

Nature of mixed iron and aluminium gels as affected by Fe/Al molar ratio, pH and citrate

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ABSTRACT: The nature and mineralogy of mixed Al and Fe(III) gels (initial Fe/Al molar ratios (Ri) of 1.0 and 2.5) formed at pH values ranging from 4.0 to 10.0, both in the presence and absence of citric acid (citrate/Fe + Al molar ratio (Rcit) of 0.01 and 0.1) and aged for a long period at room temperature and at 50°C have been studied. The complexes showed considerable differences in the mineralogy of the precipitation products. The samples formed at Ri = 1.0 contained ferrihydrite at pH 4.0, ferrihydrite + gibbsite at pH 5.0–7.0, and hematite + Al(OH)₃ polymorphs + ferrihydrite at pH 9.0–10.0. The samples formed at Ri = 2.5 had greater quantities of poorly crystallized ferrihydrite. Large amounts of Fe+Al (25–82%) were solubilized from the samples aged for 60 days at 50°C by ammonium oxalate. The addition of increasing concentrations of citrate to the gel suspensions containing equimolar amounts of Fe and Al strongly inhibited the formation of Al(OH)₃ polymorphs both at pH 5.0 or 8.5 by promoting the formation of short-range ordered materials. Citrate added initially to Fe-Al solutions (R*cit = 0.1) completely inhibited formation of crystals even after 135 days at 50°C.

The influence of time, initial pH and the presence of inorganic and organic ligands in the presence or absence of clay minerals, on the nature, chemical composition, mineralogy and reactivity of hydrolytic species of Al or Fe has been studied in detail (Cornell & Schwertmann, 1979; Huang & Violante, 1986; Loeppert, 1987; Hsu, 1989; Schwertmann & Taylor, 1989). However, there is little information available on the nature of mixed Fe(III) and Al precipitates formed at different pH values and Fe/Al molar ratios (Gastuche *et al.*, 1964; Goh *et al.*, 1987; Singh & Kodama, 1994; Colombo & Violante, 1996).

Recently, Colombo & Violante (1996) showed that mixed Fe-Al species formed when Fe(III) and Al were coprecipitated at pH 5.0 and at different initial Fe/Al molar ratios, were metastable. With time, they converted, depending on the initial Fe/Al molar ratio (Ri) and temperature, through different soluble, short-range ordered and/or crystalline

species, towards more stable crystalline Al and Fe oxides (mainly gibbsite and hematite). Even after prolonged ageing at 95°C, poorly crystallized Al-substituted ferrihydrite was still present in the precipitates at Ri ≤ 4.0. However, no information was given by these authors on the transformation of Fe-Al species formed at different pH values.

The release of low-molecular weight organic acids by plant roots and microorganisms living in the rhizosphere enhances the weathering of clay minerals at the soil-root interface. Chemical interactions between roots and rhizosphere minerals include precipitation of short-range ordered Fe and Al products and formation of organo-mineral complexes (April & Keller, 1990; Violante & Gianfreda, 1995; Vance *et al.*, 1996).

Citric acid, produced by bacteria in the rhizosphere and identified in root exudates, is one of the most abundant organic acids present in the soil environment (Huang & Violante, 1986; Violante &

Gianfreda, 1995; Vance *et al.*, 1996). Citrate interacts strongly with both Al and Fe and may influence the transformation of mixed Fe-Al species. The influence of organic ligands on the nature and crystallization of mixed Fe-Al gels has not been investigated to date.

The aim of this work was to study the nature and mineralogy of mixed Al and Fe(III) gels formed at pH values ranging from 4.0 to 10.0 both in the presence and absence of citric acid and aged for long periods at room temperature and at 50°C.

MATERIALS AND METHODS

Stock solutions of 0.01 M $\text{Al}(\text{NO}_3)_3$ and 0.01 M $\text{Fe}(\text{NO}_3)_3$ were mixed in different proportions to have samples at initial Fe/Al molar ratio (R_i) of 0, 1.0, 2.5 and ∞ . The solutions (~900 ml) were potentiometrically titrated to pH 4.0, 5.0, 7.0, 8.5, 9.0 and 10.0 by adding CO_2 -free standard 0.25 M NaOH at a feed rate of 2 ml/min. A Metrohm Herisau E 536 automatic titrator in conjunction with an automatic syringe burette 655 Dosimat was used. The final volume of all samples was adjusted to 1 l and the final Fe + Al concentration was 0.005 M. After 24 h ageing of some samples prepared at $R_i = 1.0$ and titrated to pH 5.0 or 8.5, suitable amounts of citrate were added in order to have citrate/Fe + Al molar ratio (R_{cit}) of 0.01 or 0.1. In a few samples citrate was added to the Fe-Al solutions before addition of the base. The suspensions were kept in polypropylene containers and aged at room temperature or at 50°C for up to 135 days. During the ageing process, subsamples were collected and dialysed (Molecular Weight (M.W.) cut off of 15,000) in deionized water, freeze dried and lightly ground to pass through a 100 μm mesh sieve.

