Clays and Clay Minerals, Vol. 25, pp. 49–56. Pergamon Press 1977. Printed in Great Britain

CRYSTAL NUCLEATION AND GROWTH IN HYDROLYSING IRON(III) CHLORIDE SOLUTIONS

R. J. ATKINSON*

Department of Chemistry, University of Papua New Guinea, Box 4820, University P.O., Papua New Guinea

A. M. POSNER and J. P. QUIRK†

Department of Soil Science and Plant Nutrition, University of Western Australia, Nedlands, Western Australia, 6009

(*Received* 3 *February* 1976; *and in final form* 26 *July* 1976)

Abstract—0.5 molal iron(III) chloride solutions were hydrolysed at room temperature by base additions in the range OH/Fe mole ratio 0–2.75. After an ageing period the hydrolysed solutions were used to produce amorphous hydroxide gels from which crystalline products were grown at 65°C, at low pH or high pH. Examination of crystal composition and morphology and comparison with similarly treated nitrate solutions showed that the nucleation of hematite and goethite is inhibited in chloride containing solutions, which allow growth of small rod shaped β-FeOOH to predominate or occur exclusively in gels at pH 1–2. The addition of seed crystals of hematite and goethite allows competitive growth of all three minerals. The transformations β-FeOOH → α-Fe_2O_3 and β-FeOOH → α-FeOOH at pH 1–2 proceed by dissolution and reprecipitation and are promoted by adding seed crystals.

INTRODUCTION

Crystal growth from hydrolysing iron(III) chloride solutions shows an interesting example of crystal growth being directed into a particular mineral because of the absence of suitable nuclei for the growth of other, more stable mineral species. Akaganeite (β-FeOOH) is formed from aqueous iron(III) chloride solutions, under a wide range of conditions of hydrolysis, including dilute or concentrated solutions, with base additions ranging from zero up to OH/Fe mole ratio about 2.8, at room temperature or at elevated temperatures (Feitknecht and Michaelis, 1962; Fordham, 1970; Knight and Sylva, 1974; Mackay, 1960; Murphy *et al.*, 1975; Soderquist and Jansson, 1966; Wolf *et al.*, 1967).

The formation of β-FeOOH contrasts markedly with the hydrolytic behaviour of other aqueous iron(III) solutions under comparable conditions of temperature, initial concentration of Fe, and with base additions less than base/Fe mole ratio = 3.0. Iron(III) sulphate solutions hydrolyse at elevated temperatures to produce a complex series of crystalline "basic" iron(III) sulphates (Haigh, 1967). Perchlorate solutions hydrolyse at low temperatures to α-FeOOH (goethite) and γ-FeOOH (lepidocrocite), generally with α-FeOOH predominant (Feitknecht and Michaelis, 1962; Fordham, 1970; Hsu, 1973; Knight and Sylva, 1974; Murphy *et al.*, 1975). Nitrate solutions at low temperatures are reported to hydrolyse to α-FeOOH only (Feitknecht and Michaelis, 1962; Knight and Sylva, 1974; Murphy *et al.*, 1975), with the exception of one report of γ-FeOOH formation in a nitrate solution hydrolysed at 0.0165 M Fe concentration and a base addition of OH/Fe mole ratio near 2.0 (Murphy *et al.* 1975).

At elevated temperatures the hydrolysis products of nitrate, perchlorate and sulphate solutions contain α-Fe_2O_3 (hematite), in part or exclusively, as this mineral is favored by higher temperatures (Atkinson *et al.*, 1968; Christensen 1968; Haigh, 1967; Robins, 1967; Wefers, 1966a). The identification of crystalline products of hydrolysis is complicated, especially at higher temperatures, by the possibility of slow transformations of one crystalline species into another. The transformation β-FeOOH → α-Fe_2O_3 is observed in iron(III) chloride solutions hydrolysed at elevated temperatures without added base (Mackay, 1960), and the transformation γ-FeOOH → α-FeOOH occurs at room temperature and low pH (Murphy *et al.* 1975; Wefers, 1966b).

The investigations summarized above involved iron(III) solutions which were partially hydrolysed to a pH value generally less than 3, by additions of base to give OH/Fe mole ratio ranging from zero to about 2.8. The formation of iron(III) hydroxy cations, by polymerisation processes occurring under these conditions, generally appears to inhibit the formation of crystalline species (Hsu, 1973; Knight and Sylva, 1974; Murphy *et al.*, 1975; Sylva, 1972). Little information is available on whether this is due to inhibited crystal nucleation, or inhibited growth, or both these factors.

