2^\circ 2\theta$ divergence slit, a 0.3 mm receiving slit, and a $2^\circ 2\theta$ scattering slit. Powder mounts were used and the breadth and the position of the reflections of each pattern were measured as described by Colombo *et al.* (1994), from the Cauchy integral breadth obtained

Table 1. Aluminum precipitation products, obtained in the presence of tannic acid aluminum chloride (A) and tannic acid (T), were mixed differently and neutralized by 0.5 M NaOH (OH).

Sample	R^1	Initial pH	Synthesis conditions
A5	0.01	5.0	A and T mixed and neutralized up to pH 5.0
B5	0.01	5.0	A neutralized up to pH 5.0; T added after 20 min; OH added up to pH 5.0
C5	0.01	5.0	A was neutralized up to 4.5; T added after 15 days; OH added up to pH 5.0
D5	0.05	5.0	A neutralized up to pH 5.0; T added after 20 min; OH added up to pH 5.0.
E5	0.05	5.0	A was neutralized up to 4.5; T added after 15 days; OH added up to 5.0
F5	0.1	5.0	A neutralized up to pH 5.0; T added after 20 min; OH added up to pH 5 (see sample B)
G5	0.1	5.0	A was neutralized up to 4.5; T added after 15 days; OH added up to pH 5.0 (see sample C)
A8	0.01	8.0	A and T mixed and neutralized up to pH 8.0
B8	0.01	8.0	A neutralized up to pH 8.0; T added after 20 min; OH added up to pH 8.0
C8	0.01	8.0	A was neutralized up to 4.5; T added after 15 days; OH added up to pH 8.0
D8	0.05	8.0	A neutralized up to pH 8.0; T added after 20 min; OH added up to pH 8.0
E8	0.05	8.0	A was neutralized up to pH 4.5; T added after 15 days; OH added up to pH 8.0
F8	0.1	8.0	A neutralized up to pH 8.0; T added after 20 min; OH added up to 8 (see sample B)
G8	0.1	8.0	A was neutralized up to 4.5; T added after 15 days; OH added up to 8.0 (see sample C)

¹ initial tannic acid/Al molar ratio

using the data-processing procedure of the D/Max-B system software Version 3.0, after subtracting the 100 reflection of quartz that was used as a measure of the instrumental broadening. The full width at half maximum (FWHM) was used in order to estimate mean coherence length (MCL) perpendicular to 020, 120, 140 and 051 of the boehmite (*hkl*) plane according to the Scherrer formula.

Microscope observations

The SEM images were obtained using a Zeiss DSM 940 microscope operating at 20 kV to observe the morphology of the samples. Diluted suspensions were mounted and dried at ~40°C on aluminum stubs with carbon paint, then sputter coated with gold in a vacuum evaporator. Samples for TEM were prepared by evaporating a dilute suspension on carbon-coated Formvar films supported by copper grids and subsequently coated with C to enhance conductivity. Microscope observations were conducted with a Philips CM12 electron microscope operating at 100 kV.

The AFM images were obtained by dispersing a few mg of each sample in water at pH 4.0 using an ultrasonic bath at 100 kW for 1 min. A few drops of the diluted suspensions were deposited on a freshly cleaved muscovite surface and evaporated at room temperature (Ohnesorge and Binning, 1993; Blum, 1994). The AFM images were obtained using a NanoScope III atomic

force microscope with a Multiplode SPM unit (Digital Instruments, 1993). The images were taken in air using a J model, with 125 × 125 μm scan size, and an A model, with 0.4 × 0.4 μm scan size, piezoelectric scanners. The cantilevers used were a wedge S₃N₃ tip with a force constant of 0.12 N/m in contact mode, and Si cantilevers with a force constant of 20–100 N/m in tapping mode. The images were collected at a scan rate of 1.00 Hz and the number of samples was 512. Set point voltage was ~0.77 V; integral and proportional gains were adjusted for a different scan at ~0.2 and 5, respectively. All AFM images were obtained with parallel height and amplitude images in tapping mode. The vertical height data were recorded digitally in order to obtain surface microtopography. The amplitude images are a record of the error in the height image of the sample under constant force mode and were used to analyze crystal morphology (Liu and Huang, 1999). All images were obtained from the analysis of 25 different samples prepared in different operational conditions.

RESULTS AND DISCUSSION

Samples aged for 10 months at 50°C and for 5 y at room temperature

After ageing for 10 months at 50°C and for 5 y at room temperature, the final pH of the suspensions obtained at pH 5.0 decreased to 3.95–4.09 for the

samples formed at $R = 0.01$ (A5–C5), to 4.10–4.17 for the samples formed at $R = 0.05$ (D5–E5) and to 4.22–4.24 for the samples synthesized at $R = 0.10$ (F5–G5) (Table 2). Similarly, the final pH values of the samples formed at pH 8.0 decreased more at $R = 0.01$ (pH ranging from 5.25 to 5.06) than at $R = 0.05$ or 0.1 (pH from 5.49 to 6.36; Table 2), indicating that the greater the amount of tannate coprecipitated with Al the stronger the inhibition of the hydrolytic reactions of Al and the lower the decrease in pH.