The freeze-dried samples were mounted into a holder to obtain random particle orientation and analysed using a Rigaku Geigerflex D/Max IIIC X-ray diffractometer (XRD) equipped with Fe-filtered $\text{Co-K}\alpha$ radiation generated at 40 kV and 30 mA and a scan speed of $1^\circ 2\theta \text{ min}^{-1}$. The XRD traces are the results of eight summed signals. For transmission electron microscopic (TEM) examination, one drop of previously dialysed suspension was deposited onto a carbon-coated Formvar film Cu grid. The TEM micrographs were taken with a Philips CM 120 microscope.

The Fe and Al in the freeze-dried samples were determined by atomic absorption both after dissolu-

tion with 6 M HCl and with NH_4 oxalate at pH 3.0 (Schwertmann, 1964).

RESULTS AND DISCUSSION

Mineralogy of the precipitation products of mixed iron and aluminium gels formed at different pH values

Complexes prepared at initial Fe/Al molar ratios of 1.0 and 2.5 and at pH values of 4.0–10.0 showed strong differences in the mineralogy after 60 days at 50°C (Figs. 1–4). Well-crystallized $\text{Al}(\text{OH})_3$ polymorphs formed throughout the range of pH from the end-member $R_i = 0$ and goethite and/or hematite at $R_i = \infty$ (data not shown).

In the samples at $R_i = 1.0$, well crystallized hematite formed only at pH 9.0 and 10.0, whereas at $\text{pH} \leq 8.5$ poorly crystalline ferrihydrite was the only Fe mineral identified by XRD (Figs. 1,4). Ferrihydrite was the only crystalline species present in the complex formed at pH 4.0 (Figs. 1,3a), whereas $\text{Al}(\text{OH})_3$ polymorphs with existing ferrihydrite were found in the samples formed at pH 5.0, 7.0 and 8.5 (Figs. 1,3b). At $\text{pH} \geq 7.0$ a mixture of $\text{Al}(\text{OH})_3$ polymorphs, bayerite (mainly), nordstrandite and gibbsite, formed without (pH 8.5, Fig. 4) or with hematite (pH 9.0 and 10.0, Fig. 1). Ferrihydrite was not identified by XRD in samples formed at high pH values (Fig. 1), but the presence of poorly crystalline materials was evident by TEM even at pH 10.0 (Fig. 3d).

Electron microscope observation showed hexagonal crystals of gibbsite in the sample formed at pH 5.0 (Fig. 3b) and clusters of face-to-face associations of $\text{Al}(\text{OH})_3$ crystals in the sample obtained at pH 7.0 (Fig. 3c). In the complex formed at initial pH 10.0, the crystals of hematite appeared as large particles with a spherical shape, surrounded by shapeless materials (Fig. 3d).

The samples formed at $R_i = 2.5$ (Fig. 2) contained hematite at $\text{pH} \geq 7.0$ and, surprisingly, at pH 4.0 (as will be discussed below). The XRD patterns of the samples formed at pH 4.0–7.0 revealed the presence of ferrihydrite. Some peaks, indicated by arrows in Fig. 2, suggest the presence of very poorly crystalline ferrihydrite in the samples synthesized at pH 9.0 and 10.0. Indeed, shapeless materials were observed in these materials under electron microscope (not shown).

The $\text{Al}(\text{OH})_3$ polymorphs formed in all the samples at $\text{pH} \geq 5.0$. Gibbsite and bayerite were

