

THE FORMATION OF HEMATITE FROM AMORPHOUS IRON(III)HYDROXIDE

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Abstract—The formation of hematite from amorphous Fe(III)hydroxide in aqueous systems at pH 6 and 70°C, both with and without oxalate, was followed by kinetic measurements, electron microscopy, i.r. spectroscopy and thermal analysis.

In the absence of oxalate, small amorphous particles coalesce into aggregates which eventually become single crystals of hematite. When oxalate is present, crystal growth is much faster and does not proceed through the intermediate stage of aggregation. Aggregates, when formed, consist of groups of single crystals. It is suggested that oxalate accelerates the nucleation of hematite crystals by acting as a template, the Fe–Fe distance in Fe–oxalate ions being similar to that in hematite.

INTRODUCTION

Among the iron oxides occurring in soils and sediments, hematite and goethite are by far the most common. Although hematite rarely occurs in soils of temperate climates, mixtures of both forms are often found in warmer regions. Thermodynamic evidence, although conflicting, indicates a difference in stability of the two forms, so that only one or the other should exist at equilibrium (Mohr *et al.*, 1972). Langmuir (1971) stressed the importance of particle size to explain the conflicting results but admitted sluggish kinetics as a reason for extremely slow mutual transformation. Since many of the soils in which both oxides occur are very old, the conversion of goethite into hematite and vice versa at ambient temperature must be extremely slow indeed. Furthermore, long term laboratory experiments have shown that the ratio of goethite to hematite formed at room temperature from amorphous Fe(III)hydroxide in water does not change with time (Schwertmann, unpublished results).

Apparently these two crystalline forms in soils are not inter-related genetically by a simple hydration–dehydration type of reaction ($\alpha \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \rightleftharpoons 2\alpha \text{FeOOH}$), but are formed by separate pathways from a common source. Numerous laboratory experiments have shown that amorphous or para-crystalline Fe(III)hydroxide is a suitable source. Environmental conditions play a decisive role in determining which of the two forms are produced (Schwertmann, 1969), probably because of their influence on the kinetics of the alternative reactions. However, to clarify this, it is necessary to know more about the relevant reaction mechanisms.

Fischer (1971) found that goethite is produced from amorphous Fe(III)hydroxide by a reconstructive transformation involving dissolution and reprecipitation (nomenclature after Mackay, 1960) but very little is known about the mechanism of formation of hematite. Feitknecht and Michaelis (1962) believe it to be an in-

ternal dehydration and crystallization, but do not describe the process in detail.

The aim of the present work is to elucidate the mechanism of hematite formation. Since only hematite is formed in the presence of oxalate at pH values around 7 (Schwertmann, 1969, 1970), these conditions were chosen for study.

METHODS

Iron(III)hydroxide was prepared at room temperature by the addition of 13 per cent NH_3 solution to 0.1 M $\text{Fe}(\text{NO}_3)_3$ solution (Merck, A. R.) until the NH_3 was in 30 per cent excess of the stoichiometric requirement. After centrifuging and washing three times with water, the bulk suspension was diluted to a concentration of 11.2 g Fe/l. Various amounts of ammonium oxalate were added to subsamples and the pH values were adjusted to 6.0 with H_2SO_4 . The suspensions were placed in an oven at 70°C and shaken occasionally by hand. Samples were taken for kinetic measurements at intervals up to 14 days. The samples were washed and dried and total Fe as well as oxalate soluble Fe (Schwertmann 1964) was determined by atomic absorption photometry. I.r. spectrograms were recorded with a Beckman IR-20 A, using 0.3 per cent KBr pellets. X-ray powder diffraction patterns were obtained from gently pressed specimens of random particle orientation using a Philips PW 1130 generator and $\text{Co K}\alpha$ radiation. Specific areas were measured with argon gas in an Areatron automatic single point BET instrument (Leybold). Electron micrographs were taken with a Siemens Elmiskop I instrument. TG and DTA curves were run at a heating rate of 7.8°C min and 10°C per min, respectively.