Samples aged at pH 5.0

The Al precipitation products formed at initial pH 5.0 appeared to be X-ray amorphous even when tannate was added 20 min after the formation of precipitates (B5, D5 and F5) or 15 days after a partial neutralization of Al (C5, E5 and G5) (Table 2). Violante *et al.* (1993) showed that many Al precipitates formed at pH 5.0–7.0 were non-crystalline after 7–10 y of ageing at room temperature when Al was coprecipitated with tartrate, citrate, malate, phosphate or tannate (similar to the sample A5) at ligand/Al molar ratio of 0.05–0.5.

Transmission electron microscope studies showed that the non-crystalline materials usually appeared to be agglomerates of spherical particles (Figure 1a,b) the size of which ranged from 10 to 40 nm. Under SEM the rounded particles often appeared to be of greater size (up to 300–700 nm; Figure 1c). The drying of the suspensions on the aluminum stubs at $\sim 40^\circ\text{C}$ probably promoted the condensation of many particles into greater spherical aggregates. The non-crystalline materials formed in the presence of larger amounts of tannate ($R = 0.05$ and 0.1) were often heavy precipitates consisting of very small particles strongly aggregated to each other (data not shown). The morphology of these

small particles was not easily detectable, clearly because tannate covered the surfaces of the precipitates (as discussed below) promoting the strong aggregation of the particles.

Samples aged at pH 8.0

The precipitates formed at initial pH 8.0 and at $R = 0.01$ (A8–C8) showed the presence of boehmite (peaks at ~ 0.620 , 0.319, 0.235, 0.187, 0.144 nm), whereas those obtained at $R = 0.05$ –0.1 (D8–G8) were X-ray amorphous (Figure 2). The latter precipitates showed only very broad reflections centered at ~ 0.400 –0.345 and 0.217–0.220 nm. These broad reflections may be attributed to humic-like materials formed on the surfaces of the Al precipitates. Singer and Huang (1990) found that Al precipitates obtained in the presence of humic acid showed a broad reflection at ~ 0.330 nm, characteristic of humic acid.

We have found that selected samples formed at pH 8.0 showed an organic carbon content ranging from 15% (A8 sample) to 30% (G8 sample). The organic molecules present in the precipitates were only partially oxidized (<50%) after repeated treatments by H_2O_2 , indicating that the organic ligands were strongly adsorbed on the external surfaces and/or incorporated into the network of the short-range ordered Al precipitates (Violante and Huang, 1989). After oxidation with H_2O_2 , the crystallinity of selected samples increased only slightly after further ageing at 50°C (not shown). Violante and Huang (1984) found that the amounts of some low-molecular-mass organic ligands such as citrate or tartrate which were present in the initial Al precipitates, only decreased slightly during the ageing processes. These ligands were probably partially released upon ageing, facilitating the transformation of

Table 2. Mineralogy of the aluminum precipitation products obtained in the presence of tannic acid.

Sample	R^1	Final pH	Mineralogy ²	Mineralogy ³
Initial pH 5.0				
A5	0.01	3.95	Non-crystalline	Poorly crystalline boehmite
B5	0.01	4.06	Non-crystalline	Poorly crystalline boehmite
C5	0.01	4.09	Non-crystalline	Poorly crystalline boehmite
D5	0.05	4.17	Non-crystalline	Non-crystalline
E5	0.05	4.10	Non-crystalline	Non-crystalline
F5	0.1	4.24	Non-crystalline	Non-crystalline
G5	0.1	4.22	Non-crystalline	Non-crystalline
Initial pH 8.0				
A8	0.01	5.06	Poorly crystalline boehmite	Poorly crystalline boehmite
B8	0.01	5.45	Poorly crystalline boehmite	Poorly crystalline boehmite
C8	0.01	5.25	Poorly crystalline boehmite	Poorly crystalline boehmite
D8	0.05	5.66	Non-crystalline	Poorly crystalline boehmite
E8	0.05	5.59	Non-crystalline	Poorly crystalline boehmite
F8	0.1	5.49	Non-crystalline	Non-crystalline
G8	0.1	6.36	Non-crystalline	Non-crystalline

¹ initial tannic acid/molar ratio

² after preparation, all the samples were aged for 10 months at 50°C and for 5 y at room temperature

