

EFFECT OF TIME AND TEMPERATURE ON THE CHEMICAL COMPOSITION AND CRYSTALLIZATION OF MIXED IRON AND ALUMINUM SPECIES

C. COLOMBO AND A. VIOLANTE

Dipartimento di Scienze Chimico-Agrarie, Università di Napoli "Federico II,"
80055 Portici, Napoli, Italy

Abstract—We studied the influence of time ageing (up to 120 d at 50°C or 30d at 95°C) on the mineralogical and chemical composition of hydrolytic species of mixed aluminum and iron samples formed at pH 5.0 and initial Fe/Al molar ratio (Ri) ranging from 0.1 to 10. The partitioning distribution of Fe and Al in soluble or solid phases of different sizes (<0.01, 0.2–0.01, >0.2 μm) depended on Ri and time. The ratio of Fe to Al of the <0.2 μm Fe-Al species of the samples at Ri ≤ 4 slowly increased with time. Usually the higher Ri the higher the amount of Fe + Al present in soluble or very fine solids (<0.2 μm). With time, high percentages of Fe were found mainly in the <0.01 μm while the Al increase in the >0.2 μm sizes. Gibbsite, without the presence of well-crystallized Fe-oxides was formed in the samples at Ri ≤ 0.5 after 7–120 d at 50°C. In the samples at Ri ≥ 1 low-crystalline ferrihydrite was observed after ≥60 d. Only after 120 d did gibbsite or hematite start to form in the samples at Ri = 1–10. However, even after prolonged ageing at 95°C, low-crystalline ferrihydrite was still present at Ri ≤ 4.

The Fe-Al samples at Ri ≥ 1 aged 32 d at 50°C dissolved almost completely by acid ammonium-oxalate (82–93%), but the samples at Ri ≤ 0.5 were only partially solubilized (13–60%). After further 30 d at 95°C, the percentages of Fe + Al solubilized by oxalate from the samples at R ≥ 0.5 was still relatively high (22–39%).

Key Words—Aluminum, Crystallization, Gibbsite, Iron.

INTRODUCTION

Much work has been conducted on the effect of ageing on the hydrolytic products of Al or Fe (III) at different pH values in the absence or presence of organic and inorganic ligands (Cornell and Schwertmann 1979; Huang and Violante 1986; Cornell et al. 1989; Hsu 1989; Schwertmann and Taylor 1989). The influence of Al in the crystallization process of Fe-oxides and in the formation of Al-substituted goethite and hematite has been worked out in detail (Lewis and Schwertmann 1979; Schwertmann et al. 1979; Schulze and Schwertmann 1984; Barrón et al. 1984; Torrent et al. 1987). In most of the works of Schwertmann and his coworkers (Taylor and Schwertmann 1978; Schwertmann et al. 1979; Lewis and Schwertmann 1979; Schwertmann 1988), the samples were prepared at Fe/Al molar ratio ≥2 and/or at very high pH values, and only the properties of the final products were studied. It has been shown that Al retards or inhibits the formation of some Fe-oxides in favor of others. There is little information available on the effect of time on the chemical composition, nature and crystallization of mixed Fe(III) and Al precipitates obtained at different initial Fe/Al molar ratios (Gastuche et al. 1964; Rengasamy and Oades 1979; Goh et al. 1987; Krishnamurti et al. 1995).

Rengasamy and Oades (1979) showed evidence that polymerization of Al and Fe(III) in mixed solutions (OH/Al + Fe ≤ 2.5) favored the formation of Al-Fe copoly-cations rather than a mixture of separate Al and

Fe species. Furthermore, polycations obtained by adding NaOH to Al and Fe(III) mixed solutions up to OH/Al + Fe molar ratio of 2.5 had Fe/Al molar ratios close to the original solutions. More recently, Goh et al. (1987) found that after prolonged ageing of mixed Al-Fe systems (Fe/Al molar ratio ≤ 1), crystalline Al(OH)₃ and mixed noncrystalline Fe-Al oxide or highly Al-substituted noncrystalline Fe-oxides formed at pH 6.0–7.0.

In this work, we report on the effect of time on the chemical composition, the nature and the stability of hydrolytic species of mixed aluminum and iron solutions (Fe/Al molar ratio ranging from 0.1 to 10) formed at pH 5.0 and aged up 4 months at 50° or for 32d at 50°C and 1 month at 95°C.

MATERIALS AND METHODS

Fresh stock solutions of suitable amounts of 0.01 M Al(NO₃)₃ and 0.01 M Fe(NO₃)₃ were mixed in order to have samples at initial Fe/Al molar ratio of 0, 0.1, 0.25, 0.5, 1.0, 4.0, 10.0 or ∞ (henceforth referred as R0, R0.1, R0.25, R0.5, R1, R4, R10 and R∞). The solutions were potentiometrically titrated to pH 5.0 by adding CO₂-free standard 0.25 M NaOH at a feed rate of 0.5 ml/min. A Metrohm Herisau E 536 automatic titrator in conjunction with an automatic syringe burette 655 Dosimat was used. The OH/Al + Fe molar ratio of the titrated solutions ranged between 2.65 to 3.03 by increasing the initial Fe/Al molar ratio. The final volume of all samples was adjusted to one liter.

