

FORMATION MECHANISM OF ALUMINUM HYDROXIDE POLYMORPHS

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Abstract—Substantial studies have been carried out to investigate the mechanism of the formation of $\text{Al}(\text{OH})_3$ polymorphs. The influence of the nature of Al precipitation products on the formation of $\text{Al}(\text{OH})_3$ polymorphs still remains obscure. In this study, X-ray diffraction, infrared and thermal analyses, and electron microscopic observations of the Al precipitates formed at the initial pH 8.2 and at a citric acid/Al molar ratio of 0.01 and aged for 3 hr to 60 days revealed that the transformation from the initially formed noncrystalline materials to pseudoboehmite occurred through the formation of intermediate materials with various degrees of ordering and sizes of particles that apparently had a wide range of solubility. By increasing the pH of the suspension of precipitation products of Al to 10.0 after 3 hr and 3, 11, 31, and 60 days or longer, the crystalline precipitation products were bayerite, nordstrandite and bayerite, nordstrandite and pseudoboehmite, pseudoboehmite and gibbsite, and pseudoboehmite, respectively. This work shows evidence that, as the nature of the starting Al precipitates changed, the rate of their dissolution apparently changed, and various $\text{Al}(\text{OH})_3$ polymorphs consequently formed. Therefore, the data substantiate the hypothesis that the mechanism of the formation of an $\text{Al}(\text{OH})_3$ polymorph is determined by the rate of its nucleation, which is, in turn, influenced by the rate of dissolution of the noncrystalline or poorly ordered Al-oxides initially formed.

Key Words— $\text{Al}(\text{OH})_3$ polymorphs, Bayerite, Gibbsite, Noncrystalline materials, Nordstrandite, Pseudoboehmite.

INTRODUCTION

Aluminum hydroxides (gibbsite, nordstrandite, and bayerite) and oxyhydroxides (boehmite) are present in nature. Gibbsite is the most common of the three $\text{Al}(\text{OH})_3$ polymorphs in soils and bauxites. Bayerite is rare in natural environments, but is easily synthesized in the laboratory. Occurrence of nordstrandite in some alkaline soils and bauxites (mainly in Jamaica) has been documented (Violante and Jackson, 1979; Violante *et al.*, 1982; Hsu, 1989). Boehmite frequently occurs with gibbsite and/or nordstrandite in bauxites. In many bauxite deposits boehmite consists of sub-microscopic particles, which are similar to the pseudoboehmite¹ prepared in the laboratory at low temperatures and pressures (Souza Santos *et al.*, 1953; Calvet *et al.*, 1953; Papee *et al.*, 1958; Hsu, 1967; Wefer and Bell, 1972; Tettenhorst and Hofmann, 1980; Violante and Huang, 1984, 1985). Furthermore, gibbsite and "amorphous boehmite-like alumina" have been found in many tropical soils in Australia, South Africa, Brazil, and Puerto Rico (de Villiers, 1969).

For many years, most researchers have claimed that, at ambient temperature and pressure, pseudoboehmite was only a transitional phase between the initially formed noncrystalline material and the final $\text{Al}(\text{OH})_3$

polymorphs (Souza Santos *et al.*, 1953; Calvet *et al.*, 1953; Aldcroft *et al.*, 1969; Wefer and Bell, 1972; Yoldas, 1973; Serna *et al.*, 1977). Recently it has been ascertained that at certain pHs (from 5.0 to 11.0) and critical ranges of ligand/Al molar ratios (R), inorganic and non-humified organic ligands (Violante and Violante, 1980; Violante and Jackson, 1979, 1981; Violante and Huang, 1984, 1985; Huang and Violante, 1986) as well as fulvic (Kodama and Schnitzer, 1980) and humic acid (Singer and Huang, 1993) facilitate at ambient temperature and pressure the formation of pseudoboehmite. In the presence of citric acid (R = 0.01), pseudoboehmite forms at an initial pH of 8.0–8.2 and does not change into $\text{Al}(\text{OH})_3$ polymorphs even after prolonged aging (Violante and Huang, 1985; Violante *et al.*, 1993).

Substantial studies have been conducted to investigate the mechanism of the formation of Al hydroxide polymorphs (Hsu, 1989). The significance of the nature of a series of precipitation products of Al in the formation of $\text{Al}(\text{OH})_3$ polymorphs still remains obscure. The objective of this study was to evaluate the influence of the nature of starting Al precipitation products formed in the presence of citric acid on the formation of $\text{Al}(\text{OH})_3$ polymorphs upon aging after the pH of the system was adjusted to 10.0.

MATERIALS AND METHODS

Al precipitation products were obtained by the addition with stirring of 0.5 M NaOH at ≈ 2 ml/min to

¹ Boehmite formed at room temperature and one atmosphere pressure is a poorly crystalline, highly defective and/or fine size Al-oxyhydroxide, usually called pseudoboehmite.