RESULTS

Composition of aged products

Samples taken in the early stages of the reaction were mixtures of amorphous and crystalline oxides,

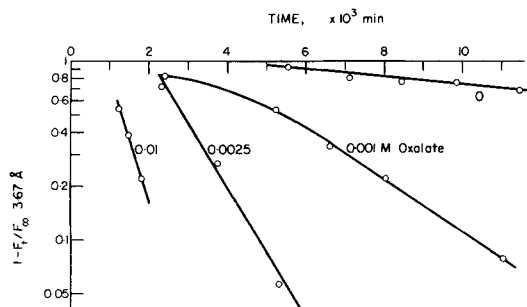


Fig. 1. First order kinetic plot of the intensity (area) of the 3.67 Å hematite reflection for various oxalate concentrations: F_∞ —peak area at complete crystallization. F_t —peak area at time t .

containing up to 1.5 per cent C derived from oxalate. After complete crystallization, small amounts of goethite were present with hematite if the oxalate concentration was 10^{-3} M or less. Only hematite was formed if the oxalate concentration was 5×10^{-3} M or higher.

Kinetics

Quantitative determination of hematite from measurements of the area under the 3.67 Å peak could be made only with sufficient accuracy during the main part of conversion. Values of $\log(1-F_t/F_\infty)$ were calculated, where F_t is the area under the hematite peak at time t and F_∞ is the area at a time when no further increase occurred. This function, which represents the non-crystalline fraction, was plotted against time. As seen on Fig. 1, all the curves, were essentially linear within the range examined. This indicates first order kinetics. The slopes give the reaction rates which increased considerably with increasing oxalate concentration. The linear parts of these curves do not extrapolate back to zero time, indicating that the main reaction was preceded by another of much slower rate. The initial slow rate of conversion is shown by the curve obtained in 0.01 M oxalate. However it is shown more clearly if the amorphous fraction of these samples (as determined chemically by dissolution in oxalate) is plotted against time (Fig. 2) on the same scales as in Fig. 1. In the main part of the conversion these curves are similar to those in Fig. 1 although in the beginning of the process the rate is gradually increas-

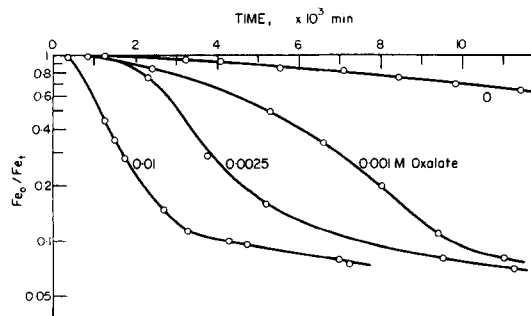


Fig. 2. First order kinetic plot of oxalate soluble iron Fe_0/Fe_t (Fe_t = total iron) for Fe-oxides aged at various oxalate concentrations.

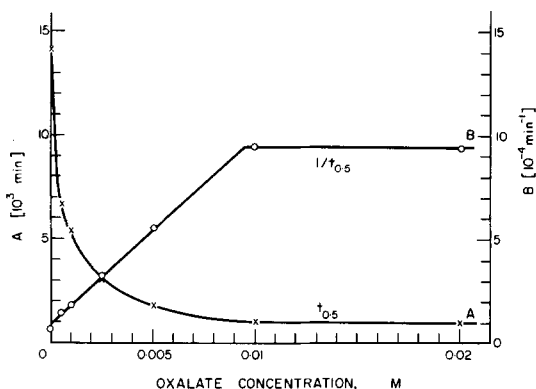


Fig. 3. Half conversion time ($t_{0.5}$, curve A) and $1/t_{0.5}$ (curve B) vs oxalate concentration. Ordinate division for A at the left, for B at the right.

ing. This is believed to be due to a nucleation process similar to that for the conversion of lepidocrocite to goethite (Schwertmann and Taylor, 1972). However treatment as a second order autocatalytic reaction, which was also applied to the latter reaction, was not successful for all curves in Fig. 1. Near the end of the conversion, Fe_0/Fe_t values do not approach zero because even hematite has a measureable, although low, solubility in oxalate solutions.