Table 1. Chemical composition of the initial solution and amounts of iron and aluminum (mmol L⁻¹) in the filtrates < 0.2 μm of the samples after 7, 20, 32 and 120 d at 50°C.

Samples	Initial chemical composition			7 d			20 d			32 d			120 d		
	Fe	Al	Ri ¹	Fe	Al	Rs ²	Fe	Al	Rs	Fe	Al	Rs	Fe	Al	Rs
R0	0	5.00	0	0	3.22	0	0	1.34	0	0	1.15	0	0	0.80	0
R0.1	0.45	4.55	0.10	0.34	3.22	0.11	0.30	1.27	0.24	0.30	1.13	0.27	0.32	0.69	0.46
R0.25	1.00	4.00	0.25	0.82	3.11	0.26	0.63	1.06	0.59	0.62	0.97	0.64	0.84	0.65	1.29
R0.5	1.66	3.34	0.50	1.49	2.59	0.58	1.32	0.91	1.45	1.32	0.89	1.48	1.50	0.42	3.57
R1	2.50	2.50	1.00	1.62	2.15	0.75	1.76	0.87	2.70	2.08	0.76	2.73	2.43	0.35	7.51
R4	4.00	1.00	4.00	2.95	0.95	3.10	3.33	0.65	5.12	3.58	0.69	5.18	3.31	0.27	12.3
R10	4.55	0.45	10.00	tr	tr	n.d.	tr	tr	n.d.	3.80	0.43	8.83	3.47	0.13	26.7
R∞	5.00	0	∞	tr	tr	n.d.	tr	tr	n.d.	2.72	tr	n.d.	0.40	tr	n.d.

¹ Ri = Initial Fe/Al molar ratio.

² Rs = Fe/Al molar ratio in the filtrates < 0.2 μm.

The final Fe + Al concentration was 0.005 M in all of the samples.

Table 1 shows the chemical composition and the initial molar ratio Fe/Al (Ri) of the starting solutions.

The suspensions were kept in polypropylene containers and aged at 20°C for one week. A pH 5.0 was maintained by adding a few drops of 0.25 M NaOH. Subsequently the suspensions were aged up to 120 d at 50°C without pH adjustment. Aliquots of the samples, previously aged for 32 d at 50°C, were kept at 95°C for another 30 d.

During the ageing process (7, 20, 32 or 120 d at 50°C), subsamples were collected and filtered through Nalgene acetate membranes (pore size < 0.2 μm) or ultrafiltered through Spectra/Por molecular porous fluorocarbon F100 membranes (Molecular Weight (M.W.) cutoff <100,000; ≈0.01 μm). The filtrates were analyzed for Fe and Al by atomic absorption spectroscopy after dissolution with 6 M HCl. Other subsamples were dialyzed (M.W. cutoff = 15,000) in deionized water until Cl⁻ free, freeze-dried and lightly ground to pass through a 100-mesh sieve.

The freeze-dried samples were mounted into a holder to obtain random particle orientation and analyzed using a Rigaku Geigerflex D/Max IIC X-ray diffractometer (XRD) equipped with iron-filtered Co-Kα radiation generated at 40kV and 30 mA and a scan speed

of 1° 2θ/min. The XRD traces are the results of 8 summed signal. Differential thermal (DTA) and thermogravimetric (DTG) analyses of selected samples were obtained using a Netzsch Thermal Analyzer STA 409 programmed from 25°C to 900°C at a rate of 10°C/min, using alumina as the reference material. For transmission electron microscopic (TEM) examination, one drop of a sample suspension, previously dialyzed, was deposited onto a carbon-coated Formvar film Cu grid. TEM electron micrographs were taken with a Philips cm 10.

Fe and Al were also determined by atomic absorption for the dialyzed samples after dissolution with 6 M HCl, pH 3.0 NH₄ oxalate (Schwertmann 1964) or dithionite-citrate-bicarbonate (Mehra and Jackson 1960).

RESULTS AND DISCUSSION

Chemical Composition of the Fe-Al Samples

Table 1 shows the amount (mmol L⁻¹) of Fe and Al present in the filtrates <0.2 μm of the samples aged 7, 20, 32, and 120 d at 50°C. The content of Al of each sample usually decreased with the time. The Fe/Al molar ratio (Rs) in the filtrates <0.2 μm of the samples R0.1–R10 usually increased with ageing. However, after 32 d at 50°C the Fe-Al species of R0.5 characterized by an initial content of 67% Al, R1 by 50% Al and R4 by 20% Al, still showed a high percentage of Al (40% for R0.5, 27% for R1 and 16% for R4), indicating that the <0.2 μm Fe-Al species initially formed were relatively stable. Only after 120 d at 50°C was the content of Al for the < 0.2 μm Fe-Al species of these samples drastically reduced (21.8% for R0.5, 11.7% for R1 and 7.5% for R4). Conversely, large quantities of Fe (71–98% of the Fe initially added) were present in the <0.2 μm fraction of samples R0.1–R10 after 120 d.