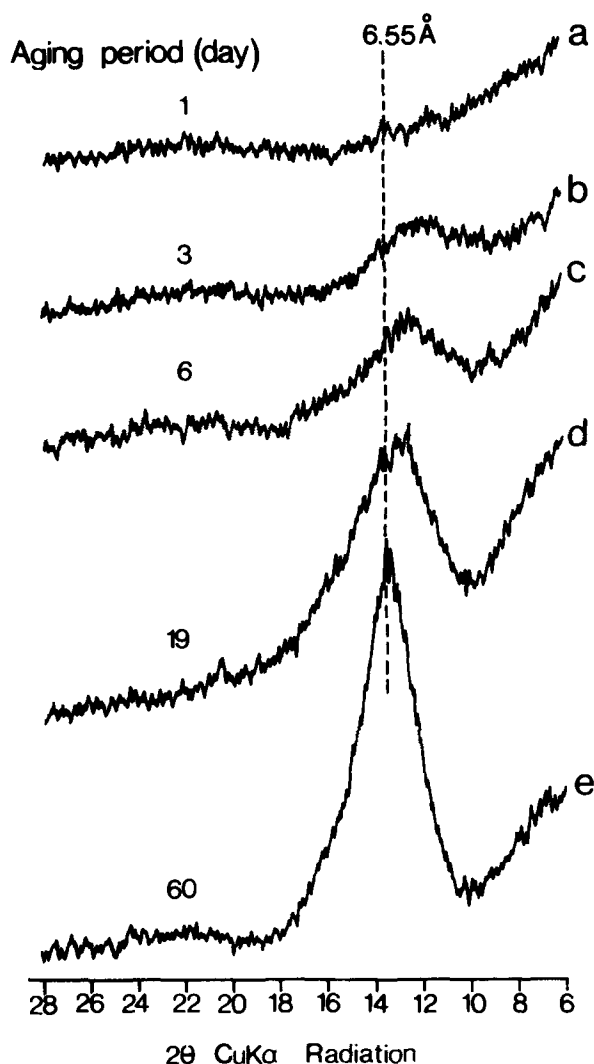


Figure 1. X-ray diffractograms (oriented aggregate specimens) of Al precipitation products formed at citric acid/Al molar ratio of 0.01 and at pH 8.2 after a) 1, b) 3, c) 6, d) 19, and e) 60 days of aging. During the aging period of 60 days to 8 months, the peak of pseudoboehmite remained practically unchanged (not shown).

a 1 liter solution containing AlCl_3 (0.1 M) and citric acid (1.0×10^{-3} M; citric acid/Al molar ratio of 0.01). The concentration of total Al in the final suspension (3 liter) was 3.3×10^{-2} M, and its final pH was adjusted to 8.2 (OH/Al molar ratio was 2.86). The suspension was aged in a polyethylene bottle, and its pH was recorded during aging by a Metrohm E436 potentiograph.

Aliquots of the suspension were collected after 3 hr; 1, 3, 6, 11, 19, 31, 43, and 60 days; and 8 months. The precipitate in the suspension was collected by ultrafiltration and washed with deionized distilled water through a Millipore M.E. filter of $0.025 \mu\text{m}$ pore size.

Some of the precipitate collected was air-dried and lightly ground to pass through a 100-mesh sieve.

Air-dried samples (<100 mesh) were mounted in a holder to obtain random orientation of particles. Oriented specimens for X-ray powder diffraction (XRD) were obtained by drying the ultrafiltered and washed precipitate of the aged samples on glass slides. Both were analyzed with a Philips X-ray diffractometer, using Ni-filtered $\text{CuK}\alpha$ radiation generated at 35 Kv and 16 mA. Infrared spectra of the precipitation products of Al were obtained from KBr discs containing air-dried samples (2 mg/100 g KBr). The spectra were recorded in the $400\text{--}4000 \text{ cm}^{-1}$ range on a Perkin-Elmer 567 IR spectrophotometer. For transmission electron microscopic (TEM) examination, one drop of a sample suspension was deposited on carbon-coated Formvar film on a Cu grid. TEM electron micrographs were taken with a Philips EM 400. Differential thermal analyses (DTA) of selected samples were carried out by using a Rigaku Differential Analyzer. About 200 mg of air-dried samples were heated in a Rigaku furnace that was programmed to raise the temperature from 25° to 1000°C at a rate of $10^\circ/\text{min}$.

The chemical composition, point of zero charge (PZC), specific surface area, and $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio of Al precipitation products during the aging process were determined by the methods described elsewhere (Violante and Huang, 1984).

The pH of 350 ml of the suspension, collected during the aging period ranging from 3 hr to 60 days, was adjusted to 10.0 by adding 0.2 M NaOH using an automatic titrator, Metrohm Herisau E 436. The systems were adjusted at this pH in order to accelerate the formation of $\text{Al}(\text{OH})_3$ polymorphs so as to facilitate the study on the factors that promote the formation of Al-hydroxides and oxyhydroxides. After the pH adjustments, all these suspensions were aged for another 8 months in polyethylene bottles and then analyzed by X-ray diffraction and electron microscopy.

