

A PECULIAR MORPHOLOGY OF GIBBSITE AND NORDSTRANDITE CO-CRYSTALLIZED IN THE PRESENCE OF TARTRATE IN A STRONGLY ALKALINE ENVIRONMENT

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Abstract—The nature and morphology of $\text{Al}(\text{OH})_3$ polymorphs obtained by precipitating Al and tartrate at pH 12.0 and at a tartrate/Al molar ratio (R) of 0.1 were studied by X-ray diffraction, transmission electron microscopy and electron diffraction. Co-crystallization of unusually long (up to 18 μm) 'stick-shaped' gibbsite with platy particles of both nordstrandite, mainly, and bayerite was observed. Face-to-face associations of plates nucleated perpendicularly on the gibbsite surfaces parallel to the c axis produced peculiar elongated 'brush'-shaped particles. In a strongly alkaline environment the inhibiting effect of tartrate on $\text{Al}(\text{OH})_3$ polymorph formation is reduced and production of co-crystallized phases with structural crystallographic similarities can be observed.

Key Words— $\text{Al}(\text{OH})_3$ Polymorphs, Alkaline pH, Electron Diffraction, Morphology, Tartaric Acid, TEM.

INTRODUCTION

The crystallization of the three $\text{Al}(\text{OH})_3$ polymorphs, gibbsite, bayerite and nordstrandite, is influenced mainly by pH, and the presence, concentration and nature of inorganic and organic anions and clay minerals (Violante and Violante, 1980; Violante and Huang, 1985; Huang and Violante, 1986; Hsu, 1989; Sposito, 1996; Violante *et al.*, 2002). These factors are inter-related. In the absence of perturbing ligands and at near-neutral or alkaline environments (say at $6.0 \leq \text{pH} \leq 11.0$), the initially formed non-crystalline Al precipitation products convert rapidly into $\text{Al}(\text{OH})_3$ polymorphs, mainly bayerite (Aldcroft *et al.*, 1969; Wefer and Misra, 1987; Hsu, 1989; Violante and Huang, 1993). On the other hand, in the presence of foreign anions, the crystallization of $\text{Al}(\text{OH})_3$ polymorphs may be substantially delayed and/or inhibited in alkaline environments. Bayerite is usually the dominant product when $\text{Al}(\text{OH})_3$ crystallization is rapid, gibbsite is usually the dominant product under conditions where $\text{Al}(\text{OH})_3$ crystallization is retarded but not inhibited, and nordstrandite is formed under intermediate conditions (Violante and Huang, 1985, 1993; Violante *et al.*, 1993). With a proper combination of pH with type and concentration of organic and inorganic ligands, gibbsite, bayerite or nordstrandite in pure or nearly pure form could be prepared in a wide range of pH values (Violante and Jackson, 1979, 1981; Violante and Violante, 1980; Violante *et al.*, 1982).

At different pH values and ligand/Al molar ratios, in the absence or presence of montmorillonite, the crystal habit of $\text{Al}(\text{OH})_3$ polymorphs varies. In particular it has been shown that at pH 9.0–11.0 the presence of strongly chelating organic anions (*e.g.* citrate or malate; ligand/Al molar ratio R of 0.02–0.1) produces nordstrandite crystals more elongated in the c direction. This is probably due to organic anion occupation of the coordination sites of Al on the edge faces parallel to the c axis (Violante *et al.*, 1982; Tait *et al.*, 1983).

The presence of appropriate concentrations of inorganic and organic anions often promotes, at a given pH, the formation of short-range ordered Al precipitation products (including poorly crystalline boehmite, the so called 'pseudoboehmite'). Tartaric acid, which is common in soil environments, mainly in the exudates of plant roots, is the low-molecular weight organic acid most effective at preventing the formation of $\text{Al}(\text{OH})_3$ polymorphs and in promoting the formation of non-crystalline or poorly crystalline Al-oxyhydroxides (Violante and Huang, 1985; Violante *et al.*, 1993, 2002). Samples obtained by precipitating Al and tartaric acid at pH 5.0–11.0 and at R values ranging from 0.01 to 0.1 showed the presence of non-crystalline materials or poorly crystalline boehmite, without the presence of $\text{Al}(\text{OH})_3$ polymorphs, even after >10 years of ageing (Violante *et al.*, 1993). In order to verify the effectiveness of tartrate in preventing $\text{Al}(\text{OH})_3$ crystallization even in strongly alkaline systems, we prepared samples obtained by precipitating Al in the presence of tartrate at R values 0.05–0.1 and at initial pH values ≥ 10.0 .