The percentages of Fe + Al present in the precipitation products (>0.2 μm) during the ageing are reported in Table 2. After 120 d, the precipitation products from sample R0 contained 84% Al and sample

Table 2. Percentages of Fe + Al present in the precipitation products (particle size > 0.2 μm) after 7, 20, 32 and 120 d of ageing at 50°C.

Samples	(Fe + Al) 7 d	(Fe + Al) 20 d	(Fe + Al) 32 d	(Fe + Al) 120 d
R0	36	73	77	84
R0.1	29	74	77	80
R0.25	21	66	68	71
R0.5	18	55	56	61
R1	25	52	43	44
R4	22	36	15	29
R10	100	100	17	26
R∞	100	100	46	92

Table 3. Amounts (mmol L⁻¹) of the iron and aluminum present in the < 0.01 μm fractions of the samples aged 7 and 120 d at 50°C.

Samples	7 d			120 d		
	Fe	Al	Rs ¹	Fe	Al	Rs
R0	0	0.92	0	0	0.76	0
R0.1	0.31	0.90	0.34	0.02	0.55	0.04
R0.25	0.81	1.22	0.75	0.16	0.48	0.33
R0.5	1.03	1.24	0.83	0.07	0.34	0.20
R1	1.19	0.42	2.83	0.01	0.16	0.06
R4	0.08	tr	n.d.	tr	tr	n.d.
R10	tr	tr	n.d.	tr	tr	n.d.
R∞	tr	tr	n.d.	tr	tr	n.d.

¹ Rs = Fe/Al molar ratio.

R∞ contained 92% Fe, of the amount initially added. In the coprecipitates of Fe and Al, after 120 d, the higher the initial concentration of Fe the lower the percentage of Fe + Al present in the solid phase. In fact, 80% of the initial amount of Fe + Al was precipitated for R0.1., 61% for R0.5, 29% for R4 and 26% for R10. Reported in Table 3 are the amounts (mmol L⁻¹) of Fe and Al present in the filtrates <0.01 μm of the samples aged 7 and 120 d at 50°C. Only traces of Fe and Al were found in the filtrates of R4–R∞ aged 7 or 120 d. After 7 d, 62–99% of Fe and 20–48% of Al found in the filtrates <0.2 μm (Table 1), were present in the filtrates <0.01 μm of the samples R0–R1 (Table 3). Consequently, the Rs values of these hydrolytic products were higher than those of the <0.2 μm fractions (compare Table 1 with Table 3). In contrast, after 120 d negligible or small amounts of Fe were contained in the <0.01 μm fractions of samples R0–R1.

The percentages of Fe + Al present in the <0.01 μm fractions of the samples R0–R1 ranged from 18% (R0) to 46% (R0.5) after 7 d, but from 15% (R0) to <5% (R0.5 and R1) after 120 d (Tables 1 and 3).

Because low or negligible amounts of Al or Fe were removed by dialysis (cut off of M.W. <15,000) during the ageing (data not reported), it appears evident that soluble species had a M.W. > 15,000. Rengasamy and Oades (1979) demonstrated that copoly-cations of Al and Fe formed by hydrolysis on addition of sodium hydroxide up to a (OH)/Fe + Al molar ratio of 2.5 (pH 3.4–5) had M.W. ranging from 20,000 to more than 100,000.

From the data reported in Tables 2–4, it was possible to calculate the percentages of Fe or Al present in the 0.2 μm fractions, between 0.2–0.01 μm and <0.01 μm of all the samples aged 7 or 120 d at 50°C (Figure 1). High percentages of Fe were found mainly in the <0.01 μm filtrates of the samples R0.1–R1 after 7 d and in the 0.2–0.01 μm fractions of the samples R0.1–R10 after 120 d. In the sample R∞, iron predominated in the solid phase >0.2 μm during the ageing period. On the contrary, in the samples R0–R4 Al pre-

Table 4. Percentages of Fe + Al solubilized by dithionite-citrate bicarbonate (DCB) or ammonium oxalate solution (OXA) from the samples aged 32 d at 50°C or 32 d at 50°C and 30 d at 95°C.

Samples	After 32 d at 50°C		After 30 d at 95°C
	DCB	OXA	OXA
R0	2	9	tr
R0.1	25	13	6
R0.25	36	36	15
R0.5	69	60	22
R1	98	82	36
R4	98	93	39
R10	92	92	36
R∞	100	74	tr

dominated in the 0.2–0.01 μm or <0.01 μm fractions after 7 d. With time, its concentration in the solid phase >0.2 μm strongly increased (Table 1; Figure 1) mainly because of the formation of crystals of gibbsite (as discussed below; Figures 2–5).