RESULTS

Effect of aging on the nature of Al precipitation product

Figure 1 shows the XRD patterns of the Al precipitation products formed at pH 8.2 during the aging process. Initially, a noncrystalline material formed (Figure 1a), but pseudoboehmite began to appear a few days after the sample preparation (Figure 1b). The 020 reflection increased in intensity upon aging (Figures 1b–1e), and a variation in its peak breadth and position from the lower (Figure 1b) to higher 2θ values (Figure 1e) was observed. The variation in the peak breadth and position of the 020 reflection during the aging process seems to be due to an increase in size and/or in crystallinity of the Al precipitation products (Tettenhorst and Hofmann, 1980; Violante and Huang, 1984,

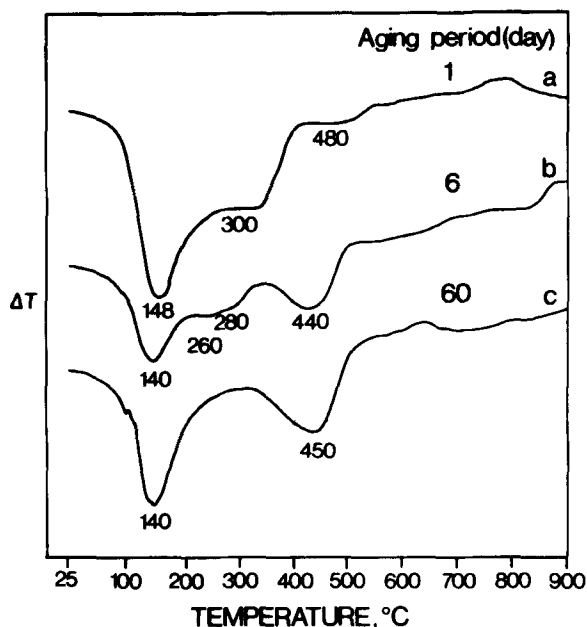


Figure 2. Differential thermal analysis patterns of Al precipitation products formed at citric acid/Al molar ratio of 0.01 and at pH 8.2 after a) 1, b) 6, and c) 60 days of aging.

1985; Violante *et al.*, 1989, 1993) as well as to a partial removal of H₂O molecules situated between the elemental layers (Papee *et al.*, 1958; Hsu, 1967, 1989; Yoldas, 1973; Tettenhorst and Hofmann, 1980).

The infrared analysis (not shown) strengthens the findings of XRD analysis. The Al precipitation products collected after 3 hr or 1–2 days did not show bands of boehmite. After 11 days broad bands characteristic of pseudoboehmite at about 3300, 3100, 1080, 760 and 490 cm⁻¹ (Wefer and Bell, 1972; Violante and Huang, 1984, 1985; Hsu, 1989) appeared quite well resolved. Some of these bands (at ≈3100, 1080 and 490 cm⁻¹) increased in intensity during the aging process.

DTA patterns show a continuous gradation of bonding energy for the water (Figure 2). The endotherm at 140°–148°C was attributed to sorbed water. The very broad endotherms at 260°–300°C of the samples aged 1 and 6 days (Figures 2a and 2b) indicate the presence of strongly bound water molecules. According to Baker and Pearson (1974), some excess water was likely bonded to the surfaces of the crystallites. They noted that for very small crystals the amount of such water can be significant. The endotherm at 260°–300°C decreased with aging and was absent in the pattern of the sample aged 60 days (Figure 2c), whereas the broad endotherm of boehmite centered at 440°–480°C increased in intensity during the aging (Figures 2a–2c), showing a transition from a very short-range ordered material into pseudoboehmite. During the first 30 days

of aging the structural water decreased from 22.2 to 20.0% (Violante and Huang, 1984).

Electron microscope studies (Figure 3) show that the morphology of the precipitates also changed gradually from agglomerates of spherical particles, characteristic of noncrystalline materials (Souza Santos *et al.*, 1953; Violante and Violante, 1980; see Figure 3a) through fibrous materials which still contained spherical particles (Figure 3b) to agglomerates of fibrils, which appeared to be randomly interlaced (Figure 3c). After 8 months of aging, the precipitate showed highly developed fibers (Figure 3d) that often appeared at high magnification to be double lines with a separation of ≈50 Å. TEM micrographs seem to indicate that, during the early stages of the transformation of the initial noncrystalline material into pseudoboehmite, the products were not homogeneous, but probably a mixture of materials with a wide range of crystallinity and crystallite size.