The formation of crystalline iron oxides has been investigated also in completely hydrolysed systems, in which base additions are sufficient to give

* Present address: Department of Soil Science and Plant Nutrition, University of Western Australia, Nedlands, Western Australia 6009.

† Present address: Director, Waite Agricultural Research Institute, Glen Osmond, South Australia.

https://doi.org/10.1346/CCMN.1977.0250108 Published online by Cambridge University Press

OH/Fe $\simeq$ 3.0 or greater, corresponding to a final pH greater than about pH 4.5. Rapid and complete hydrolysis results in amorphous iron(III) hydroxide gels, from which α-Fe_2O_3, or α-FeOOH, or mixtures of both may be grown according to the chosen conditions of pH and temperature (Atkinson *et al.*, 1968, and references cited therein; Wefers, 1966a; Collepardi *et al.*, 1972, 1973). Iron(III) hydroxide gels containing chloride form only trace amounts of β-FeOOH when the pH is greater than about 5 (Collepardi *et al.*, 1972), and β-FeOOH formation appears to be completely prevented by washing the gels free or nearly free of chloride (Mackenzie and Meldau, 1959; Schwertmann and Fischer, 1966). Nucleation and growth of β-FeOOH occur only at relatively low pH in the presence of chloride (or fluoride) ions, and the crystals contain small, variable amounts of chloride (or fluoride) (Mackay, 1960).

The process of forming iron(III) hydroxide gels from nitrate solutions allows the simultaneous formation of nucleating material for α-Fe_2O_3 or α-FeOOH, or both. The presence of nucleating material in the parent gel may be demonstrated by growing it into goethite, at high pH, and examining the crystal size and morphology, which are found to be related to the extent of hydrolysis in the iron solution prior to gel formation (Atkinson *et al.*, 1968).

This study examines whether processes of hematite and goethite nuclei formation, similar to those observed for iron(III) nitrate solutions, can occur in iron(III) chloride solutions, at the pH conditions which normally lead to β-FeOOH formation.

EXPERIMENTAL

Solutions were prepared in Pyrex glass vessels by rapid dissolving of A.R. grade $FeCl_3.6H_2O$ or $Fe(NO_3)_3.9H_2O$ followed immediately by the rapid addition and mixing of the necessary amounts of additional water and 2.5 M NaOH to attain the required OH/Fe mole ratio and initial total Fe concentration 0.5 molal. The solutions were allowed to stand for a period ("ageing time", Table 1) at 25°C, with occasional shaking. The pH of the aged solution was then measured, and a second rapid addition of 2.5 M NaOH was made to attain OH/Fe mole ratio 2.68–2.95, or in some cases excess NaOH was added to attain pH $\simeq$ 12. After the second addition of NaOH the precipitated solutions contained typical brown gels, amorphous to XRD, with the exception of the $FeCl_3$ solutions which had been aged for long periods (>6 days), which contained some β-FeOOH. The precipitated solutions were placed in an oven at 65 $\pm$ 1°C. Samplings for XRD, electron microscopy and pH measurements ("pH after crystal growth") were made at various times.

In some experiments, small amounts of aqueous suspensions of synthetic α-Fe_2O_3 and α-FeOOH were added to the solid iron salt (chloride or nitrate) prior to dissolution, to provide seed crystals for artificial nucleation. An amount equal to $\sim$5% of the expected final mass of FeOOH was used. Other preparations of β-FeOOH, having the larger spindle shaped crystal morphology (Gallagher, 1970; Mackay, 1960; Soderquist and Jansson, 1966; Wolf *et al.*, 1967), were made from dilute iron(III) chloride solutions (0.04 M) without added base which was allowed to stand at 65°C (10 days) or room temperature (3 months). Other details, and methods used for XRD, electron microscopy and electron diffraction, are given by Atkinson *et al.* (1968). Phosphate adsorption experiments utilised conventional techniques (Atkinson *et al.*, 1972).

RESULTS AND DISCUSSION

Inhibition of goethite nucleation

The size and morphology of goethite crystals grown at pH 12 and 65°C from iron(III) hydroxide gels are related to the ageing history of the parent iron solution. Iron(III) chloride solutions, which have been hydrolysed to a moderate extent (OH/Fe 0–0.75, ageing time 50 hr) and subsequently precipitated to pH 12, produce goethites which closely resemble the goethites from similarly treated nitrate solutions (Plates 1(a)–1(c), Atkinson *et al.*, 1968). However, differences between chloride and nitrate solutions occur when hydrolysis is more extensive, at greater OH/Fe or longer ageing times.