Mineralogy of the Precipitation Products

The x-ray diffraction patterns (XRD), DTG and DTA curves and electron micrographs of the dialyzed precipitation products of the samples prepared at different initial Fe/Al molar ratios and aged for 7–120 d at 50°C or for 62 d (32 d at 50°C followed by 30 d at 95°C) are shown in Figures 2–5.

X-RAY DIFFRACTION ANALYSES. Figure 2 shows XRD of the samples aged 32 d at 50°C. Well crystallized gibbsite formed from the end member R0 and goethite for R∞, respectively (Figures 2a and 2f). Gibbsite was found in samples R0.1–R0.5. But in sample R0.5, some broad peaks of ferrihydrite were also evident (Figure 2b). The presence of gibbsite was ascertained by XRD in the samples R0–R0.5 after 7 d of ageing (not shown). In samples R1–R10, ferrihydrite was observed after 32–60 d of ageing at 50°C. X-ray diffraction traces show a very broad 2-lines pattern characteristic of poorly crystalline material called 2-lines ferrihydrite in Figures 2c–2e (Schwertmann and Cornell 1991). It was only after further ageing (120 d at 50°C) that we ascertained the formation of gibbsite in samples R1 (Figure 3b) and hematite in R10 (Figure 3d). However in sample R4, ferrihydrite was the only crystalline species identified by XRD (Figure 3c). A few extremely small gibbsite crystals were observed in this sample under the electron microscope (Figure 5d).

After 32 d at 50°C and further ageing for 30 d at 95°C, gibbsite without the co-presence of well crystallized Fe-oxides was found in the samples R0.1–R4 (Figures 3e–f), but in the sample R10, well-crystallized hematite had formed (Figure 3g). The XRD patterns of samples R1 and R4 still showed the presence of ferrihydrite.