³ after further ageing for 3 days at 140°C

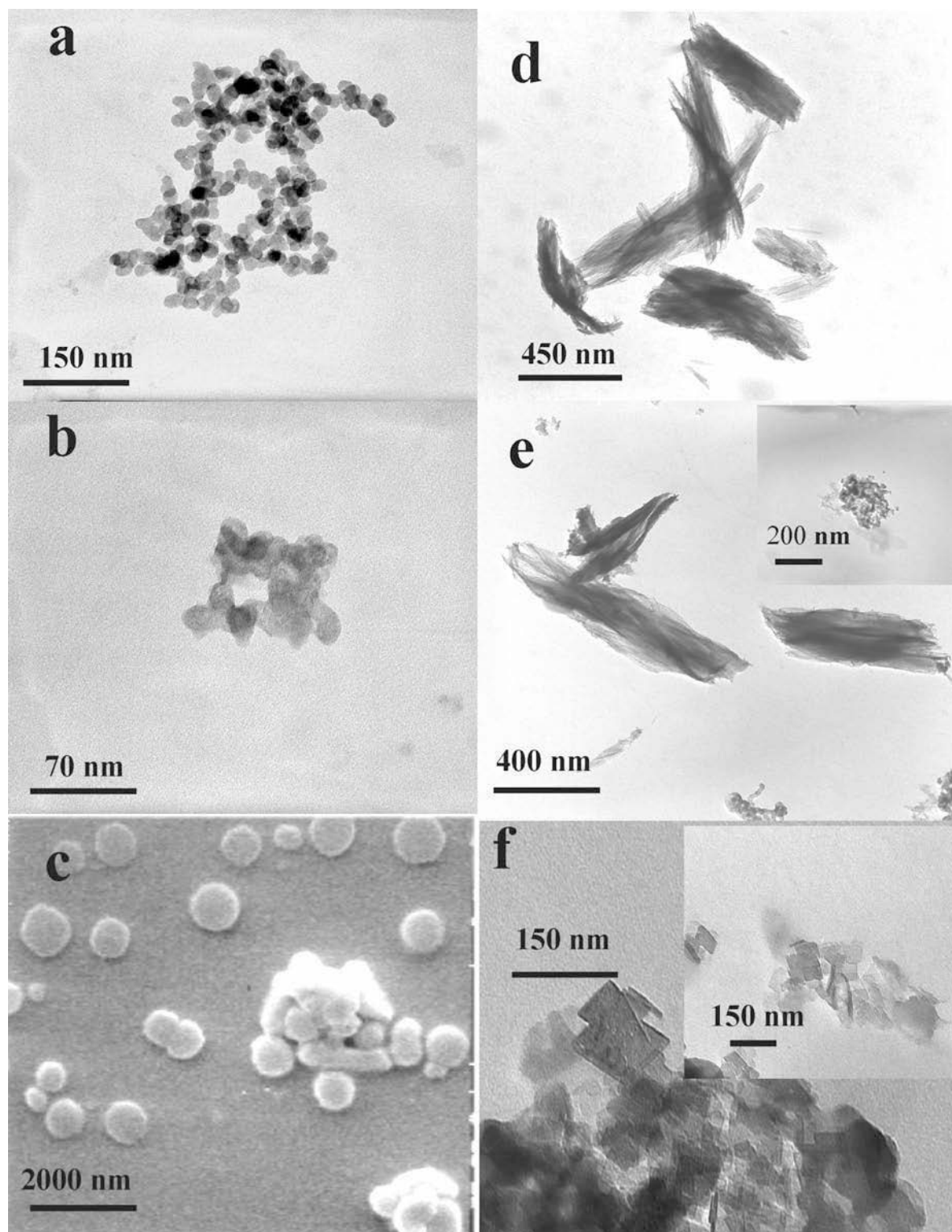


Figure 1. TEM (a, b, d, e and f) and SEM (c) images of selected samples formed at an initial tannate/Al molar ratio of 0.01 obtained at pH 5.0: sample A5 aged for 10 months at 50°C, then for 5 y at room temperature (a, b, c) and after further ageing for 3 days at 140°C (d, e); sample B5 aged for 10 months at 50°C, then for 5 y at room temperature and, finally, for 3 days at 140°C (f). See Table 1 for the synthesis conditions.