Chloride solutions aged at OH/Fe = 0.75 until visible precipitation was observed (190 hrs) grew acicular goethite after precipitation to pH 12 (Figure 1), in contrast to similarly treated nitrate solutions which grew smaller, aggregated acicular crystals (similar to Plate 2(b), Atkinson *et al.*, 1968). Chloride solutions aged 50 hr at OH/Fe = 1.50–2.75 and subsequently precipitated to pH 12 grew acicular goethite, similar to Fig. 1. However, the corresponding nitrate solutions resulted in significantly smaller acicular crystals at OH/Fe = 1.50–2.50 (similar to or smaller than Plate 1(d), Atkinson *et al.*, 1968), and a mixture of acicular goethite and larger, twinned goethite at OH/Fe = 2.75 (Fig. 2).

These results show that the number of goethite crystals initiated in gels from extensively hydrolysed Fe(III) chloride solutions generally is smaller than is found from similarly treated nitrate solutions. Twinned goethite crystals, which derive from hematite nuclei (Atkinson *et al.*, 1968; Cornell *et al.*, 1974a; Wefers, 1966a), are not initiated when extensively hydrolysed chloride solutions (OH/Fe = 2.75) are brought to pH 12, although this occurs in similarly treated nitrate solutions (Figure 2).

Inhibition of hematite and goethite formation in low pH gels

A series of experiments similar to those described above was carried out, using smaller amounts for the second addition of NaOH giving final OH/Fe = 2.68–2.95, resulting in pH 1–2 after crystal growth at 65°C. This treatment of Fe(III) chloride

https://doi.org/10.1346/CCMN.1977.0250108 Published online by Cambridge University Press

https://doi.org/10.1346/CCMN.1977.0250108 Published online by Cambridge University Press