These results clearly reveal that initially mixed Fe-

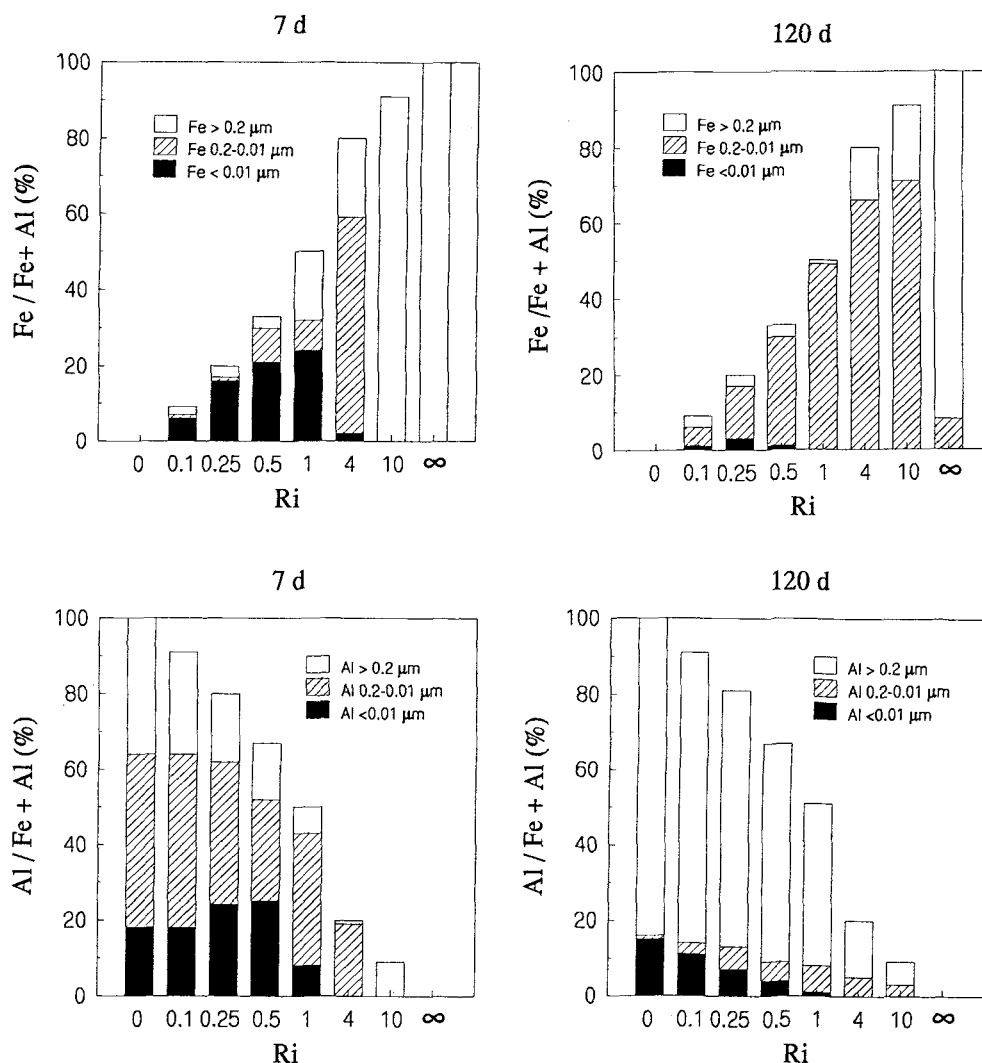


Figure 1. Percentages of Fe and Al in the fractions $>0.2 \mu\text{m}$, between $0.2\text{--}0.01 \mu\text{m}$ and $<0.01 \mu\text{m}$ of the samples aged 7 and 120 d at 50°C . Ri indicates the initial Fe/Al molar ratio.

Al species formed rather than a mixture of separate Al or Fe species. These Fe-Al species were particularly stable and the formation of gibbsite (R1 and R4) or hematite (R10) required many days, up to 120 d or more of ageing at high temperatures. On the contrary, at pH 5.0, gibbsite or hematite and/or goethite formed in a few days or weeks within $0.005\text{--}0.0005 \text{ M}$ Al or Fe solutions aged at 50°C (data not shown).

THERMAL ANALYSES. DTG (Figure 4Aa) and DTA (not shown) curves of sample R0 showed the presence of well-crystallized gibbsite (a strong peak at $300\text{--}310^\circ\text{C}$) after only 7 d at 50°C . In contrast, only short-range ordered materials were present in sample R ∞ after 7 d (Figures 4Af and 4Bf). The DTG curve of this sample aged 7 d showed two broad peaks at ≈ 100 and 300°C (Figure 4Af). Whereas, that of the same sample aged

120 d (Figure 4Ag) showed that the peak at $\approx 100^\circ\text{C}$ strongly decreased and a strong and asymmetric peak at $\approx 310^\circ\text{C}$, attributed to the presence of goethite (confirmed by XRD, Figure 2f) with a shoulder at 260°C formed.

Gibbsite was found in sample R0.5 aged 32–120 d (Figures 4Ab, 4Ba and 4Bb). An increase of gibbsite formation appeared evident with the passage of reaction time (compare Figure 4Ba with Figure 4Bb).

The DTG curves of the samples R1 and R4 aged 32 d or 120 d at 50°C (Figures 4Ac–e), in which the presence of ferrihydrite had been confirmed by XRD (Figures 2c, 2d and 3c), differed from each other. This was probably due to differences in the chemical composition, nature and particle size of the Fe-Al-species (Tables 1–3). The DTA curves of these samples

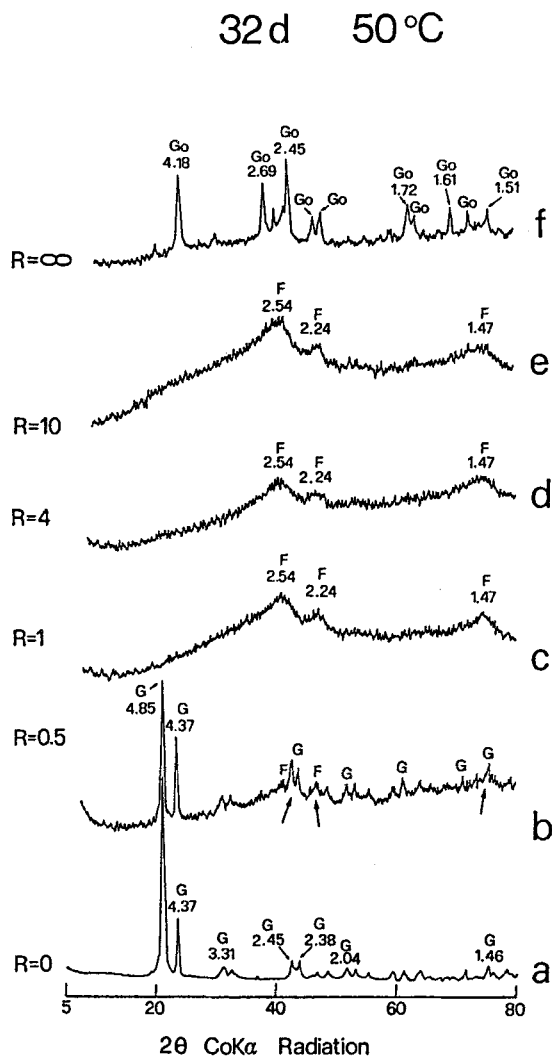


Figure 2. X-ray powder diffractograms of the samples aged 32 d at 50°C. Go stands for goethite, F for ferrihydrite and G for gibbsite. The arrows indicate a possible presence of ferrihydrite. R indicates the initial Fe/Al molar ratio.

showed a strong exotherm between 150 and 350°C with a maximum centered at $\approx 280^\circ\text{C}$ and a shoulder at about 300°C (Figures 4Bc–e). Schwertmann et al. (1979) and Lewis and Schwertmann (1979) found that pure ferrihydrite had a strong and sharp exothermic peak in DTA curve between 300 and 350°C due to the crystallization of hematite, whereas Al-substituted ferrihydrites showed broader peaks the temperatures of which increased with increasing Al substitution up to 564°C at 25 mole percent of added Al. Similar differences were not ascertained in our samples. The Fe–Al species (R1 and R4) showed DTA curves almost similar to that of R_∞ aged 7 d (Figure 4Bf), with only the maximum at 280°C much more evident.