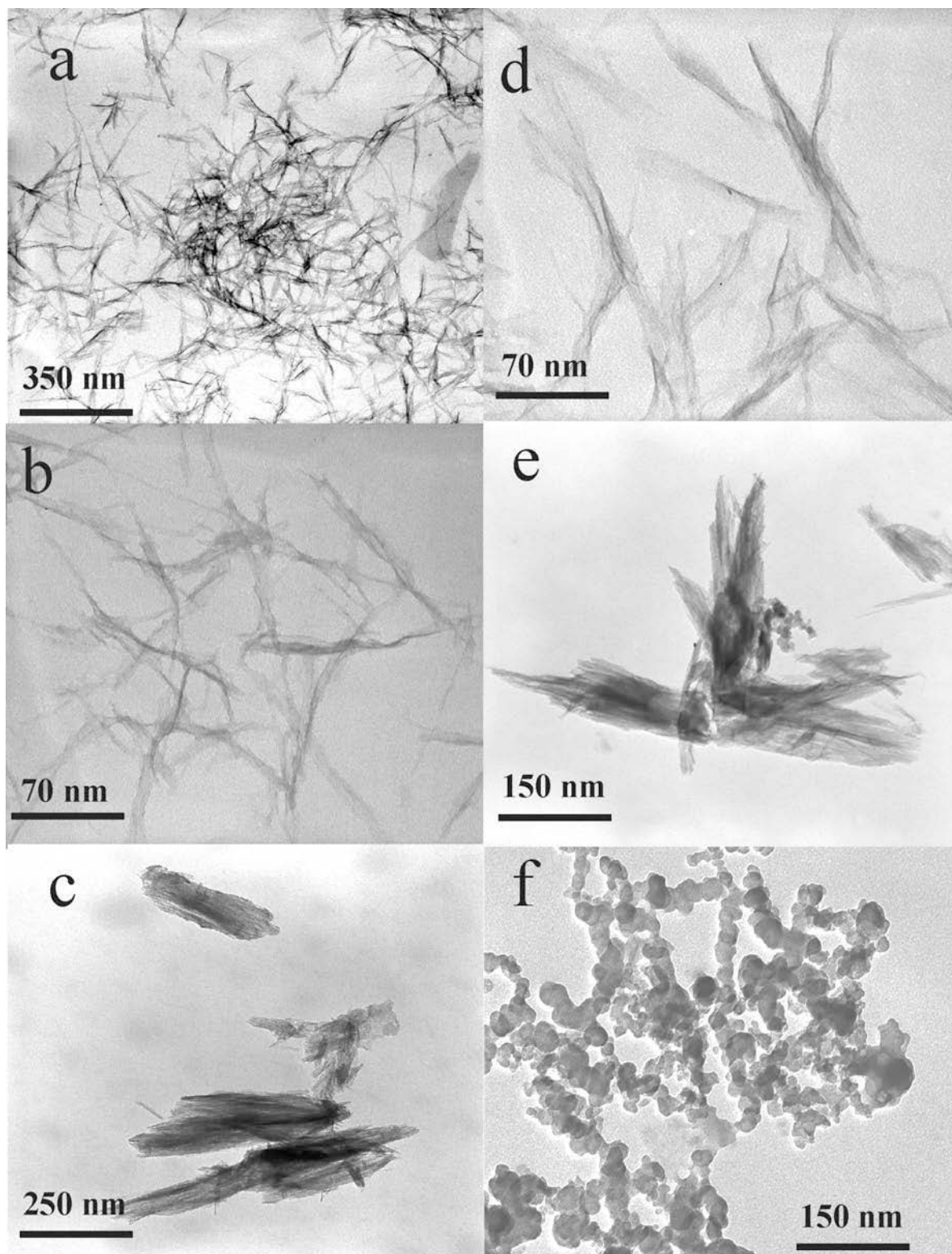


Figure 3. TEM images of Al precipitation products obtained at pH 8.0 at the initial molar ratio of 0.01: sample A8, aged for 10 months at 50°C and then for 5 y at room temperature (a,b) and then after further ageing for 3 days at 140°C (c); sample C8, aged for 10 months at 50°C and for 5 y at room temperature (d) and after further ageing for 3 days at 140°C (e). The non-crystalline Al precipitation product formed at an initial molar ratio of 0.1 (sample F8) and aged for 10 months at 50°C and for 5 y at room temperature and after further ageing for 3 days at 140°C (f). See Table 1 for the synthesis conditions.