For first order reaction kinetics the rate of conversion is inversely proportional to the half conversion time $t_{0.5}$ (where $Fe_0/Fe_t = 0.5$). If the reciprocal of $t_{0.5}$ is plotted against oxalate concentration, a linear relationship is obtained (Fig. 3) up to a concentration of 0.01 M. This leads to the conclusion that the oxalate anion accelerated the formation of hematite in direct proportion to its concentration, up to a value of saturation where no further acceleration occurred (0.01 M under the condition of this experiment). During this process the oxalate concentration in the supernatant solution dropped to an undetectably small value as determined by the $KMnO_4$ oxidation test.

Morphology

Electron microscopy yields some information about the changes in particle morphology during ageing. The initial amorphous hydroxide consisted of finely dispersed particles with an average dia. between 50 and 100 Å (the fine-grained material between the denser particles in Fig. 4a). The first visible change was the formation of denser aggregates 10–20 times as large as the initial particles (Fig. 4a).

Without the oxalate or with low concentrations, these aggregates gradually assumed the approximately hexagonal shape which is commonly found in hematite. These crystals, however, appear to have fissures, holes and other imperfections (Fig. 4b). Under the same conditions as in Fig. 4a but with higher oxalate concentrations, the aggregates were ellipsoid (Fig. 5a) and, after complete crystallization to hematite (Fig. 5b), had an internal laminar or chain structure and considerable thickness (shaded electron micrograph of Fig. 5c).

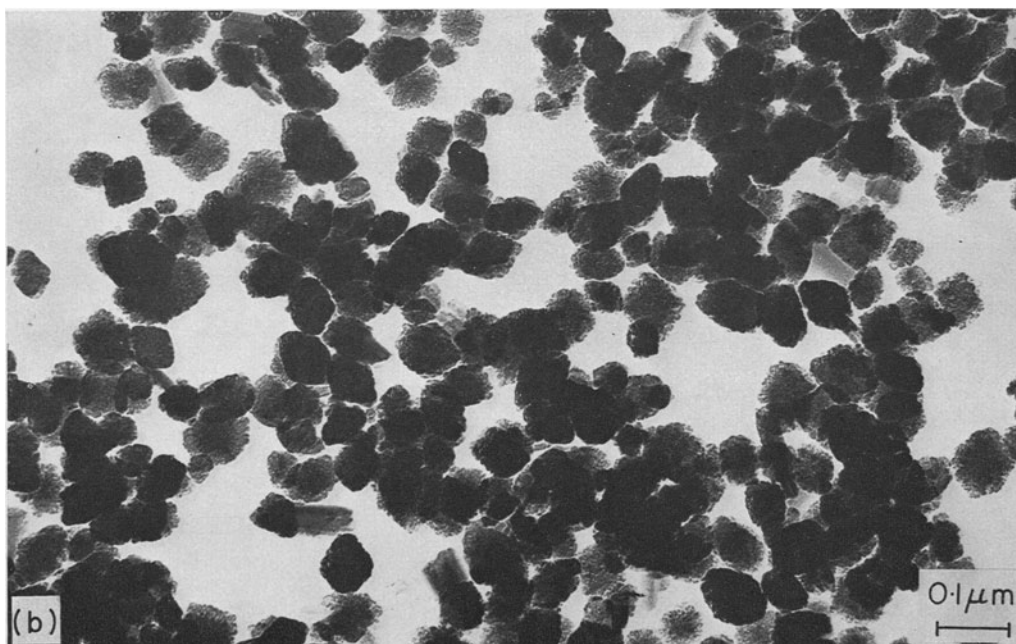
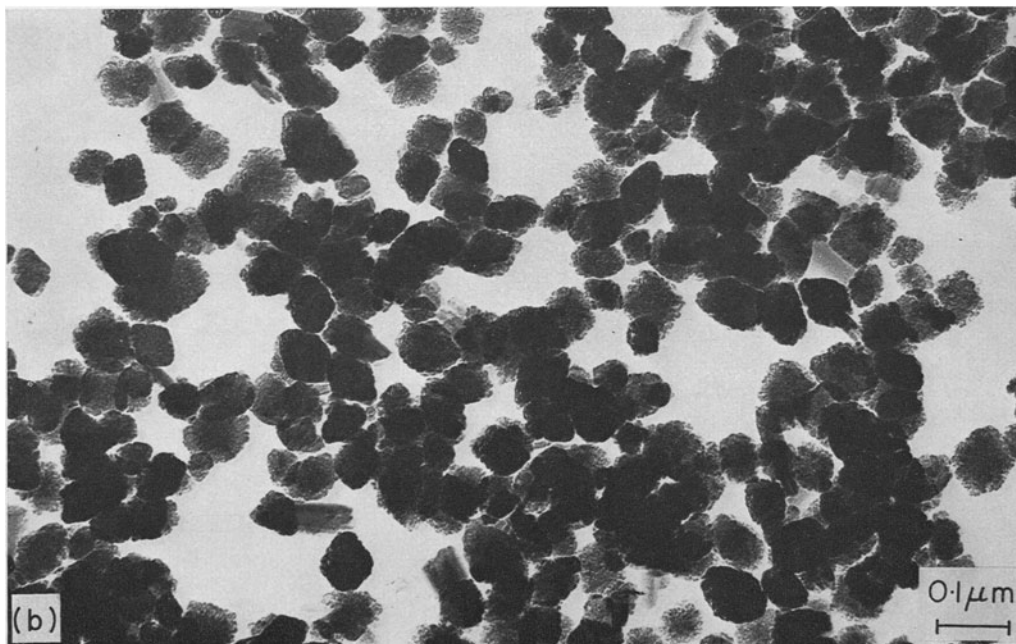