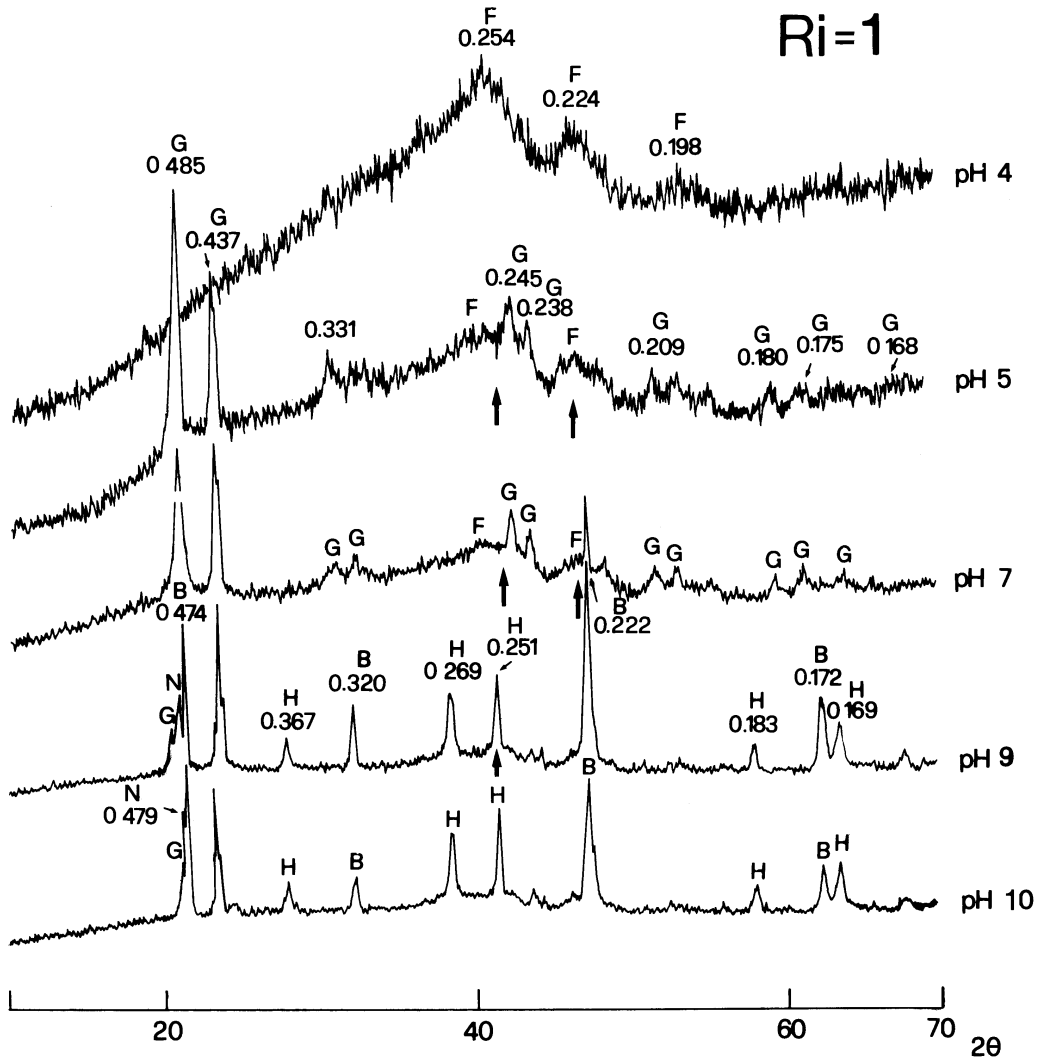


FIG. 1. X-ray powder diffractograms of the precipitation products obtained at pH 4.0–10.0, at initial Fe/Al molar ratio of 1 and aged for 60 days at 50°C. F: ferrihydrite; H: hematite; G: gibbsite; N: nordstrandite; B: bayerite.

the only crystalline Al hydroxides identified by XRD in the samples formed at pH 5.0 and 10.0, respectively. At pH 7.0, much more bayerite was found in the sample at $Ri = 2.5$ than in that at $Ri = 1.0$. In the former, a rapid formation of hematite probably also promoted crystallization of bayerite. In fact, the development of the three $Al(OH)_3$ polymorphs is related to the rate of crystallization. A rapid crystallization leads to the formation of bayerite, whereas a slow rate promotes gibbsite. The intermediate conditions favour nordstrandite

(Huang & Violante, 1986). Similar results were obtained by Gastuche *et al.* (1964). These authors observed that, in samples formed at pH 4.5 by increasing Ri from 0.33 to 1.0, gibbsite was obtained but it decreased in favour of bayerite.