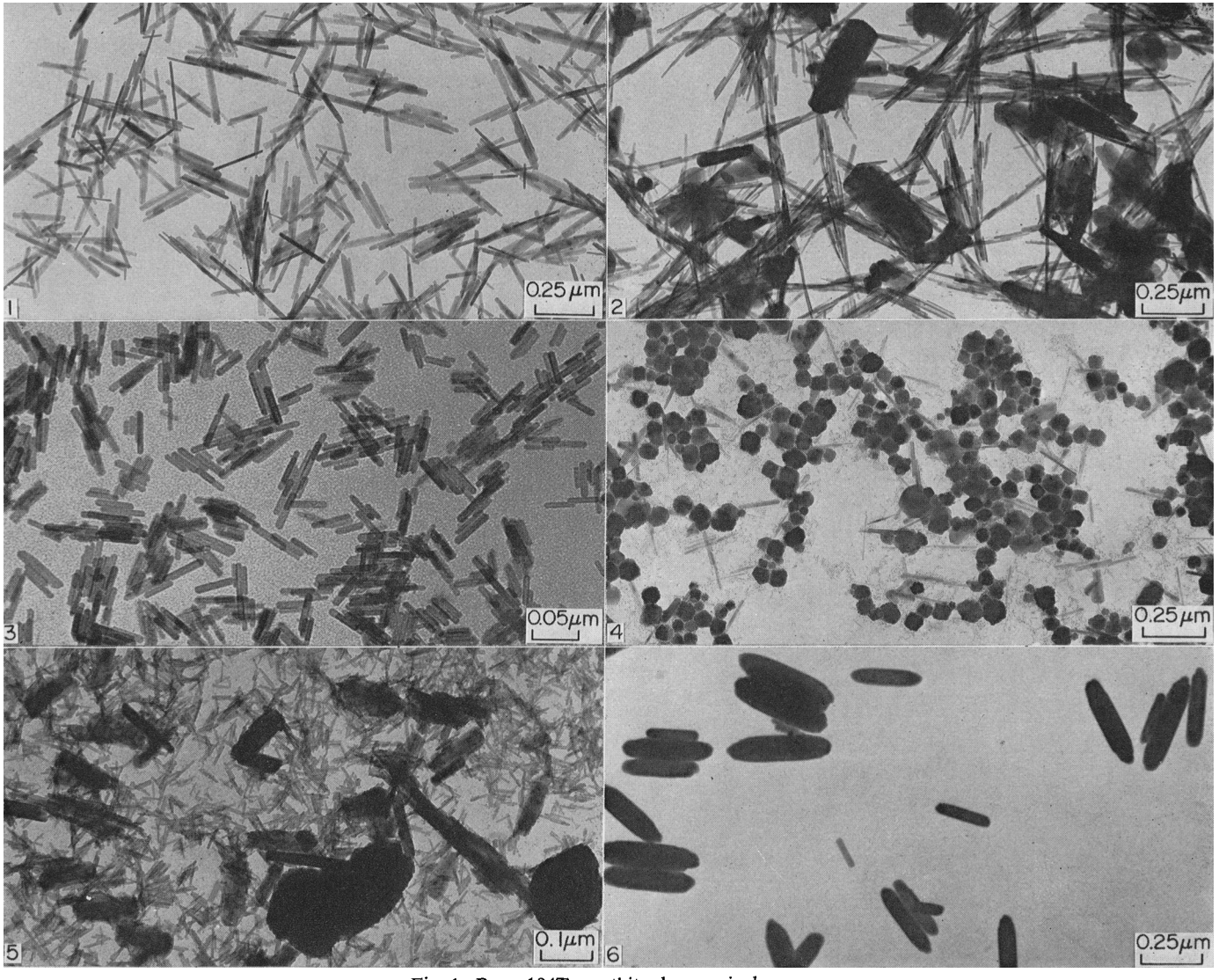


Fig. 1. Prep. 104T, goethite, large acicular.
Fig. 2. Prep 88T, goethite, acicular and twinned.
Fig. 3. Prep. 58, β–FeOOH small rod.
Fig. 4. Prep. 108T, hematite with minor acicular goethite.
Fig. 5. Prep. 123, β–FeOOH with goethite (intermediate sized crystals) and hematite (large rounded crystals). Some amorphous gel particles are present.
Fig. 6. Prep. 57, large spindle shaped β–FeOOH.

Table 1. Composition and morphology of crystalline products from gels produced by precipitation of aged Fe(III) solutions

Prep. No.	OH/Fe	Anion	Ageing time (hr)	pH before ppt.	pH after crystal growth	Composition and morphology of initial crystalline product (6 days) (XRD, e.m.; see text)
104T	0.75	Cl^-	190	1.37	12.2	G, larger acicular (Fig. 1.)
103T	2.75	Cl^-	50	2.35	12.0	Very similar to 104T
88T	2.75	NO_3^-	50	2.50	12.0	G, acicular and twinned (Fig. 2)
118	0	Cl^-	50	1.1	1.40	β-FeOOH, traces H, G.
58	0.75	Cl^-	50	1.2	1.66	β-FeOOH (Fig. 3)
121	2.75	Cl^-	50	2.35	1.88	β-FeOOH
105T	0	NO_3^-	50	1.0	1.52	H major, G trace.
108T	0.50	NO_3^-	50	1.58	1.77	H major, G minor (Fig. 4)
109T	0.75	NO_3^-	50	1.64	1.90	G major, H minor
110T	2.00	NO_3^-	50	1.79	2.05	G, very small acicular
122	0	Cl^-	50	1.1	1.34	*G major, H minor, β minor
61	0.75	Cl^-	50	1.2	1.70	*β-FeOOH
123	2.75	Cl^-	50	2.58	1.24	*β-FeOOH major, G minor, H minor (Fig. 5)
70	0.75	Cl^-	90 days	1.1	1.19	*β-FeOOH
71	0.75	Cl^-	90 days	1.1	1.12	*β-FeOOH

* These preparations were artificially seeded with H and G (122, 61, 123) or with G only (70), or H only (71). (H = hematite, G = goethite)

solutions produced only β-FeOOH as the initial crystalline product, at all conditions of ageing examined (OH/Fe 0–2.75, 50 hr ageing). Crystal sizes were generally very small (e.g. Figure 3).

The corresponding experiments with nitrate solutions produced hematite and goethite mixtures. Slight hydrolysis (OH/Fe = 0, 50 hr) produced 0.1–0.3 μm hematite of ellipsoid shape, with very little goethite. More extensive hydrolysis resulted in progressively smaller amounts of hematite and greater amounts of acicular goethite. The nitrate solution preparation from OH/Fe = 0.50, 50 hr ageing, contained smaller hematite crystals, tending to show a hexagonal outline with the (0001) face normal to the electron beam, together with a smaller proportion of acicular goethite, twinned goethite and epitaxial goethite on hematite (Figure 4). Acicular goethite predominated in a OH/Fe = 0.75, 50 hr ageing preparation, and smaller acicular goethite without hematite occurred in a preparation from OH/Fe = 2.0, 50 hr ageing (Table 1).