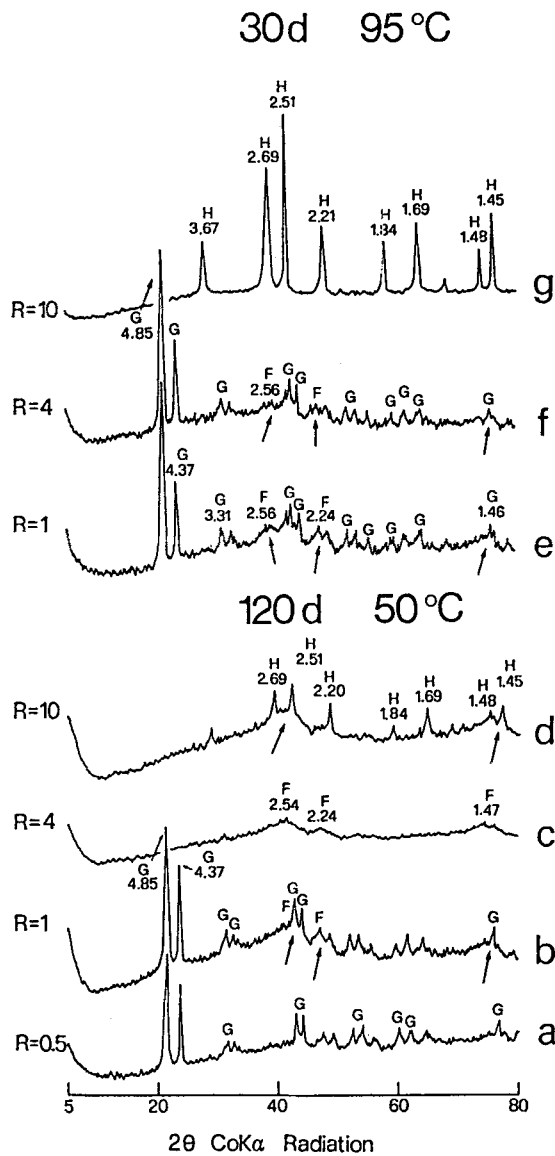


Figure 3. X-ray powder diffractograms of the samples aged 120 d at 50°C and 32 d at 50°C plus 30 d at 95°C . H stands for hematite, F for ferrihydrite and G for gibbsite. R indicates the initial Fe/Al molar ratio.

ELECTRON MICROSCOPE OBSERVATION. Electron microscopy of the samples aged 120 d at 50°C showed evidence that the higher the initial Fe/Al molar ratio the greater the amount of poorly crystalline or noncrystalline materials present in the samples. Morphologically ill-defined materials rarely appeared in samples R_0 – $R_{0.25}$ (Figure 5a). They appeared more often in samples $R_{0.5}$ – $R_{1.0}$ (Figures 5b, 5c) and they were predominant in samples R_4 – R_{10} (Figure 5d, 5e). At high magnification these formless materials appeared to be aggregates of extremely small spherical particles ($< 5\text{ nm}$). Gibbsite crystals which formed in the Fe rich samples