Fig. 4a. Ageing product under low oxalate concentration ($5 \cdot 10^{-4} \text{M}$) after 86 hr at 70°C amorphous material and hematite containing aggregates ($\text{Fe}_0/\text{Fe}_t = 0.71$).
Fig. 4b. Ageing product without oxalate after 400 hr boiling: complete crystallization to hematite ($\text{Fe}_0/\text{Fe}_t = 0.012$).

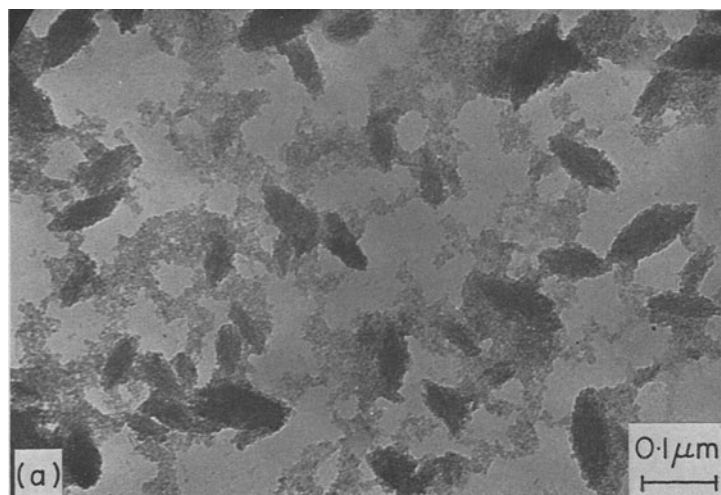


Fig. 5a. Ageing product under high oxalate concentration ($2 \cdot 10^{-2} M$) after 20 hr at $70^{\circ}C$ amorphous material and ellipsoidal aggregates containing hematite ($Fe_o/Fe_t = 0.53$).

Fig. 5b. Same as Fig. 5a but after 165 hr: almost complete crystallization to hematite ($Fe_o/Fe_t = 0.059$).