The pH values found after crystal growth from nitrate containing gels increased in the series OH/Fe = 0–2.0 (Table 1). This does not appear to have significantly affected the relative amounts of hematite and goethite. A preparation similar to 105 T, but at pH 1.91, showed a similar result, and a preparation similar to 110 T, but at pH 1.45, showed a similar result.

Preparations of β-FeOOH from chloride containing gels in the pH range 1–2 were examined after crystal growth was complete or nearly complete, requiring about 6 days at 65°C. At longer times goethite and hematite formed very slowly from β-FeOOH (see below). Crystal growth was much slower from nitrate containing gels, compared with β-FeOOH growth from chloride containing gels under similar conditions. Some amorphous particles usually remained after 1 month's growth from nitrate containing gels (e.g. Figure 4).

The mechanism of chloride inhibition of α-Fe_2O_3 and α-FeOOH growth was investigated further by experiments using artificially seeded Fe(III) chloride solutions.

Artificially seeded iron(III) chloride solutions

A series of experiments, similar to those described above for low pH gels, were carried out with iron(III) chloride solutions which were artificially seeded by adding small amounts of synthetic hematite and goethite at the commencement of solution ageing. Although the additions of hematite and goethite each amounted to only ~5% of the expected final mass of FeOOH, this represents a relatively large number of seed crystals which is desirable to minimise a possible limitation to the growth of these minerals. Results are illustrated by Preps. 122, 61, 123 (Table 1) which are described after 6 days' growth at 65°C. The comparable non-seeded preparations, which all showed only β-FeOOH at 6 days, are 118, 58 and 121.

Growth of hematite and goethite is promoted by the addition of seed crystals to slightly hydrolysed (OH/Fe = 0, 50 hr) and extensively hydrolysed (OH/Fe = 2.75, 50 hr) Fe(III) chloride solutions (e.g. Figure 5). These results show that the absence of hematite and goethite from chloride containing gels at low pH is due in part to inhibition of nuclei forming processes for these crystals.

Growth of hematite and goethite may be inhibited also by competitive growth of β-FeOOH. This circumstance is illustrated by Prep. 61 (OH/Fe = 0.75, 50 hr) which had conditions favoring an earlier commencement of β-FeOOH growth. In this case the addition of seed crystals did not promote the growth of hematite and goethite. Also, growth of β-FeOOH

https://doi.org/10.1346/CCMN.1977.0250108 Published online by Cambridge University Press

was observed to be faster in Prep. 61, compared with Prep. 122 and 123. This suggests that rapid growth of β-FeOOH, promoted by earlier and more rapid nucleation, also may prevent growth of hematite and goethite. When β-FeOOH nucleation is slower (illustrated by Preps. 122 and 123), the growth of β-FeOOH was slower and less effective as a competitor with hematite and goethite growth.

The solubility of amorphous gel particles is greater than the solubility of β-FeOOH (Fordham, 1970). The rate of dissolution is probably greater for amorphous gel particles, compared with crystalline β-FeOOH (Cornell *et al.*, 1974b). Thus both thermodynamic and kinetic considerations indicate that there should be a faster rate of growth for hematite and goethite from amorphous gel particles, compared with the rate of growth through the transformations β-FeOOH → α-FeOOH, and β-FeOOH → α-Fe_2O_3.

Transformations β-FeOOH → α-Fe_2O_3 and α-FeOOH

Rates of growth of hematite and goethite from dissolving β-FeOOH, in the absence of amorphous gel particles, were examined qualitatively by extended observations on a number of the β-FeOOH preparations which have been described above. These were left at 65°C, without washing, and examined at 21, 100 and 150 days. In some cases the β-FeOOH suspension was adjusted down to pH 1.1–1.4 by HCl addition (to increase the concentration of dissolved iron for the low pH transformation), or to pH 12–12.5 by NaOH addition to study transformation at high pH.

Suspensions of β-FeOOH brought to pH 12–12.5 undergo slow transformation to α-FeOOH at 65°C, without α-Fe_2O_3 growth occurring. Seeding with α-FeOOH accelerates the transformation. At pH 1–2, 65°C, β-FeOOH transforms to both α-Fe_2O_3 and α-FeOOH, or to α-Fe_2O_3 only, depending on conditions. Some examples of low pH transformations are given in Table 2 (refer to Table 1 for details, and products found at 6 days).