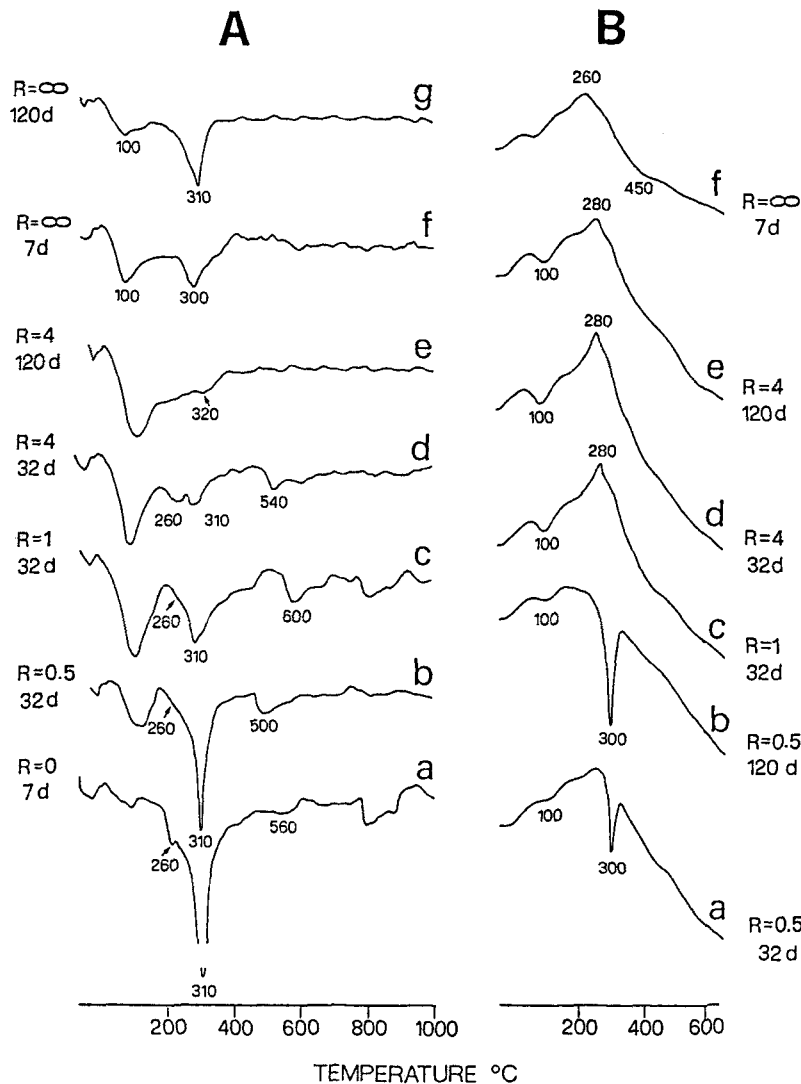


Figure 4. Differential thermogravimetric DTG (A) and differential thermal analysis (DTA) (B) curves of the samples aged 7, 32 or 120 d at 50°C. R indicates the initial Fe/Al molar ratio.

($R > 1$) appeared distorted (Figure 5d) and of extremely small size. In sample R10, the sparse crystals of hematite appeared to have been formed of fine-grained particles with spherical shape and an inner granular structure (Taylor and Schwertmann 1978). Finally, in sample R^∞ , acicular goethite and few small hexagonal crystals of hematite were evident (Figure 5f).

Nature of Fe-Al precipitation products. Table 4 shows the percentages of Fe + Al solubilized by DCB or oxalate solution at pH 3.0 from the samples aged 32 d at 50°C or 32 d at 50°C plus 30 d at 95°C, as referred to the total amounts of Fe and Al solubilized by 6 M HCl.

Samples R1–R10 aged 32 d at 50°C, which showed only low-crystalline ferrihydrite by XRD (Figures 2c–e), were almost completely solubilized by DCB and

oxalate (82–98%). On the contrary, samples R0–R0.5, which showed gibbsite by XRD were only partially solubilized. The amounts of Fe + Al removed from these samples by oxalate ranged from 9% (R0) to 60% (R0.5), confirming that increasing amounts of short-range ordered and/or finely divided Fe-Al materials were formed by increasing the initial Fe/Al molar ratio. From the sample R^∞ , which principally contained goethite and traces of hematite (Figures 2f–5f), 74% of the Fe was solubilized by oxalate. This indicates the presence of large quantities of ferrihydrite or very poorly crystalline Fe-oxides.

After ageing at 95°C, samples R0, R0.1, R0.25 and R^∞ had negligible quantities of Fe + Al solubilized by oxalate ($\leq 15\%$), but the percentages of Fe + Al solubilized by oxalate from the samples R0.5–R10