The formation of hematite in the sample formed at pH 4.0 is surprising because hematite did not form at pH 5.0 and $Ri = 2.5$, nor at pH 4.0–8.5 and $Ri = 1.0$. Furthermore, Colombo & Violante (1996) showed evidence that in mixed Fe-Al samples obtained at pH 5.0, hematite formed in materials at $Ri > 4.0$, i.e. in

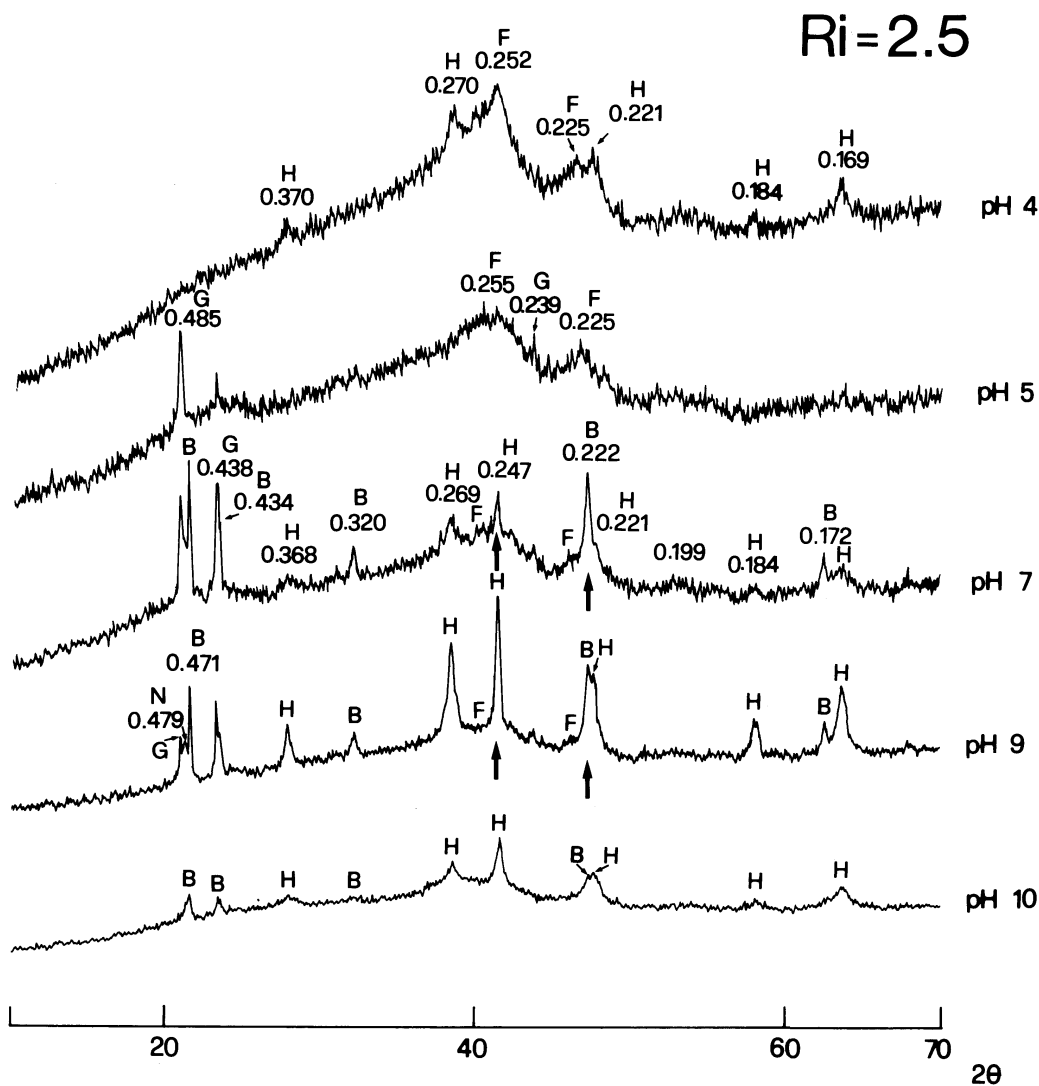


Fig. 2. X-ray powder diffractograms of the precipitation products obtained at pH 4.0–10.0, at initial Fe/Al molar ratio of 2.5 and aged for 60 days at 50°C. Symbols as in Fig. 1.

samples particularly rich in Fe, but only after prolonged ageing at high temperature (50–95°C) (see their Fig. 3). This finding deserves an explanation. It is likely that because at pH 4.0 Al was present mainly in soluble species (monomers and polymers), it is possible that in this sample the Fe-Al precipitation products were particularly rich in Fe, whereas soluble Fe-Al polycations were richer in Al (Colombo & Violante, unpublished data). Colombo

& Violante (1996) also demonstrated that partitioning distribution of Fe and Al in soluble and solid phases of different sizes depended on Ri and time. The effect of pH on the partitioning distribution of Fe and Al in soluble and solid phases and on the transformation of Fe-Al species during ageing process is under investigation; however, the first results indicate that during the ageing the precipitates in the sample formed at Ri = 2.5 and pH 4.0 were