Table 2. Transformations of β-FeOOH at low pH

Prep. No.	Products found (see Table 1 for initial products)
118	H major, G minor (21 days)
58	β-FeOOH (21 days) → H only (150 days)
121	β-FeOOH (21 days → β major, H trace (50 days) → H only (150 days)
122*	G, H both major (21 days)
61*	β major, H trace, G trace (21 days) → β major, G minor, H minor (250 days, 28°C)
123*	H major, G minor (21 days)
70*	G major, β minor, H trace (100 days) → G major, H minor (150 days)
71*	H only (150 days)

* Seeded. See Table 1 for details.

The growth of hematite and goethite from amorphous gel particles at low pH in the presence of chloride ions (e.g. the seeded Preps. 122, 123 at 6 days) is relatively rapid compared with growth of hematite and goethite occurring only by transformation from well developed β-FeOOH (e.g. Preps. 58, 61, 70, 71). The β-FeOOH produced from moderately hydrolysed solutions (OH/Fe = 0.75, Preps. 58, 61, 70, 71) transforms more slowly at pH 1–2 than β-FeOOH produced under other conditions (OH/Fe = 0, 2.75). An exception to this observation is Prep. 121 (OH/Fe = 2.75, not seeded), for which the relative slowness of the transformation appears to be due to a long induction period being required for hematite nucleation to occur, as the comparable seeded preparation (Prep. 123) lost β-FeOOH relatively quickly.

The growth of goethite as a major product of β-FeOOH transformation at pH 1–2, 65°C, appeared to require seeding which was goethite alone (Prep. 70). Goethite was a minor component, or was absent, in unseeded preparations undergoing transformation. Thus the transformation β-FeOOH → α-Fe_2O_3 appears to occur more readily than β-FeOOH → α-FeOOH. Both transformations can proceed together, possibly with the former occurring at a slightly greater rate, in β-FeOOH seeded with both hematite and goethite. In one example (Prep. 70) the results suggest that there may have been some growth of hematite through the transformation α-FeOOH → α-Fe_2O_3.

The transformation of β-FeOOH to hematite and goethite at low pH does proceed at a measurable rate at room temperature (28°C), provided that hematite and goethite nuclei are present initially. For example, Prep. 61, after growth at 65°C for 0–21 days, showed significant further growth of both hematite and goethite during subsequent standing (21–250 days) at room temperature. However, unseeded preparations of β-FeOOH are quite stable. For example, a preparation similar to Prep. 58, but grown entirely at room temperature, showed no detectable α-Fe_2O_3 or α-FeOOH after 4 yr.

The relatively slow rates of the transformations of β-FeOOH to hematite and to goethite, and the promotion by seeding, indicate that both these transformations proceed by dissolution and reprecipitation of low molecular weight species.

Crystal morphology and properties of β-FeOOH.

Nearly all studies on β-FeOOH have noted only the familiar "spindle" or "cigar" shaped crystals (Figure 6), which have much larger sizes than the rod shaped β-FeOOH crystals prepared by the methods described above. The small rod shaped crystals show widths of 50–100 Å and lengths 200–600 Å (Figure 3 and other Preps, not shown). These crystals are a dark brown to reddish brown color (typically Munsell 10YR 2/3 when dried on ceramic tiles) while the spindle shaped crystals appear much lighter brown (10YR 4/6).

https://doi.org/10.1346/CCMN.1977.0250108 Published online by Cambridge University Press

The small rod shaped β-FeOOH crystals show well defined electron diffraction ring patterns, and *d* spacings from both electron diffraction and XRD show very good agreement with standard data (Mackay, 1960). However, the XRD patterns show weaker and considerably broadened lines compared with patterns from spindle shaped crystals. The small rod shaped crystals readily develop a mottled appearance during prolonged exposure to an electron beam. In some examples it appears possible that the rods are hollow tubes, as proposed by Gallagher (1970), but in general a hollow rod appearance was not detected.