A decrease in pH from 8.20 to 7.04 was observed during the aging of Al precipitation products in the first 60 days of aging. However, the amounts of NaOH required to raise the pH of 350 ml suspension to 10.0 steadily decreased with aging (Table 1). This is attributed to the hydrolytic reactions of Al with a subsequent reorganization and crystallization of the precipitation products (Figures 1, 2, and 3). At an initial pH of 8.2, Al³⁺ was not fully neutralized and could be described as basic salts. A part of the positive charge of Al³⁺ was neutralized by citrate or Cl⁻ ions. The basic salts further hydrolyzed to neutral Al oxyhydroxide or Al(OH)₃ polymorphs during aging, and therefore pH decreased.

As reported elsewhere (in Tables 2 and 3; Violante and Huang, 1984), the chemical composition, specific surface area, and PZC of the Al precipitation product changed continuously with aging (from 0 to 30 days). Surface area decreased from 518 m²/g to 400 m²/g, Al content increased from 39.4 to 41.0%, citrate anions present in the precipitate decreased from 153 μmol/g to 125 μmol/g, and the PZC increased from 8.5 to 8.9.

The changes of the physicochemical and thermal properties as well as the chemical composition of the Al precipitation products during aging (Figures 1–3) must be attributed to an increase in the degree of ordering of the arrangement of the elementary units and/or in crystal size. The presence of perturbing ligands in the Al precipitation product initially caused a structural disorder (Figures 1a, 2a, and 3a). The formation of a more well-ordered boehmite after aging (Figures 1e and 2c) is attributed to the partial and gradual removal of H₂O molecules and foreign ligands (citrate) from the noncrystalline materials and the subsequent reorganization of these phases in solid state (Wefer and Bell, 1972; Yoldas, 1973; Violante and Huang, 1984, 1985). This transformation is gradual and occurs more rapidly during the first few months of aging, but it