The purpose of this paper is to report the identification of peculiar crystal forms of $\text{Al}(\text{OH})_3$ polymorphs co-crystallized in the presence of tartaric acid at pH 12.0.

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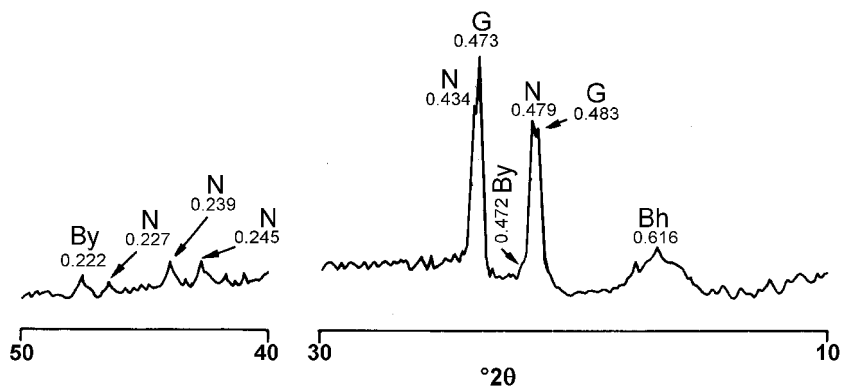


Figure 1. XRD pattern ($\text{CoK}\alpha$ radiation) of oriented clay-aggregate Al products obtained at pH 12.0 and at a tartaric acid/Al molar ratio of 0.1. G = gibbsite, N = nordstrandite, By = bayerite, Bh = poorly crystalline boehmite.

EXPERIMENTAL

An Al precipitation product was obtained by adding, with stirring, 0.1 M NaOH to a mixture of AlCl_3 (1×10^{-2} M) and tartaric acid until a pH of 12.0 was reached; the concentration of tartaric acid was chosen to have a tartaric acid/Al molar ratio, R , of 0.1. The sample was aged in a polyethylene bottle for up to 4 y. The pH of the suspension increased to 12.2 in the first 5–6 months and then decreased to pH 11.4–11.0 after 2–4 y. Aliquots of the aged sample were centrifuged at 10,000 g for 20 min, and the supernatant liquids were filtered through a Millipore membrane filter (pore size 0.025 μm). The precipitation products were dialyzed and analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD analysis was performed on oriented clay-aggregate samples using

Rigaku Geigerflex D/MaxB diffractometer with Fe-filtered $\text{CoK}\alpha$ -radiation generated at 40 kV and 30 mA. The TEM specimens were prepared by drying a drop of dilute suspensions onto a carbon film supported on a copper grid and examined using Siemens Elmiskope 102 and Philips EM300 instruments. Electron diffraction patterns were obtained at 200 kV and calibrated with the diffraction pattern produced by a 10 nm thick preparation of Au in exactly the same conditions of diffraction.

RESULTS AND DISCUSSION

The XRD pattern of the sample synthesized at pH 12.0 and at a tartaric acid/Al molar ratio, R , of 0.1 showed the presence of gibbsite (0.483, 0.437 nm) and

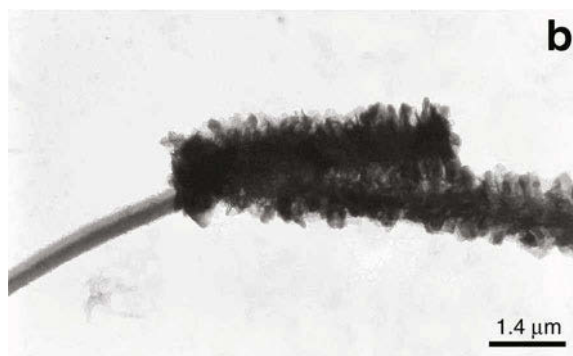
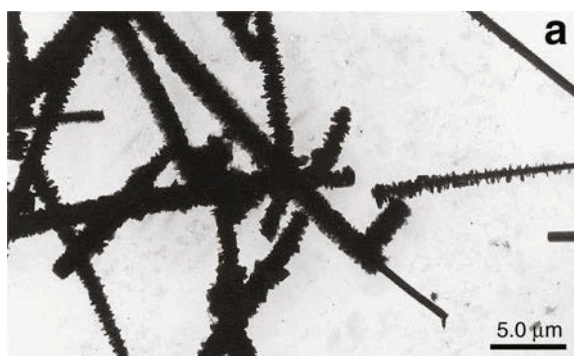