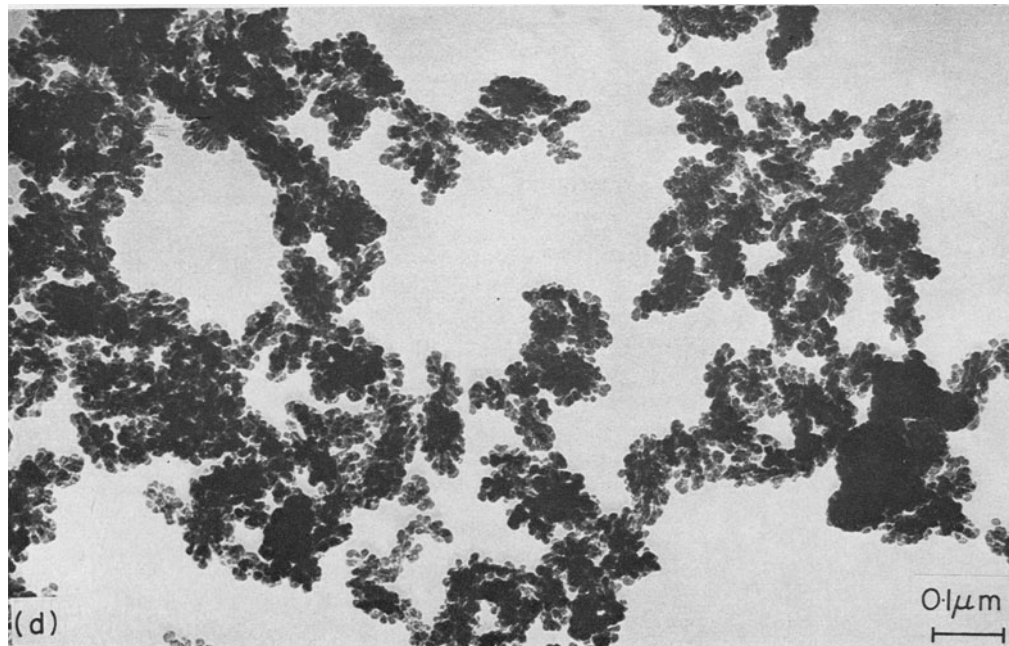
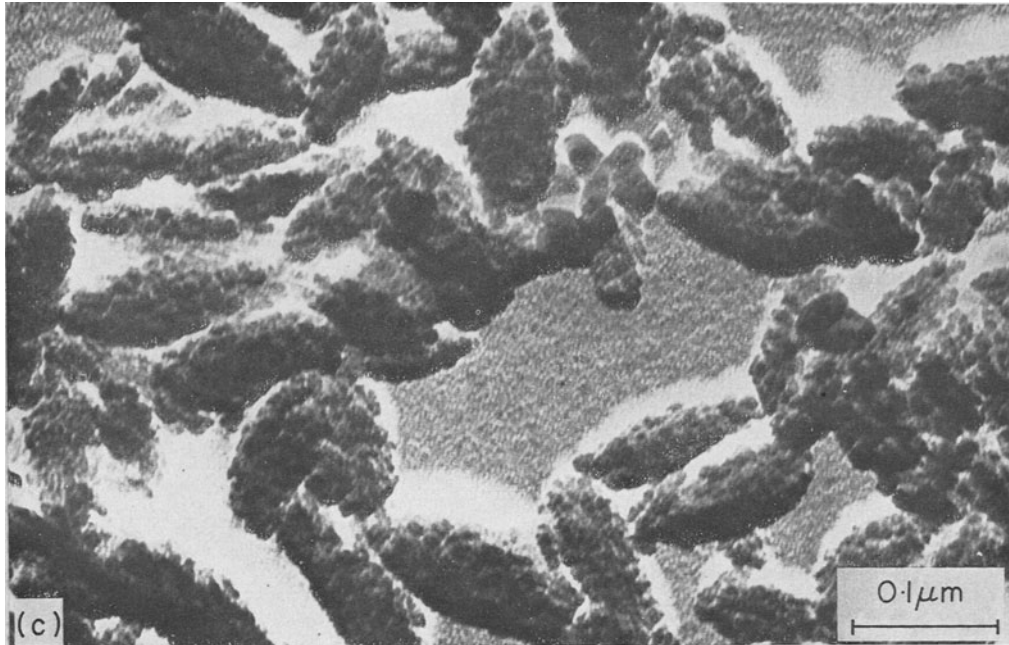


Fig. 5c. Same as Fig. 5b but shaded with Pt/C under 55°C.