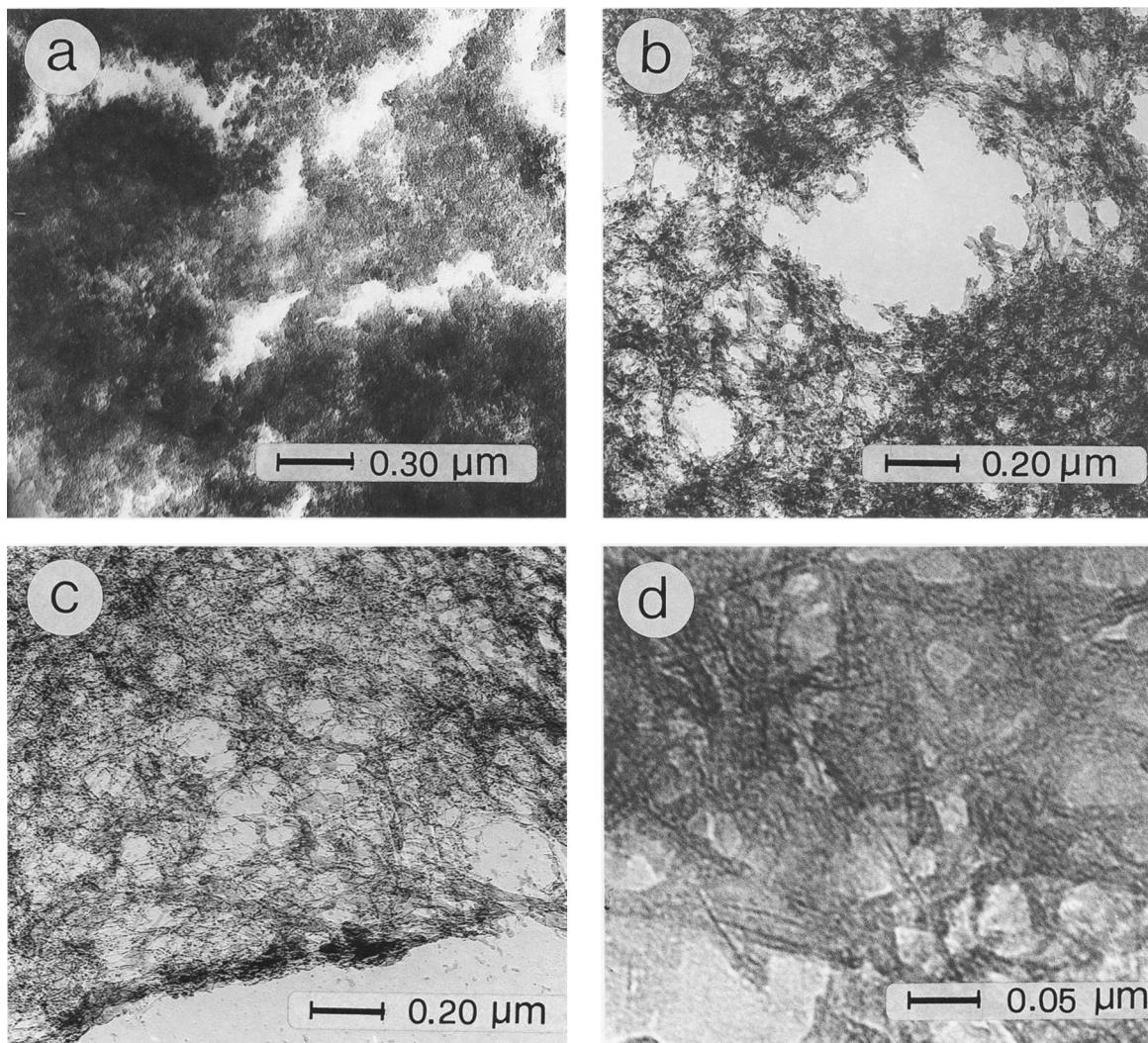


Figure 3. Transmission electron micrographs of Al precipitation products formed at citric acid/Al molar ratio of 0.01 and at pH 8.2 and aged a) 3 hr. b) 3 days. c) 43 days. and d) 8 months, showing a change in morphology of the precipitates by aging in the mother solution.

continues much more slowly after prolonged aging (Violante *et al.*, 1993).

Effect of the nature of short-range ordered Al precipitation products and pH on the Al transformation

Figures 4 and 5 show the influence of previous aging periods on the nature of the Al precipitation products formed after increasing the pH of the precipitate suspension to pH 10.0. Compared with Figures 1–3, it is evident that the mineralogical composition of the final precipitation products after the pH adjustment changed tremendously. The relative amounts of bayerite, nordstrandite, gibbsite, and/or pseudoboehmite present in the precipitation products varied with the length of previous aging periods (Figures 4 and 5). Many large

Table 1. Amounts of NaOH required to raise the pH of the suspension of the precipitation products of Al to 10.0 during the aging process.

Aging (days)	pH	μ moles of NaOH added to 350 ml of suspension to raise pH to 10.0
0.1	8.20	1860
1	8.05	1750
2	7.85	1575
3	7.33	1500
6	7.31	1375
11	7.29	635
19	7.10	610
31	7.09	560
43	7.07	480
60	7.04	465

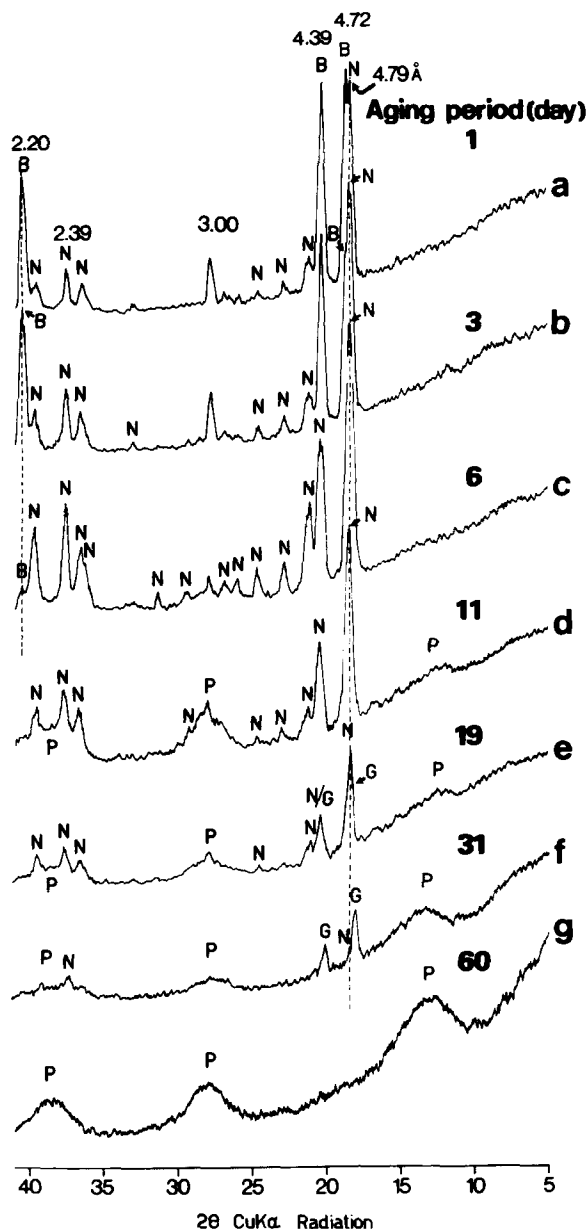


Figure 4. X-ray diffractograms (random orientation) of Al precipitation products that were aged for 8 months after the pH adjustment to 10.0 following the initial Al precipitation at a citric acid/Al molar ratio of 0.01 and at pH 8.2 and aging for a) 1, b) 3, c) 6, d) 11, e) 19, f) 31, and g) 60 days. B stands for bayerite, N for nordstrandite, G for gibbsite, and P for pseudoboehmite.