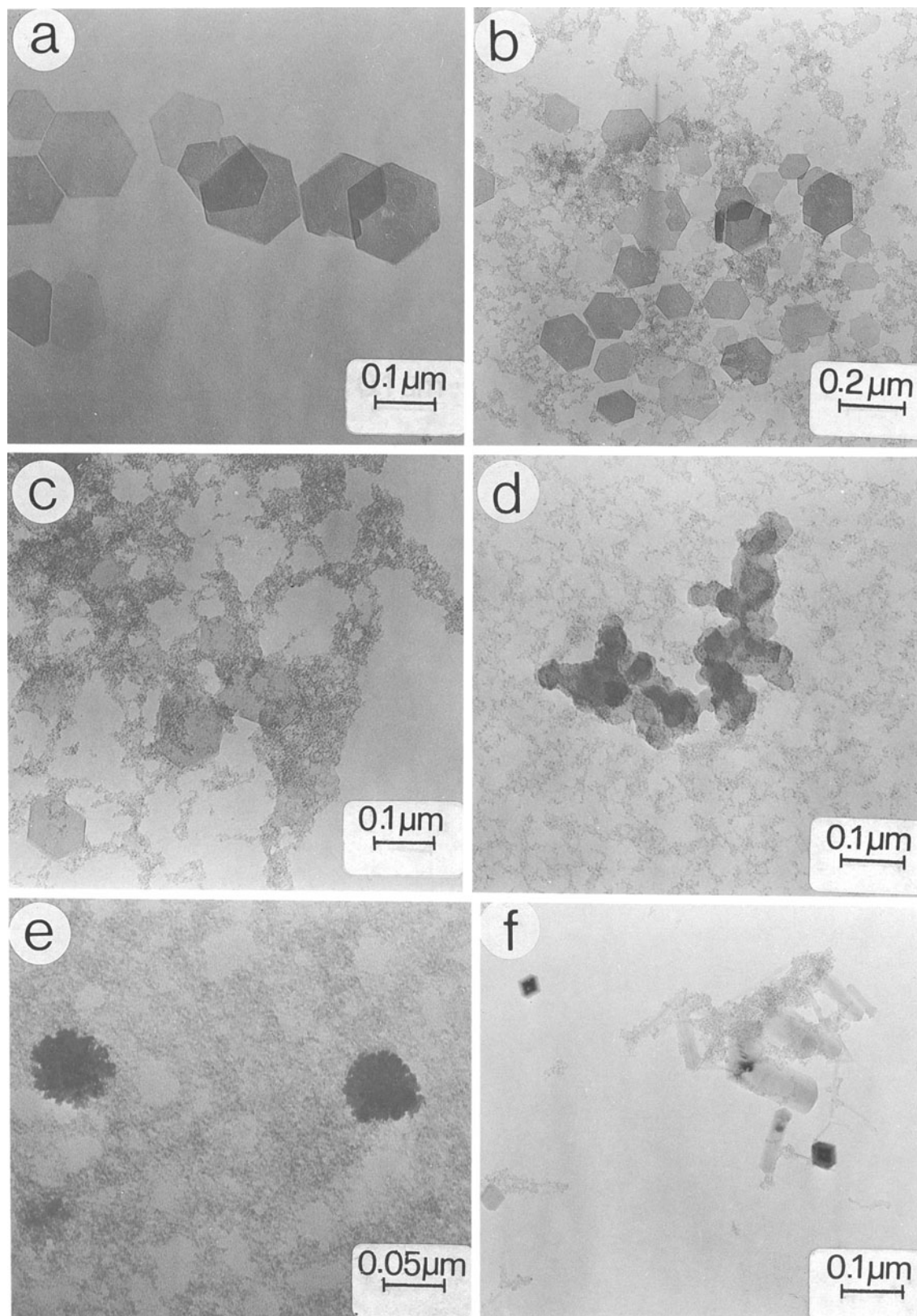


Figure 5. Transmission electron micrographs (TEM) of selected samples aged with 120 d at 50°C. a) R0.1, b) R0.5, c) R1, d) R4, e) R10 and f) R ∞ .

were still relatively high. They ranged from 22% (R0.5) to 36–39% (R1–R10). These results indicate that coprecipitation of Al and Fe at certain initial Fe/Al molar ratios promote the formation of stable poorly crystalline or noncrystalline Fe-Al species.

The ratio R_0 (Fe_0/Al_0), which indicates the ratio of Fe and Al solubilized by ammonium oxalate, for samples aged at 95°C were: R0.5, 4.9; R1, 4.9 and R4, 8.1 (data not shown). This indicates that after prolonged ageing at high temperatures the short-range ordered Fe-Al precipitation products of these samples were particularly rich in Fe, but still contained relatively high amounts of Al (11–17% of Al).

CONCLUSIONS

The data reported in this study show evidence that mixed Fe-Al species form when Al and Fe are coprecipitated at different Fe/Al molar ratios. The initially formed mixed Fe-Al products were metastable and slowly converted, depending on the initial Fe/Al molar ratio (R_i), and temperature, through different soluble, short-range ordered and/or crystalline species toward more stable crystalline Al or Fe-oxides (mainly gibbsite and hematite; Figures 2–6). The Fe/Al molar ratio of the $<0.2 \mu\text{m}$ Fe-Al species slowly increased by ageing (Table 1). The distribution of Fe and Al in soluble or solid phases of different sizes seemed to depend on the initial R value and on the ageing period. Usually, the higher the initial Fe/Al molar ratio the higher the amounts of Fe + Al present in soluble or very fine precipitation products.

The high stability of mixed Fe-Al species appeared also evident. In fact, whereas in unmixed Al or Fe solutions (0.005–0.0005 M) gibbsite or hematite and/or goethite crystallized in a few days or weeks at pH 5.0 and 50°C, in the Fe-Al samples well-crystallized Fe-oxides could not be detected in the samples R0.1–R4 even after prolonged ageing at 50° and 95°C.

Results demonstrate that in soil environments especially acidic conditions and at certain critical Fe/Al ratios, Fe and Al ions may interact with each other forming short-range ordered materials of different chemical composition, size and nature. In addition, it probably exhibits a different reactivity toward nutrients and pollutants, which may persist in soils for indefinite periods of time.

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