Figure 2. TEM images of complex crystals in which $\text{Al}(\text{OH})_3$ polymorphs have co-crystallized at pH 12.0 and at a tartaric acid/Al molar ratio of 0.1, showing (a and b at higher magnification) long stick-shaped crystals formed by elongated core units (gibbsite) covered by aggregates of thin platy particles of nordstrandite and (c) long crystals without the 'stick core'.

nordstrandite (0.479, 0.434, 0.245, 0.239, 0.227 nm) as well as poorly crystalline boehmite (0.616 nm) and a very small amount of bayerite (0.472 and 0.222 nm) (Figure 1). The mineralogy of the sample did not change significantly with ageing (from 6 months to 4 y). The relative intensities of the 0.483 nm gibbsite 002 reflection and the 0.479 nm nordstrandite 010 reflection were much lower than the published XRD data for Al compounds (Brown, 1980). On the contrary the relative intensities of the 0.437 nm gibbsite 110 reflection and the 0.434 nm nordstrandite 001 reflection were stronger than indicated in the literature (Brown, 1980). This observation suggests the presence of crystals elongated in the crystallographic *c* direction, which enhances the

orientation of the crystals in a sedimented aggregate with their *c* axis parallel to the plane of the glass slide (Violante *et al.*, 1982).

The TEM observations showed unusually long (up to 18 μm) 'stick-shaped' crystals apparently consisting of elongated core units covered entirely or partly by aggregates of thin platy particles (Figure 2a). These particles showed a clear face-to-face association, with their principal face disposed perpendicularly to the stick core (Figure 2b). In many cases, at higher magnification, the long crystals appeared to consist entirely of stacks of tabular particles (*i.e.* no stick-core unit) (Figure 2c). Well developed, thoroughly uncovered stick-shaped crystals were also observed (Figure 3a–c). Typical