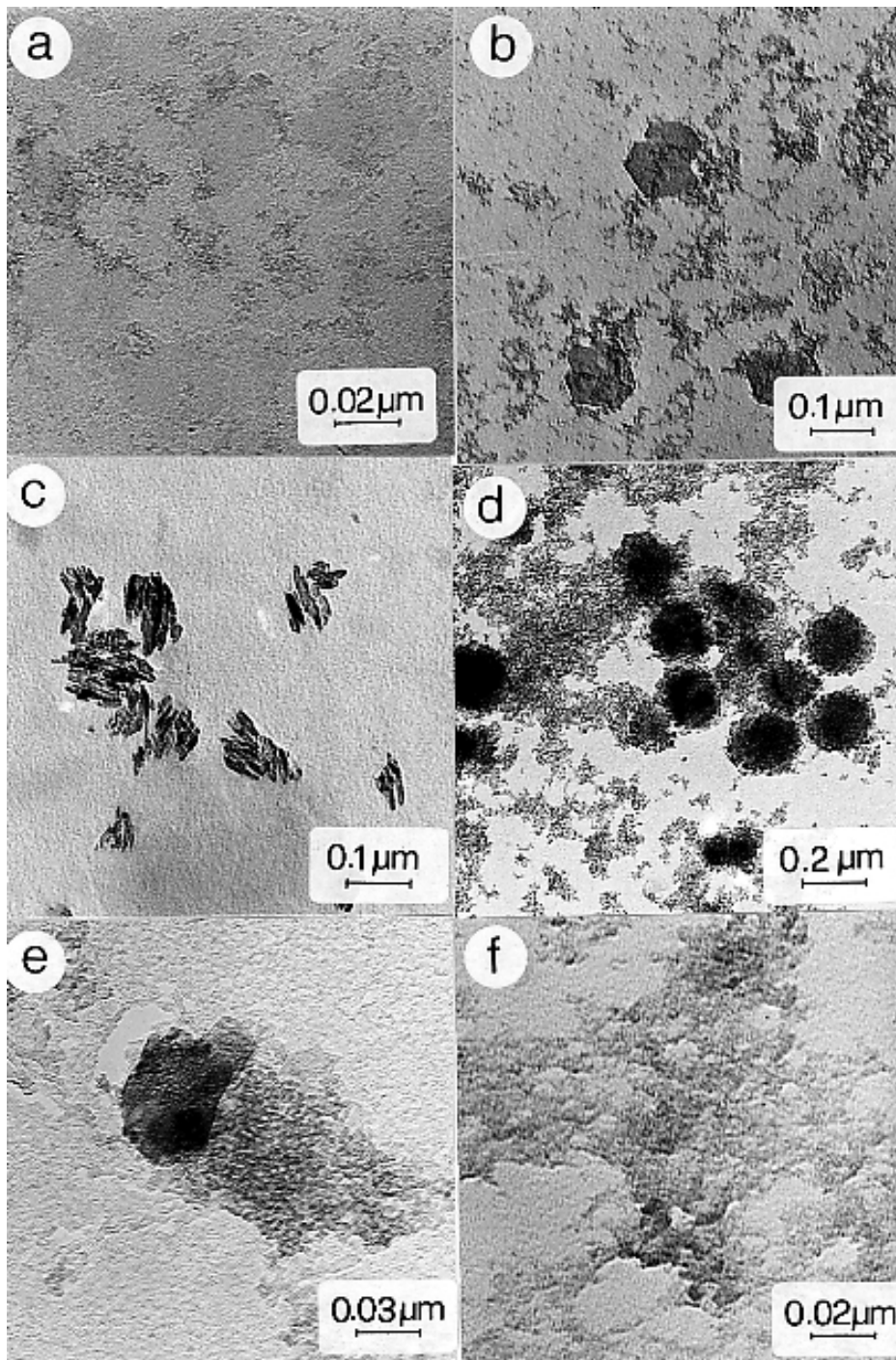


FIG. 3. Transmission electron micrographs of the samples obtained at initial Fe/Al molar ratio of 1, at pH 4.0 (a), 5.0 (b), 7.0 (c) and 10.0 (d) after 60 days at 50°C, and in the presence of citrate (e and f) at pH 5.0 and citrate/Fe+Al molar ratio of 0.1 after 135 days at 50°C. Citrate was added after 24 h (e) and initially with Fe+Al (f).