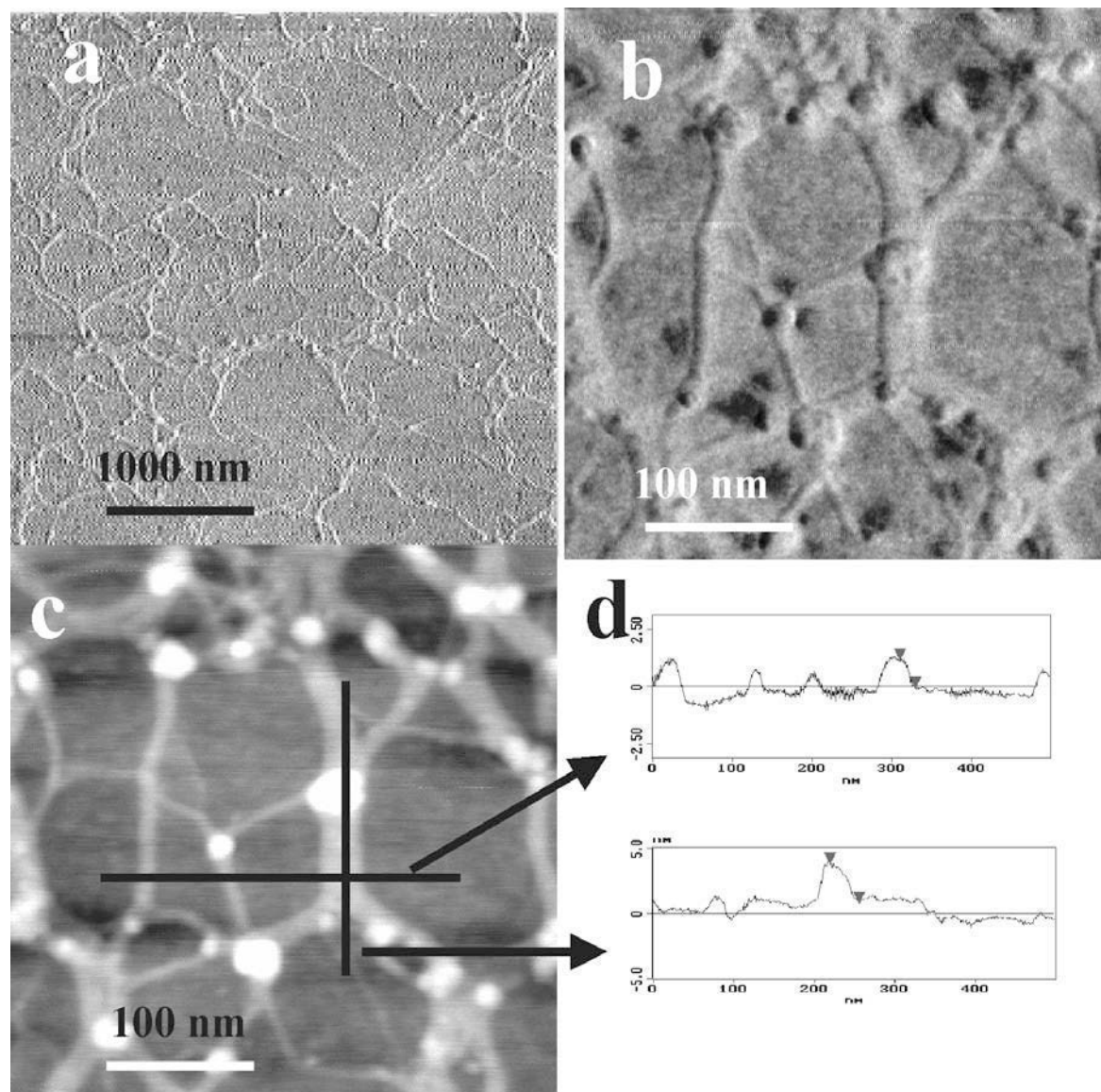


Figure 4. AFM images (a,b,c) of sample A8 obtained at pH 8.0 at the initial molar ratio of 0.01, aged for 10 months at 50°C and for 5 y at room temperature; section profile analysis of the same sample (d). See Table 1 for the synthesis conditions.

features (Figure 2). The XRD peaks of these samples were not uniformly broad and reasonably symmetrical as found by Tettenhorst and Hofman (1980) in their synthetic Al oxyhydroxides. In particular, in the A8–B8 samples the high-angle reflections at ~ 0.235 and 0.187 nm appeared sharper and/or stronger than the low-angle reflections at 0.638 – 0.620 and 0.318 – 0.319 nm (Figure 2). In particular, the B8 sample showed very broad and small peaks at 0.620 nm and 0.318 nm, whereas the C8 sample had relatively sharp and symmetrical peaks at 0.629 , 0.235 and 0.187 nm, but the peak at 0.319 nm was particularly broad.

These findings shows that boehmite formed in the presence of strongly chelating ligands and under mild conditions is usually poorly crystalline, having the same

atomic arrangement of boehmite but with a short-range order (Papee *et al.*, 1958; Violante and Huang, 1979, 1994; Singer and Huang, 1990; Violante *et al.*, 1993, 2002). Furthermore, it appears evident that the samples obtained by varying the order of mixing of Al, tannate and NaOH also differed in crystallinity (Figure 2). Table 3 shows the variation in position and FWHM of some reflections and the mean coherence length (MCL) of the samples A8, B8 and C8. According to Tettenhorst and Hofmann (1980), the greater the shift of the reflections to lower 2θ values and the greater their breadth (FWHM), the smaller is the crystallite size of the material synthesized. The data indicate that the A8 sample appears to have crystallite dimensions slightly smaller than those present in the C8 and B8 samples (in

the order listed). These findings are extremely important, because they demonstrate that tannate is more effective in preventing or perturbing the growth of the crystals of boehmite, when coprecipitated with Al than when added to soluble $\text{Al}(\text{OH})_x$ species or Al precipitates already formed. Clearly, in all the precipitates, tannate was not merely a surface sorbate, but, mainly, an integral part of the precipitates that formed and transformed into boehmite. Obviously, the organic ligands were present in the network of the precipitates more in the sample obtained coprecipitating tannate with Al than in samples B8 and C8. As a consequence, the inhibition and perturbation of the growth of the crystals of boehmite in sample A8 were particularly evident (Figure 2, Table 3).

The fibrous morphology of boehmite formed in the A8 (Figure 3a,b), B8 and C8 samples (Figure 3d) was similar to that described in previous works (Violante and Huang, 1979, 1984, 1994) and no difference was noted from sample to sample.