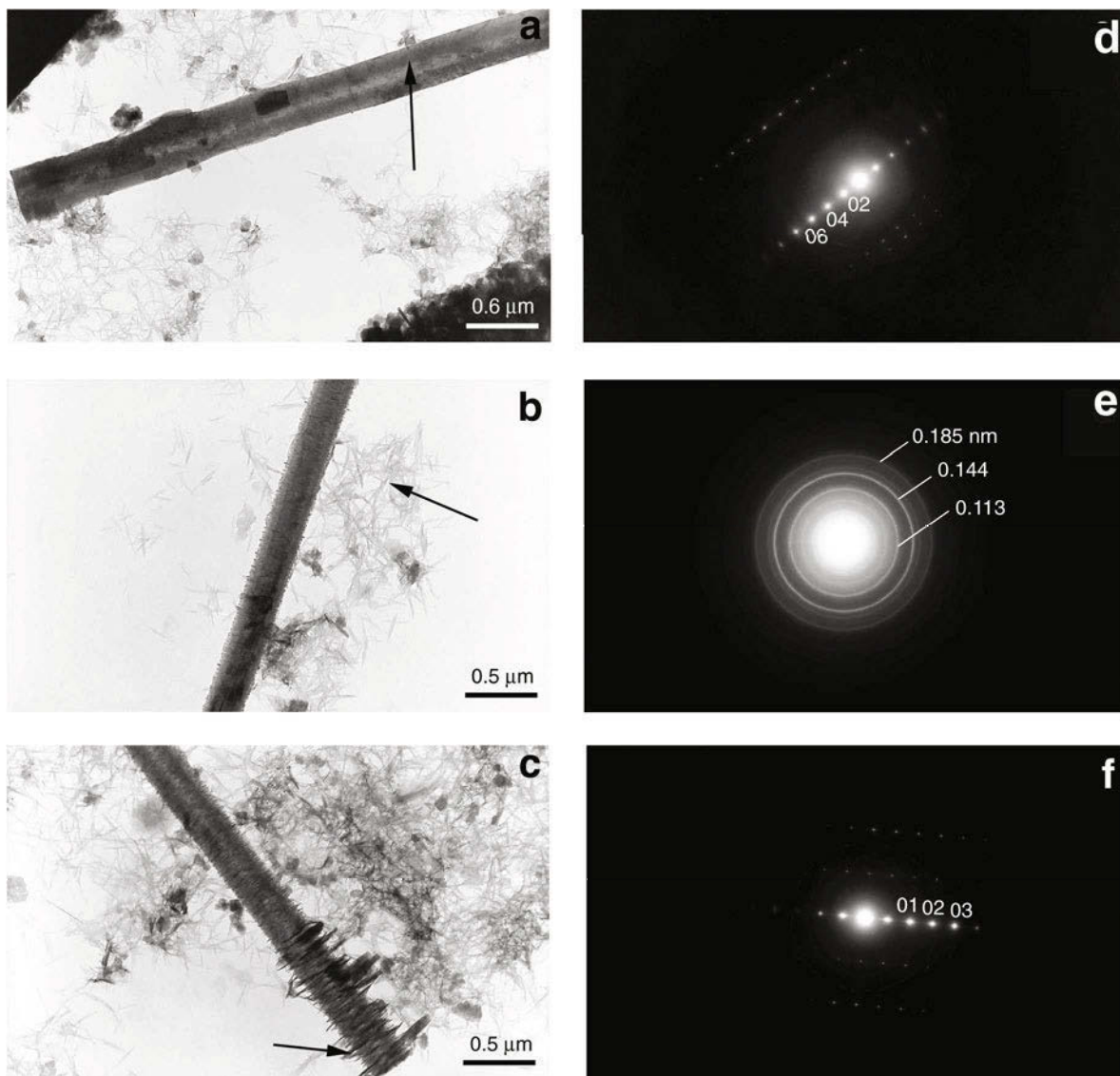


Figure 3. TEM images (a, b, c) and electron diffraction patterns (d, e, f) of complex crystals in which $\text{Al}(\text{OH})_3$ polymorphs have co-crystallized at pH 12.0 and at a tartaric acid/Al molar ratio of 0.1. Well developed, stick-shaped crystals of gibbsite (a, b, c and d) surrounded by a matrix of gel-like/acicular particles of poorly crystalline boehmite (b, c and e). Bayerite (f) from the edge faces of the units covering the 'stick-core' crystal in (c). Arrows show the areas selected for electron diffraction.

selected area electron diffraction patterns from the elongated bare particles (Figure 3a) gave a network of spots with a repeat distance of 0.484 nm in the direction of elongation of the crystal, representing the 001 planes of gibbsite (Figure 3d). Unfortunately, no clear electron diffraction pattern was obtained from the long-stick-shaped crystals, which were partly covered (Figure 2a,b) or which consist entirely (Figure 2c) of particles with a thin tabular morphology. In these cases a prevailing gibbsite electron pattern was superposed upon one or more other patterns preventing their differentiation (data not shown).

The above-mentioned XRD data suggest that the platy particles around the gibbsite-stick core (Figure 2) were mainly nordstrandite; in fact these two Al hydroxide polymorphs were the prevailing phases in the studied sample (Figure 1). Moreover, the crystal habit shown by nordstrandite resembles very closely that formed in the presence of montmorillonite, as identified by Violante and Jackson (1979, 1981) and Violante *et al.* (1982). These authors also observed that at pH 9.0–10.0, nordstrandite crystals nucleated on the montmorillonite surfaces and condensed in clusters of weak face-to-face associations of plates. In the present context, the gibbsite-stick surfaces may act as nucleation centers for the growth of nordstrandite in the form of stacking platy or bladed crystals to give the extraordinarily long 'brush'-shaped particles observed. The long crystals of gibbsite were often surrounded by a matrix of gel-like/acicular particles that seemed to arrange around the stick core to give features (Figure 3b,c) that could be considered intermediates of those described previously (Figure 2a,b). Electron diffraction patterns from the matrix gave a concentric series of rings identifying the presence of poorly crystalline boehmite (Figure 3b,e). Indeed, in a few cases the edge faces of the polycrystalline units covering the stick-core crystals (Figure 3c) gave electron diffraction patterns consistent with bayerite (Figure 3f). This result is consistent with the XRD data showing the presence of small amounts of bayerite in the studied sample, and it suggests that bayerite had co-crystallized with the platy nordstrandite. Nevertheless, bayerite crystals in the usual shape of triangular pyramids were not observed.

In conclusion, when the pH level is particularly high, the inhibiting effect of tartaric acid on Al hydroxide polymorphs formation is reduced and crystallization of gibbsite, nordstrandite and bayerite can be obtained. The tendency of the phases that are characterized substantially by common structural elements in their framework to co-crystallize makes possible the formation of complex crystals with the very peculiar morphology described.

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