crystals of bayerite ($> 1\text{--}3\ \mu\text{m}$) were observed by electron microscope in the sample whose pH was increased after 3 hr (Figure 5a), whereas a mixture of bayerite and nordstrandite was found in the sample whose pH was raised after 1 day (Figure 4a). The increase of pH of the suspensions previously aged 3 and 6 days (Figures 4b and 4c) resulted in an increase of the formation of nordstrandite and the subsequent decrease of bay-

erite content. The reflections at 4.72 and 2.2 Å characteristic of bayerite were very strong in the samples previously aged 1 or 3 days (Figures 4a and 4b), but barely detectable in the sample whose pH was raised after 6 days of aging (Figure 4c). The intensity of the peaks of nordstrandite (4.79, 4.20, 4.15, 2.45, 2.39, 2.27 Å) steadily increased in samples after previous aging for 3, 6, and 11 days (Figures 4b–4d). In the samples previously aged 11, 19, 31 and 60 days (Figures 4d–4g) the peaks of bayerite were not observed, but the presence of nordstrandite, gibbsite and/or pseudoboehmite was evident. In the sample previously aged 31 days (Figure 4f) the Al precipitation products were pseudoboehmite, gibbsite, and a small amount of nordstrandite. The relative amount of pseudoboehmite over $\text{Al}(\text{OH})_3$ polymorphs increased with aging periods from 11 to 60 days prior to pH adjustment (Figures 4d–4g). Electron microscope observations are in accord with XRD analysis. Rectangular crystals of nordstrandite were predominant in the sample whose pH was raised after 11 days (Figure 5b); whereas in the samples previously aged 19 and 43 days (Figures 5c and 5d), only a few crystals of gibbsite and/or nordstrandite blended into a gelatinous material, characteristic of pseudoboehmite, were found. Pseudoboehmite (peaks at about 6.60, 3.20, 2.35 and 1.90 Å; the last peak is not shown in Figure 4) was the only component detected by XRD in the Al precipitation products formed by increasing the pH of the suspension to 10.0 after 60 days or more of previous aging (Figure 4g).

DISCUSSION

The results obtained in this study show that the nature of the noncrystalline or poorly crystalline materials formed during the early stages of the aging process (Figures 1–3 and Table 1) had an important bearing on the Al transformation when the pH of the suspension was increased (Figures 4 and 5). The transformation of noncrystalline Al precipitation products to citrate-stabilized pseudoboehmite evidently occurs through a series of poorly ordered intermediate materials that increase in structural order and particle size and decrease in solubility during aging (Figure 6).

It has been reported that the rate of crystallization controls the final aluminous products (Hsu, 1966, 1989; Violante and Jackson, 1979, 1981; Violante and Violante, 1980). A rapid crystallization yields bayerite and slow crystallization promotes gibbsite, whereas intermediate conditions favour the formation of nordstrandite. It is also generally agreed that crystallization of $\text{Al}(\text{OH})_3$ polymorphs in slightly acidic, neutral, or alkaline media takes place via a dissolution-reprecipitation reaction (Souza Santos *et al.*, 1953; Calvet *et al.*, 1953; Papee *et al.*, 1958; Bye and Robinson, 1964, 1974; Wefer and Bell, 1972; Violante and Violante, 1980; Van Straten *et al.*, 1984; Violante and Huang,