Using AFM, we observed that the particles of sample A8 appeared as a net of fibrillar structure characterized by irregular, slightly elongated crystals (Figure 4a,b). These particles were 150–800 nm long (average of 350 nm) and 1–4 nm wide (average 2.5 nm). The AFM images also show that the fibrillar structure was covered

by small thin subspherical particles with a diameter of 25–50 nm (Figure 4c). Application of AFM enabled us to distinguish the nanosized globular features on the surface particle which were not observed in the TEM micrographs. For example, Figure 4d shows the particle profiles of two kinds of surface shapes: (1) elongated needle particle 100–400 nm long and 3–4 nm thick; and (2) smaller structural globular particles 20–50 nm long and 1.2–1.8 nm thick. This indicates that very poorly crystalline materials (or Al tannate precipitates) were probably present over the elongated crystals of boehmite as strongly aggregated globular nanoparticles.

Effect of heating at 140°C on boehmite crystallization

In the A5, B5 and C5 samples obtained at $R = 0.01$ and pH 5.0 (Tables 1, 2; Figure 5) which were non-crystalline after prolonged ageing at temperatures $\leq 50^\circ\text{C}$ (Table 2), boehmite formed when the suspensions were kept for a further 3 days at 140°C. In sample B5 the high-angle reflections at 0.236 and 0.187 nm appeared relatively sharper and stronger than the low-angle reflections at 0.628 and 0.318 nm. These findings confirm that the order of addition of components (Al, tannic acid and NaOH) has an influence on the nature and crystallinity of boehmite, as ascertained for the samples formed at pH 8.0 and aged at temperatures

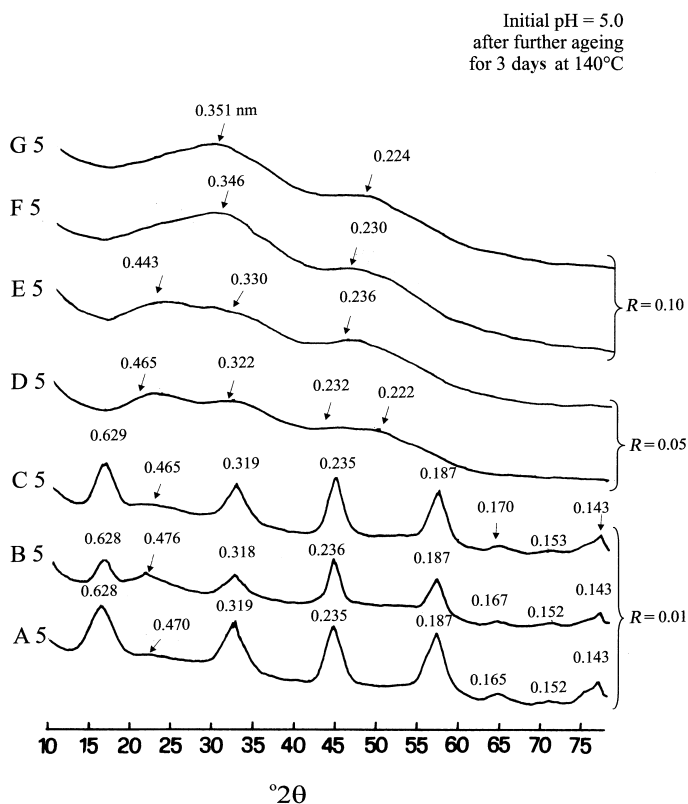


Figure 5. Powder XRD patterns of Al precipitation products, obtained at pH 5.0, aged for 10 months at 50°C and for 5 y at room temperature and after further ageing for 3 days at 140°C, formed at the initial ligand/Al molar ratio of 0.01 (A5, B5, C5), 0.05 (D5, E5) and 0.1 (F5, G5). See Table 1 for the synthesis conditions.

$\leq 50^\circ\text{C}$ (Figure 2). The TEM observations of sample A5 (Figure 1d,e), B5 and C5, kept for 3 days at 140°C , showed fibrous materials formed by aggregation of needle particles. However, spherical particles were also observed in these samples, indicating the presence of non-crystalline or very short-range ordered material (Figure 1e). In sample B5, particularly at very high magnifications, some crystals showed a rhombic, tabular morphology (Figure 1f). A similar morphology was described by Mackenzie *et al.* (1971) and by Tettenhorst and Hofmann (1980, see their Figure 1). More crystals showing a rhombic habit were observed in the samples aged for >3 days at 140°C , but the fibrous morphology still predominated after 15 days at 140°C .

Heating for 3–15 days at 140°C did not promote the formation of boehmite in the samples synthesized at pH 5.0 and $R \geq 0.05$ (D5–G5; Figure 5), indicating that the presence of critical concentrations of tannate strongly prevented the formation of boehmite even after prolonged ageing at high temperatures. However, we have found that when sample G5, aged at 50°C and room temperature, was brought to pH 12.0 and aged for a further 6 months at 50°C , poorly crystalline boehmite formed, indicating that the non-crystalline material formed in the presence of a large amount of tannate

converted under critical conditions into boehmite *vs.* $\text{Al}(\text{OH})_3$ polymorphs (data not shown).