Preparations of spindle shaped β-FeOOH adsorbed 120–130 μmole phosphate per g, at pH 4.0 and solution phosphate concentration about 2.2 mM, in 0.1 M NaCl medium. Greater phosphate adsorption, 600–700 μmole/g, under similar conditions, occurred with the small rod shaped crystals, which have a greater surface area. Constant concentrations of phosphate in solution were found after 1 day for spindle shaped crystals, in contrast to adsorption experiments with small rod shaped crystals which required reaction periods greater than 8 days. Gallagher (1970) has proposed a structure for the larger spindle shaped crystals, based on square tubular subcrystals of size similar to the small rod shaped β-FeOOH crystals. However in phosphate adsorption reactions there is no breakdown of the larger spindle shaped crystals into smaller subcrystals. If such breakdown or fragmentation were to occur, the amount of phosphate adsorption by the larger spindle shaped crystals would be expected to increase from 120–130 μmole/g to 600–700 μmole/g.

The phosphate adsorption by small rod shaped β-FeOOH is considerably larger than that of high surface area goethite (Atkinson *et al.*, 1972), but still much smaller than phosphate adsorption by amorphous iron hydroxide gels (about 2000 μmole/g, under comparable conditions).

The transformation β-FeOOH → αFeOOH at pH 12–12.5, 65°C, requires much longer periods for the spindle shaped crystals, compared with periods of several weeks required for small rod shaped β-FeOOH. This observation, and the results for amount of phosphate adsorption, are not inconsistent with a tubular subcrystal structure for spindle shaped β-FeOOH (Gallagher, 1970). However, it appears that the spindle shaped crystals are quite resistant to breakdown into individual small rod shaped crystals.

CONCLUSIONS

The hydroxide gels prepared from hydrolysed iron(III) chloride solutions differ from gels produced from similarly hydrolysed iron(III) nitrate solutions. At high pH, the gels produced from extensively hydrolysed iron(III) chloride solutions (aged at OH/Fe = 1.50–2.75 prior to precipitation) grow larger acicular goethite, and do not initiate the twinned goethite crystals which derive from hematite nuclei. In the extensively hydrolysed solutions, the presence of chloride ions tend to inhibit hematite and goethite nucleation, compared with similarly hydrolysed nitrate solutions.

These results are confirmed by crystal growth experiments with iron(III) hydroxide gels at low pH. Inhibition of hematite and goethite crystal nucleation in hydrolysing iron(III) chloride solutions delays or prevents growth of these minerals. Consequently, low pH gels prepared from hydrolysed iron(III) chloride parent solutions have crystal growth directed into β-FeOOH with no growth or only slight growth of hematite and goethite, at 65°C. The addition of seed crystals of hematite and goethite to chloride containing gels at pH 1–2, 65°C, allows competitive growth of all three minerals at the expense of amorphous gel particles.

Growth of hematite and goethite can continue at pH 1–2 by dissolution of β-FeOOH, at a relatively slow rate compared with growth from amorphous gel particles. Thus extended periods of observation of α-Fe_2O_3, α-FeOOH and β-FeOOH mixtures at low pH are required to show the eventual disappearance of β-FeOOH. The transformations of β-FeOOH occur more readily when seed crystals are present. Seeding with hematite alone directs the transformation towards pure hematite, and seeding with goethite alone directs the transformation largely into this mineral with only minor hematite. The transformation β-FeOOH → α-FeOOH appears to occur only when seeded with goethite. The influence of seed crystals in promoting both transformations suggests that these proceed by dissolution of β-FeOOH and reprecipitation on goethite and hematite surfaces. These processes would involve low molecular weight species in solution, in contrast to the growth of hematite from amorphous gel particles by aggregation (Fischer and Schwertmann, 1975).

The existence of two distinctly different morphological types of β-FeOOH, the small rod shaped crystals generally observed in this study and the larger spindle shaped crystals observed in earlier studies, offers potentially interesting comparisons for adsorption reaction studies.

Acknowledgements—Part of this work (electron microscopy) has been generously supported by the Australian Research Grants Committee. We thank Mr. T. Armitage and Mr. G. Hewson for assistance with electron microscopy.

REFERENCES

Atkinson, R. J., Posner, A. M. and Quirk, J. P. (1968) Crystal nucleation in Fe(III) solutions and hydroxide gels: *J. Inorg. Nucl. Chem.* **30,** 2371–2381. (Note: Legends to plates should read: Electron micrographs of goethite. Magnification ×40,000).

Atkinson, R. J., Posner, A. M. and Quirk, J. P. (1972) Kinetics of isotopic exchange of phosphate at the α-FeOOH–aqueous electrolyte interface: *J. Inorg. Nucl. Chem.* **34,** 2201–2211.

https://doi.org/10.1346/CCMN.1977.0250108 Published online by Cambridge University Press

Christensen, A. N. (1968) Hydrothermal preparation of goethite and hematite from amorphous iron(III) hydroxide: *Acta Chem. Scand.* **22,** 1487–1490.