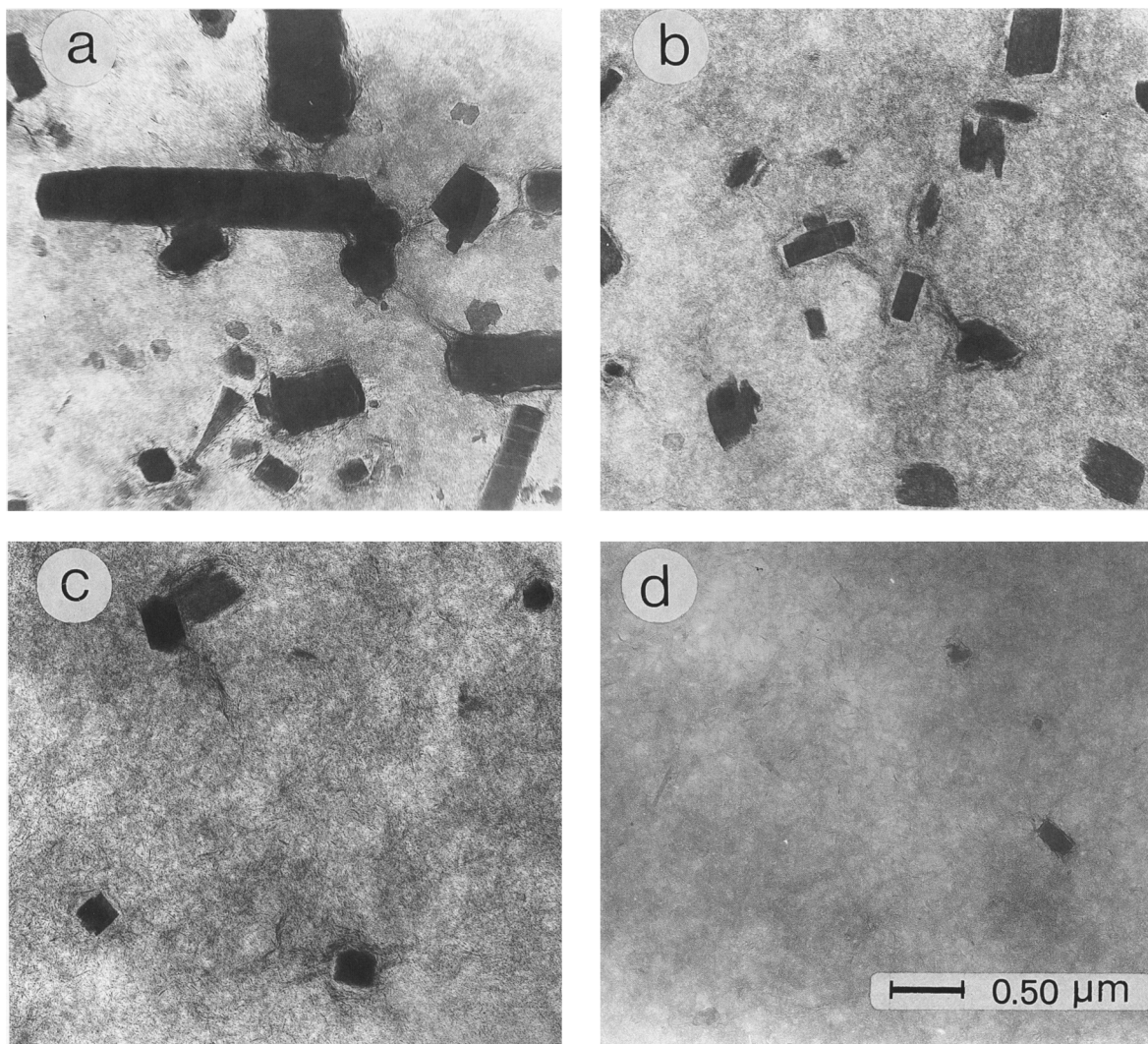


Figure 5. Transmission electron micrographs of Al precipitation products that were aged for 8 months after the pH adjustment to 10.0 following the initial Al precipitation at a citric acid/Al molar ratio of 0.01 and at pH 8.2 and aging for a) 3 hr, b) 11, c) 19, and d) 43 days.

1985; Hsu, 1989). Consequently, the rate determining step in the crystallization process of $\text{Al}(\text{OH})_3$ polymorphs in the samples whose pH was raised to 10.0 is the dissolution of the poorly ordered intermediate Al precipitation products present in each system.

An increase of pH to 10.0 evidently facilitated the solubilization of noncrystalline materials and poorly ordered intermediate Al precipitation products and the subsequent crystallization of $\text{Al}(\text{OH})_3$ polymorphs (pathway A and B in Figure 6). By increasing the pH of the suspension of the Al precipitation products to 10.0 immediately after the sample preparation the noncrystalline material initially formed rapidly dissolved and mainly bayerite formed (Figure 5a) as depicted in Figure 6 (pathway A).

By increasing the pH of the original suspension to

10.0 during the early stages of aging (1 to 6 days of aging), a mixture of bayerite and nordstrandite formed with the latter being more prominent than the former at longer previous aging periods (Figures 4a–4c). The solid materials, which had different crystallinity and/or particle size (Figures 1b, 1c, 2a and 2b), apparently dissolved at different rates, resulting in the formation of various $\text{Al}(\text{OH})_3$ polymorphs. A slower rate of crystallization promoted the formation of nordstrandite over bayerite (Violante and Violante, 1980; Violante *et al.*, 1982; Huang and Violante, 1986). By increasing the pH of the suspension to 10.0 after 11 to 60 days, bayerite was not found (Figures 4d–4g, and 5b–5d) evidently because very disordered and soluble materials were no longer present.