Fig. 5d. Same as Fig. 5b, but after an additional 16 days refluxing in water: hematite only ($Fe_o/Fe_t = 0.022$).

The individual particles had a size similar to that of the initial amorphous hydroxide but had developed a hexagonal morphology indicative of their hematitic nature. This became clearly visible when the aggregates formed at 70°C were boiled (Fig. 5d). Besides dispersion some additional crystal growth occurred at this higher temperature.

Thus the oxalate induced differences both in external form and internal structure. Single, highly defect, hexagonal crystals were formed in its absence, and thick, ellipsoidal aggregates of small hexagonal crystals formed when it was present. These differences are reflected in the uncorrected widths at half height of the 3.67 Å X-ray diffraction peak, namely 0.43° and 0.25° with and without oxalate, respectively.

Thermal behavior

The differential thermal curves changed markedly with increasing crystallinity. Curve A of Fig. 6 shows the DTA curve of a sample at the initial stage (10^{-2} M oxalate added, no ageing). The different peaks are due to the loss of absorbed water (endo 150°C), oxidation of the oxalate (exo 240°C), and crystallization of hematite (exo 420°C). In agreement with the intense DTA dehydration peak the TG weight loss up to 200°C in a thermogravimetric experiment was about 14 per cent (curve in B, Fig. 6). In contrast, the final product of the same ageing series had only the oxalate oxidation peak at 235°C (curve A, Fig. 7), and the weight loss from the dehydration of surfaces up to 200°C was about 4.5 per cent (curve B, Fig. 7).

Infrared spectra

The i.r. spectrum of a well-crystallized synthetic hematite (prepared by ignition of Fe(III)hydroxide) shows three strong bands at 565, 465 and 330 cm^{-1} . These bands, although broadened, occurred also in a typical spectrum of hematite prepared in the presence of oxalate (Fig. 8), but there were a number of bands

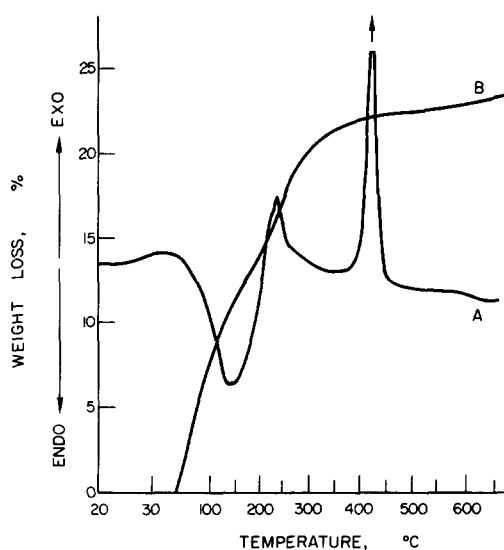


Fig. 6. DTA curve (A) and TG curve (B) for an amorphous Fe(III)-hydroxide precipitated in the presence of 10^{-2} M oxalate.

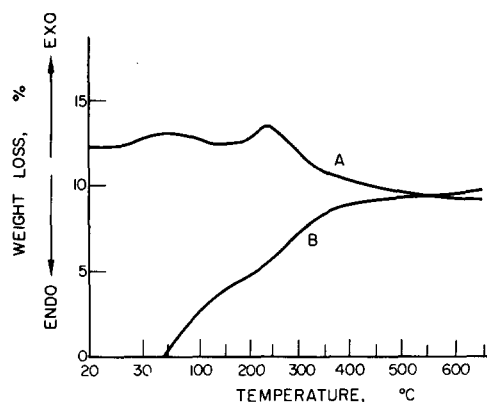


Fig. 7. DTA curve (A) and TG curve (B) for a completely crystallized hematite from 10^{-2} M oxalate.

of low intensity (Table 1). The additional bands could not be removed by thorough water washing combined with ultrasonic treatment, or by dissolving part of the oxide by a 1-hr treatment with 1 N HCl. Schmelz (1957) reported a similar system of bands in the 1700–1200 cm^{-1} range for $\text{K}_3(\text{Fe}(\text{C}_2\text{O}_4)_3) \cdot 3\text{H}_2\text{O}$. The bands were different from those of a mechanical mixture of solid hematite and ammonium oxalate, but could be produced by slowly drying hematite in oxalate solution for 2 days. This indicates the existence of Fe-oxalato-complexes.