The XRD patterns of samples A8–C8, which showed the presence of boehmite after heating at temperatures $\leq 50^\circ\text{C}$ (Figure 2), showed that the high-angle reflections at 0.235 and 0.187 nm were not sharper than the first reflections at the lowest diffraction angle (0.638 and 0.318 nm), as ascertained before heating at 140°C (as discussed above). This suggests that the crystallinity of these oxyhydroxides increased (Table 3). However, even after heating at 140°C for 3 days, sample A8 appeared to have crystallite sizes relatively smaller than those present in C8 and B8 (Table 3).

The XRD patterns of samples D8 and E8 obtained at $R = 0.05$ showed very small, diffuse and asymmetric peaks (Figure 6), indicating that the crystals were very distorted and/or very finely divided. However, the E8 sample appeared to be of lower crystallinity than the D8 sample. Fibrous materials were not easily detected under TEM or AFM, clearly because of the presence of large amounts of non-crystalline materials in these precipitates (data not shown).

Of the samples synthesized at initial pH 8.0 only those formed at $R = 0.1$ (F8 and G8) did not contain boehmite after further heating for 3 days at 140°C (Figures 3f, 6).

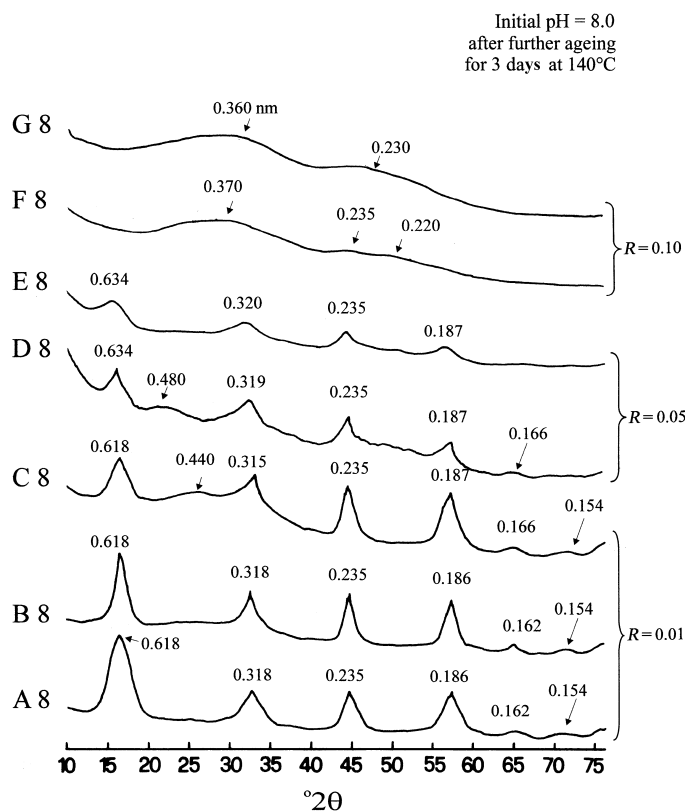


Figure 6. Powder XRD patterns of Al precipitation products, obtained at pH 8.0, aged for 10 months at 50°C and for 5 y at room temperature and after further ageing for 3 days at 140°C , formed at the initial ligand/Al molar ratio of 0.01 (A8, B8, C8), 0.05 (D8, E8) and 0.1 (F8, G8). See Table 1 for the synthesis conditions.

However, the samples containing greater amounts of tannate showed extremely small peaks of boehmite only after heating at 140°C for 15 days. Figure 7 shows the XRD patterns of the oriented E8 and F8 samples after prolonged ageing at temperatures $\leq 50^\circ\text{C}$ (a) and after further ageing for 3 days (b) or 15 days (c) at 140°C. The transformation from non-crystalline materials into boehmite appears evident. Only a very broad hump was ascertained for the F8 sample after 15 days at 140°C, in spite of the fact that oriented poorly crystalline and/or finely divided boehmite yields a more intense peak at $\sim 0.620\text{--}0.650\text{ nm}$ than when randomly oriented with the remaining peaks being undetectable (Violante and Violante, 1980; Hsu, 1989; Violante and Huang, 1979, 1984, 1994). This indicates that the crystallinity of these samples is very poor. Electron microscope observations of these samples showed materials comprising non-crystalline spherical particles. Very few, if any, fibrous particles were observed.

These results reinforce the conclusion of Violante and Huang (1993) that the transformations from the initially formed non-crystalline materials into boehmites occur through the formation of intermediate materials with various degrees of ordering and sizes of particles. The boehmite formed in the presence of strongly chelating ligands even after prolonged ageing may be a mixture of materials of boehmite character differing in

the degree of ordering, crystallinity and crystal habit as well as of non-crystalline precipitates. Kawano and Tomita (1996) and Kawano *et al.* (1997) have demonstrated that at the earliest weathering stages of K-feldspars or volcanic glass, Al precipitates, exhibiting distinct habits (fibrous, spherical particles or very thin flaky particles) formed. These materials, containing small amounts of Si, were similar to boehmite, but were metastable and converted into gibbsite and/or halloysite.