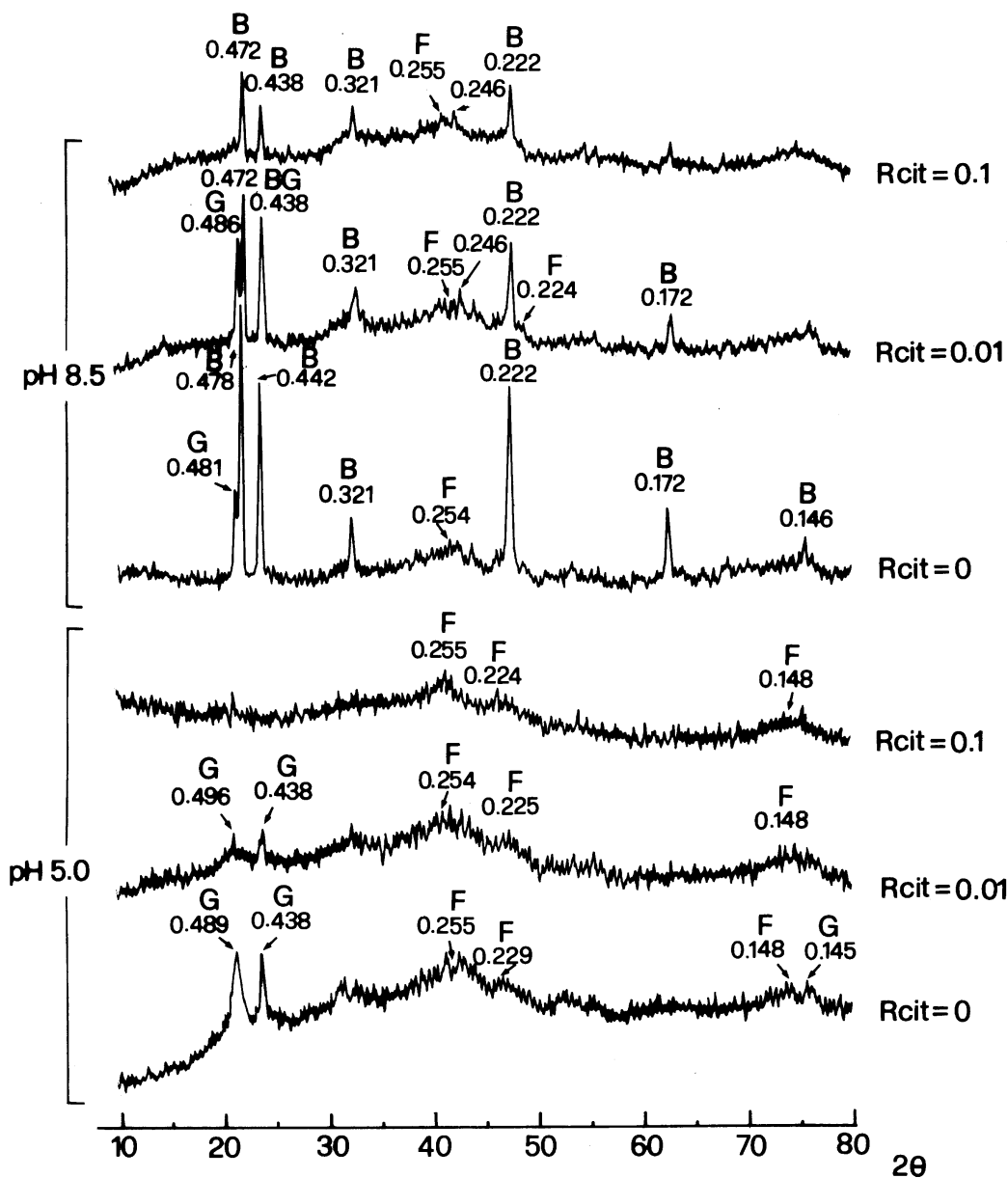


FIG. 4. X-ray powder diffractograms of the precipitation products obtained at pH 5.0 and 8.5, at a citrate/Fe-Al molar ratio of 0.01 and 0.1 and aged for 30 days at room temperature. F: ferrihydrite; G: gibbsite; and B: bayerite.

particularly rich in Fe, so that the formation of hematite from ferrihydrite was possible.

Large percentages of Fe + Al were solubilized by ammonium oxalate solution from the samples at Ri = 1.0 and 2.5, even after 60 days ageing at 50°C

(Fig. 5). Larger amounts of Fe + Al were solubilized, in all the range of pH studied, from the precipitates obtained at Ri = 2.5 (from 82 to 62%) than from those ones formed at Ri = 1.0 (from 58 to 24%).