After aging for 11 to 31 days, pseudoboehmite ap-

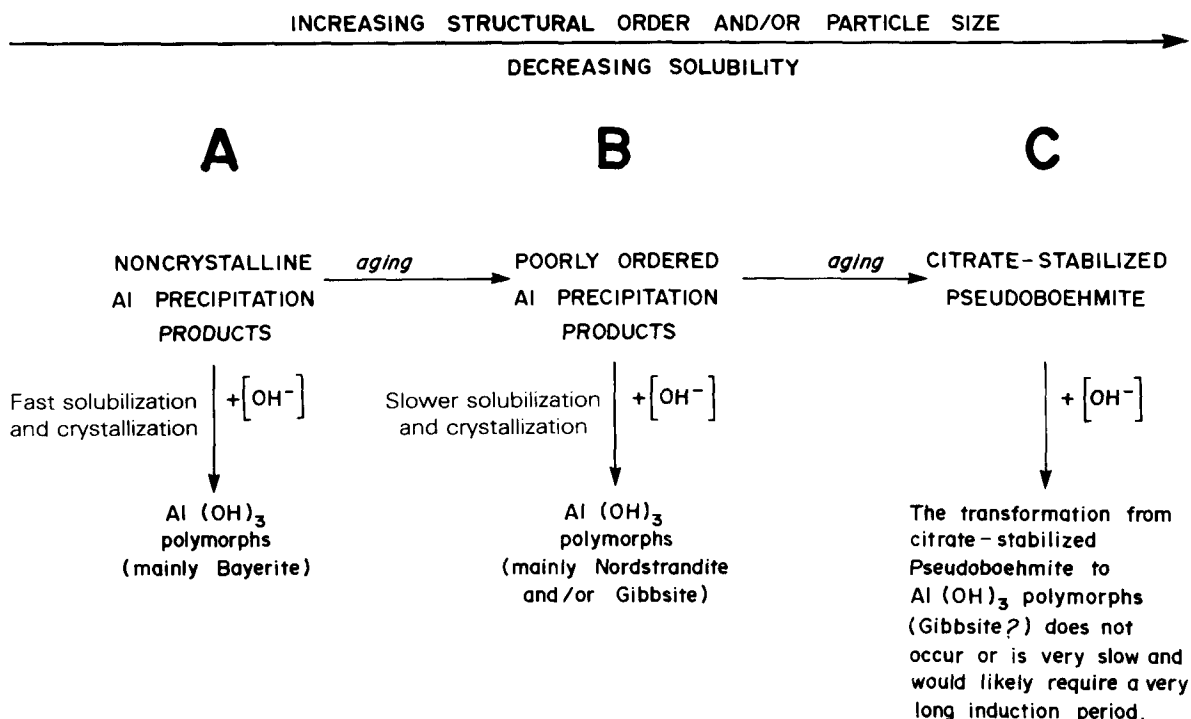


Figure 6. Proposed pathway of transformations of Al precipitation products as influenced by aging and change of pH in alkaline conditions. Citrate is present in Al transformation.

peared to form as shown by the persistence of its peaks in the XRD patterns (Figures 4d–4f). Intermediate Al precipitation products must be still predominant since nordstrandite and/or gibbsite along with pseudoboehmite were found in these systems, whose pH was brought to 10.0 (Figures 4d–4f, and 5b–5d). Pathway B in Figure 6 illustrates this transformation process.

Some intermediate Al precipitation products, which were still present at the end of 31–43 days, must have a very low solubility. By increasing the pH of these systems to 10.0, these materials dissolved very slowly. Gibbsite, present in small amounts, was the only Al(OH)₃ polymorph detected (Figures 4f and 5d).

Finally, after 60 days or more (Figures 1e, 2c, and 3d), the increase of pH did not change the final Al precipitation products (Figure 4g) even after 8 months of aging (not shown). Evidently, the pseudoboehmite samples, which formed at the citric acid/Al molar of 0.01 and pH 8.2, were sufficiently stable and the rate of their solubilization was extremely slow, apparently because of their relatively more ordered structure and/or larger crystals. The formation of Al(OH)₃ (gibbsite) from such citrate stabilized pseudoboehmite samples, even if it occurs, would likely require a very long induction period (Figure 6, pathway C).

Our proposed mechanism of formation of Al(OH)₃ polymorphs in alkaline systems could be, at least in part, compared to that proposed by Hsu (1988) in partially neutralized aluminum chloride solutions (pH <

4.1). According to Hsu, the initial OH-Al polymers in the freshly prepared solutions were unstable and transformed, in the absence of nuclei, to stable OH-Al polymers by internal organization; on the contrary, in the presence of nuclei the unstable OH-Al polymers dissociated into monomeric ions, which deposited onto nuclei to form gibbsite. In our experiments the initial noncrystalline Al precipitation products formed at pH = 8.2 and citric acid/Al molar ratio of 0.01 were converted into pseudoboehmite upon aging apparently by a solid state transformation; the citrate stabilized pseudoboehmite was not affected by increasing pH to 10. On the other hand, the formation of nuclei of Al(OH)₃ polymorphs from dissolution of noncrystalline and poorly ordered Al precipitation products evidently occurred by increasing pH to 10. These solubilized monomeric Al species then deposited onto nuclei of Al(OH)₃ polymorphs forming bayerite, nordstrandite, and/or gibbsite.

In conclusion, the nature and solubility of Al precipitation products play a vital role in influencing the subsequent formation of an Al(OH)₃ polymorph that is determined by the rate of its nucleation and crystal growth. A rapid crystallization yields bayerite, a very slow crystallization favors gibbsite, and intermediate conditions favor nordstrandite. Transformations of citrate-stabilized pseudoboehmite to Al(OH)₃ polymorphs were not observed and would likely require a very long induction period.

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