CONCLUSIONS

Boehmites formed at pH 5.0 and $R = 0.01$ and at pH 8.0 and $R = 0.01\text{--}0.1$ after prolonged ageing at $20\text{--}50^\circ\text{C}$ and further ageing for 3–15 days at 140°C either by precipitating mixtures of Al and tannic acid or by varying the order of addition of Al, tannic acid and NaOH. These findings show that tannate promoted the formation of Al oxyhydroxides versus crystalline $\text{Al}(\text{OH})_3$ polymorphs even when added on preformed soluble and precipitated $\text{Al}(\text{OH})_x$ species. Most of the Al oxyhydroxides formed appeared to be largely poorly crystalline materials. However, tannate was more effective in preventing and/or perturbing the growth of the crystals of boehmite when coprecipitated with Al than when added to soluble $\text{Al}(\text{OH})_x$ species or Al precipitates already formed.

Microscope observations (TEM, SEM and AFM) indicated the presence, in most of these samples, of fibrous materials or agglomerates of fibrils and spherical particles, also suggesting the presence of non-crystalline materials. Many samples in which the presence of boehmite was indicated by XRD were formed of materials with various degrees of ordering, crystallite size and morphology (fibrous or rhombic habit). Even after oxidation with H_2O_2 the crystallinity of selected samples increased only slightly after further ageing at 50°C . Mean coherence length data indicate that boehmites formed at pH 8.0 and $R = 0.01$ coprecipitated with Al have crystallite sizes slightly smaller than those present in boehmite formed in samples with tannate added to soluble $\text{Al}(\text{OH})_x$ species or Al precipitates already formed. The crystallinity of some boehmites formed after ageing at $20\text{--}50^\circ\text{C}$ (Figure 1) increased substantially after further ageing for 3–15 days at 140°C (Figures 6, 7), but samples formed at $R = 0.05\text{--}0.1$ and pH 5.0 remained non-crystalline even after ageing for 15 days at 140°C , indicating that tannate strongly prevented the transformation of non-crystalline materials into boehmite (Violante and Huang, 1994). However, some of these materials converted into boehmite by increasing the pH to 12.0 and after further ageing for 6 months at 50°C . The hypothesis of Tettenhorst and Hofmann (1980) that synthetic boehmites formed under mild conditions are only submicroscopic in size and must be considered as finely divided boehmite cannot be

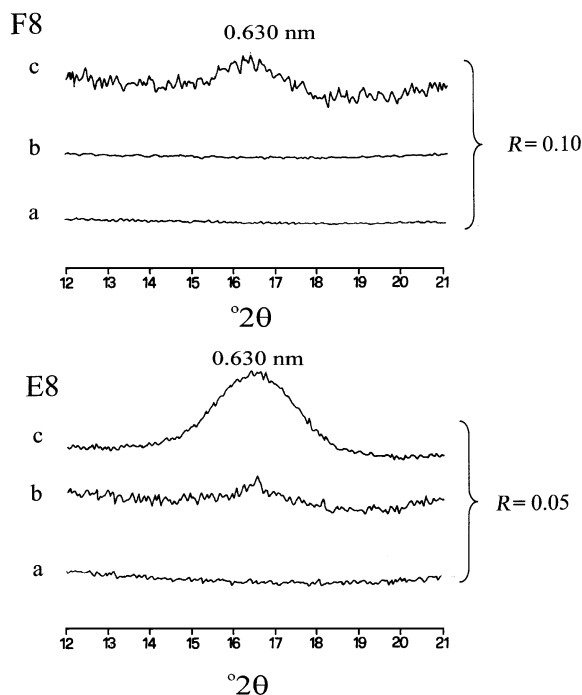


Figure 7. XRD patterns of Al precipitation products (oriented aggregate specimens), obtained at pH 8.0 at the initial ligand/Al molar ratio of 0.05 (E8) and 0.1 (F8): (a) aged for 10 months at 50°C and for 5 y at room temperature; (b) aged for 3 days at 140°C ; (c) aged for 15 days at 140°C .

completely accepted. When boehmites are synthesized in the presence of inorganic and organic ligands with a low affinity for Al (e.g. Cl^-) at high temperatures (between 100 and 300°C), it is possible that the final materials are mainly finely divided crystalline boehmites. However, boehmites synthesized in the presence of strongly chelating ligands, particularly high-molecular-mass ligands such as tannate, fulvate and humate (Kodama and Schnitzer, 1980; Violante and Huang, 1979, 1984; Singer and Huang, 1990) and at temperatures not particularly high, are substantially materials with the same structure as boehmite but with a poorly ordered and defective ion arrangement (Papee *et al.*, 1958; Violante and Huang, 1984). Indeed, most of these samples, even after prolonged ageing, appear to be mixtures of materials with varying degrees of ordering, sizes of particles and morphology.

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