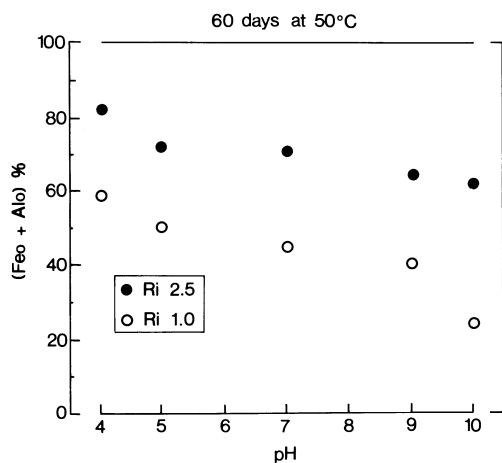


FIG. 5. Percentages of Fe + Al dissolved by ammonium oxalate from the complexes obtained at pH 4.0–10.0 and at an initial Fe/Al molar ratio of 1 and 2.5 after 60 days at 50°C.

Effect of citrate on Fe-Al species transformation

Figure 4 shows XRD patterns of Fe-Al samples formed at pH 5.0 and 8.5 and in the presence or absence of citrate at citrate/Fe + Al (R_{cit}) the molar ratio of 0.01 and 0.1, after 30 days ageing at room temperature. In these samples citrate was added 24 h after the Fe-Al species formation. Increasing concentrations of citrate strongly inhibited the crystallization of $Al(OH)_3$ polymorphs by promoting the formation of short-range ordered materials. At pH 5.0 the presence of well crystallized gibbsite and poorly-ordered ferrihydrite was observed in the absence of citrate ($R_{cit} = 0$), as found in the sample aged for 60 days at 50°C (Fig. 1). A strong reduction ($R_{cit} = 0.01$) or absence of gibbsite ($R_{cit} = 0.1$) occurred for the samples containing increasing quantities of citrate. The presence of poorly crystalline or non-crystalline materials increased by increasing the citrate concentrations even at pH 8.5, but bayerite was still found at $R_{cit} = 0.1$. Hematite did not crystallize in the samples obtained at pH 8.5 after 30 days at room temperature.

After a much longer ageing period (135 days at 50°C) large amounts of poorly crystalline ferrihydrite were still present in all the complexes, particularly in those formed at $R_{cit} = 0.1$ and even in the complexes synthesized at pH = 8.5 (Fig. 6). Only few distorted crystals of gibbsite

were found in the sample obtained at pH 5.0 and $R_{cit} = 0.1$, indicating that citrate strongly inhibited the hydrolytic reactions of the Fe-Al species (Figs. 3e,6). However, it is interesting to note that Violante & Huang (1985) and Violante *et al.* (1993) found that the presence of citrate in Al suspensions (citrate/Al molar ratio of 0.01–0.1) at pH 5.0–11.0 promoted the formation of short-range ordered Al oxyhydroxides (pseudoboehmites) or non-crystalline Al precipitation products and completely prevented $Al(OH)_3$ crystallization even after years of ageing. Evidently, citrate inhibits more strongly Al (and Fe) crystallization when precipitated with Al (or with Fe or with Al+Fe) than when added after Fe and/or Al precipitation. In fact when citrate was added initially to the Fe-Al solutions, the XRD patterns of the samples formed at citrate/Fe-Al = 0.1 ($R_{cit} = 0.1$) indicated non-crystalline materials even after 135 days at 50°C (Figs. 3f,6).

CONCLUSIONS

In Fe-Al gels containing equimolar amounts of Fe and Al ($R_i = 1.0$), hematite formed only at pH > 8.5, whereas in the samples at $R_i = 2.5$ it formed at pH ≥ 7.0 and at pH 4.0. The crystallization of $Al(OH)_3$ polymorphs was prevented at pH 4.0 both in the samples at $R_i = 1.0$ and 2.5 even after a long ageing. Poorly crystalline ferrihydrite was easily identified by XRD in the samples formed at pH ≤ 7.0 . Shapeless precipitates were observed by electron microscopy even in the samples synthesized at pH 10.0, after a long ageing period. Large quantities of Fe and Al (24–80%) were solubilized by ammonium oxalate from the samples aged for 60 days at 50°C, indicating that co-precipitation of Fe and Al promotes the formation of short-range ordered materials (mainly aluminous ferrihydrite). Increasing the concentrations of citrate in samples containing equimolar amounts of Fe and Al strongly inhibited the formation of $Al(OH)_3$ polymorphs by promoting the formation of short-range ordered materials. At $R_{cit} = 0.01$ and 0.1, the crystallization of hematite was completely restrained even at pH 8.5 and after a long ageing period.