Collepardi, M., Massidda, L. and Rossi, G. (1972) Ageing of iron oxide gels: *Trans. Instn. Mining Metall. (Sect. C. Mineral Process. Extr. Metall.)* **81,** C43–C46.

Collepardi, M., Massidda, L. and Rossi, G. (1973) Effect of pH and salt additions on ageing of ferric iron oxide gels: *Trans. Instn. Mining Metall. (Sect. C. Mineral Process. Extr. Metall.)* **82,** C88–C91.

Cornell, R. M., Posner, A. M. and Quirk, J. P. (1974a) Crystal morphology and the dissolution of goethite: *J. Inorg. Nucl. Chem.* **36,** 1937–1946.

Cornell, R. M., Posner, A. M. and Quirk, J. P. (1974b) The dissolution of synthetic goethites: the early stage: *Soil Sci. Soc. Proc.* **38,** 377–378.

Feitknecht, W. and Michaelis, W. (1962) Ueber die Hydrolyse von Eisen(III)-perchlorat-Loesungen: *Helv. Chim. Acta.* **45,** 212–224.

Fischer, W. R. and Schwertmann, U. (1975) The formation of hematite from amorphous iron(III) hydroxide: *Clays & Clay Minerals* **23,** 33–37.

Fordham, A. W. (1970) Sorption and precipitation of iron on kaolinite III. The solubility of iron(III) hydroxides precipitated in the presence of kaolinite: *Aust. J. Soil. Res.* **8,** 107–122.

Gallagher, K. J. (1970) The atomic structure of tubular subcrystals of β-Iron(III) oxide hydroxide: *Nature* **226,** 1225–1228.

Haigh, C. J. (1967) The hydrolysis of iron in acid solutions: *Proc. Aust. Inst. Mining and Metallurgy* **223,** 49–56.

Hsu, Pa Ho (1973) Appearance and stability of hydrolysed $Fe(ClO_4)_3$ solutions: *Clays & Clay Minerals* **21,** 267–277.

Knight, R. J. and Sylva, R. N. (1974) Precipitation in hydrolysed iron(III) solutions: *J. Inorg. Nucl. Chem.* **36,** 591–597.

Mackay, A. L. (1960) β-Ferric oxyhydroxide: *Mineralog. Mag.* **32,** 545–557.

Mackenzie, R. C. and Meldau, R. (1959) The ageing of sesquioxide gels I. Iron oxide gels: *Mineralog. Mag.* **32,** 153–165.

Murphy, P. J., Posner, A. M. and Quirk, J. P. (1975) Chemistry of iron in soils. Ferric hydrolysis products: *Aust. J. Soil Res.* **13,** 189–201.

Robins, R. G. (1967) Hydrothermal precipitation in solutions of thorium nitrate, ferric nitrate and aluminium nitrate: *J. Inorg. Nucl. Chem.* **29,** 431–435.

Schwertmann, U. and Fischer, W. R. (1966) Zur Bildung von α-FeOOH und α-Fe_2O_3 aus amorphem Eisen(III)-hydroxid: *Z. Anorg. Allgem. Chem.* **346,** 137–142.

Soderquist, R. and Jansson, S. (1966) On an X-ray and electron microscope study of precipitates formed by the hydrolyses of iron(III) in 0.5 M NaCl ionic medium: *Acta Chem. Scand.* **20,** 1417–1418.

Sylva, R. N. (1972) The hydrolysis of iron(III): *Rev. Pure Appl. Chem.* **22,** 115–132.

Wefers, K. (1966a) Zum System Fe_2O_3-H_2O. 1. Teil: *Ber. Dtsch. Keram. Ges.* **43,** 677–684.

Wefers, K. (1966b) Zum System Fe_2O_3–H_2O. 2. Teil: *Ber. Dtsch. Keram. Ges.* **43,** 703–708.

Wolf, R. H. H., Wrischer, M. and Sipalo-Zuljevic, J. (1967) Electron-microscope investigation of the formation of colloidal beta FeOOH during slow hydrolysis of an aqueous ferric chloride solution at room temperature: *Kolloid-Zeit. u. Zeit Polymere* **215,** 57–60.

https://doi.org/10.1346/CCMN.1977.0250108 Published online by Cambridge University Press