In a soil environment, and mainly in the rhizosphere, the mutual interaction of Al and Fe ions, released from clay minerals, and organics (root exudates) may promote the formation of short-range ordered and crystalline materials of different chemical composition, mineralogy, surface properties, stability and reactivity. The effect of organic

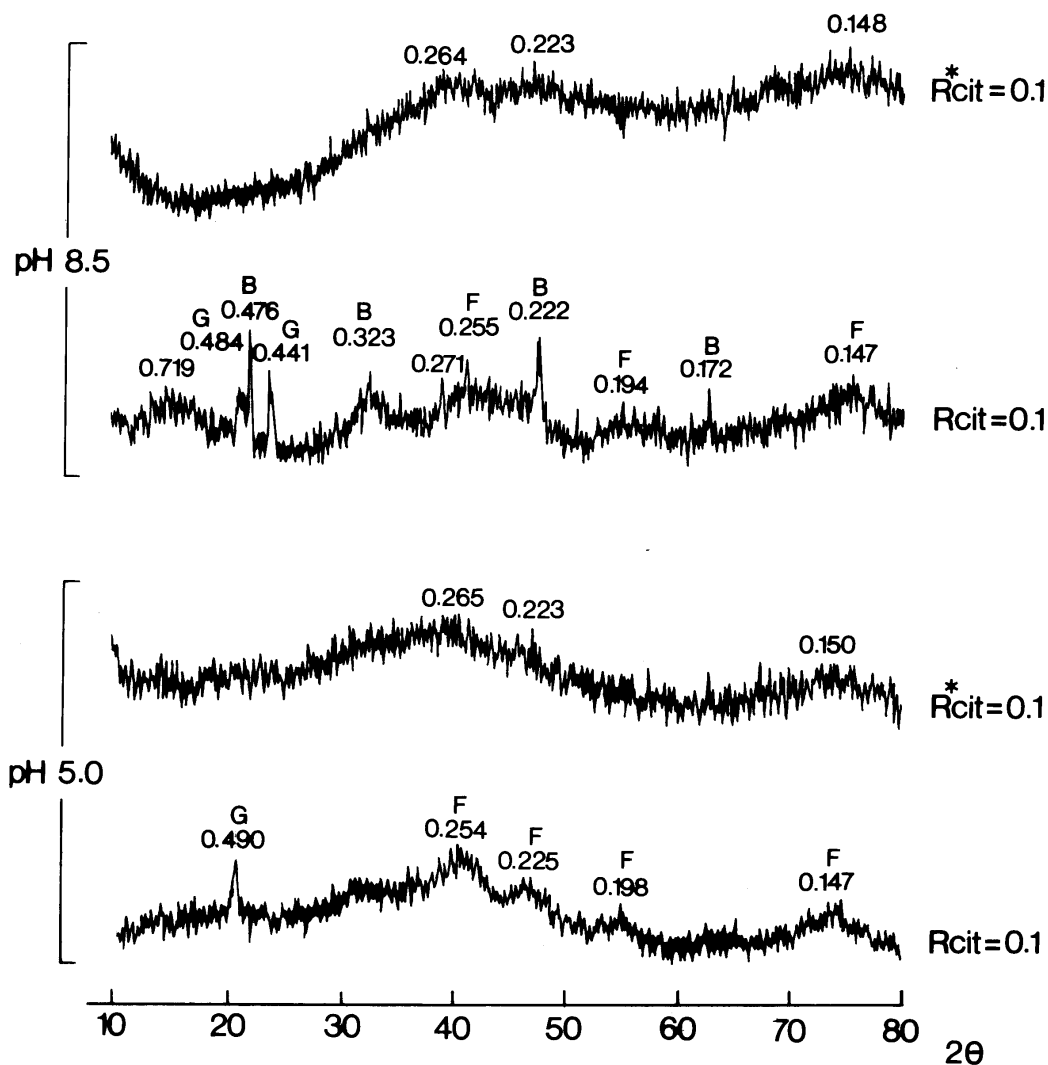


FIG. 6. X-ray powder diffractograms of the precipitation products obtained at pH 5.0 and 8.5, at citrate/Fe-Al molar ratio of 0.1 and aged for 135 days at 50°C. R_{cit} = added in the suspensions after 24 h and R*_{cit} = citrate added initially to the Fe-Al solutions. Symbols as in Fig. 4.

ligands on the chemistry and mineralogy of Fe-Al gels deserves closer investigation.

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