The position of the bands is also in agreement with that of Farmer and Mitchell (1963) for ionized carboxyl groups of oxalate (1410 cm^{-1}) and for chelated oxalate (at 1690 and 1270 cm^{-1}) in peroxidized soil clays. The COO^- band at 1590 cm^{-1} , reported by Farmer, may be overlapped by the very intensive system between 1700 and 1600 cm^{-1} .

During the ageing experiment the shape and intensity of the bands changed in a typical way. Due to the loss of adsorbed water, the band at 1670 cm^{-1} becomes sharper and splits into three different features: a main absorption line at 1680 cm^{-1} with shoulders at 1710 and 1625 cm^{-1} , the latter being caused by HOH deformation. The weak bands in the 700–1300 cm^{-1} range developed during the reaction as did the hematite lattice vibration lines, whereas the 1271 cm^{-1} band became smaller. This is surprising in view of the fact that the oxalate should be fixed as a complex, as indicated by the washing experiments. The 785 and 885 cm^{-1} bands are normally typical of the occurrence of goethite. They occurred in all spectra of oxalate-treated amorphous Fe(III)hydroxides including those with a very low oxalate concentration. Figure 8 compares the spectra of two preparations at oxalate concentrations of 10^{-3} (curve A) and 2×10^{-2} M (curve B). The bands in question were stronger at a lower oxalate concentration which confirms that they are due to goethite and not to any direct influence of oxalato-complexes. The bands in the range between 900 and 1200 cm^{-1} of the i.r. spectra have not yet been identified. In agreement with electron microscopy and X-ray diffraction results, the hematite bands were sharper in the low oxalate material, indicating better crystallinity.

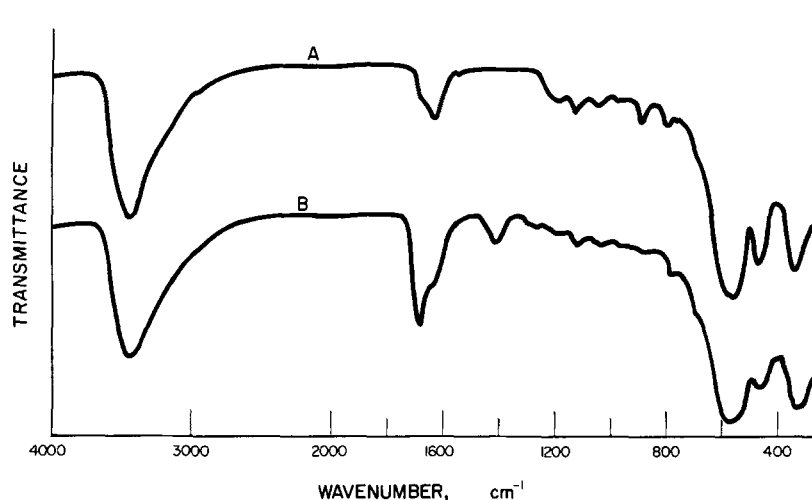


Fig. 8. I.r. spectra of the final products prepared at oxalate concentrations of 10^{-3} M (curve A) and $2 \cdot 10^{-2}$ M (curve B).

Table 1. List of i.r. bands obtained from hematites prepared with oxalate

Wavenumber (cm^{-1})	Intensity	Remarks
325	s	hematite
465	m	hematite
557	vs	hematite
785	w	goethite
887	vw	goethite
1030	vw	?
1118	vw	?
1190	vw	? removable by H_2O washings
1270	w	COO^- or chelated
1410	m	oxalate
1625	sh*	adsorbed H_2O
1680	s	same as 1270
1708	sh	?
3410	vs	adsorbed H_2O

* sh = shoulder.

Effect of similar organic acids

In order to find out whether the effect of oxalic acid is due to the particular distance between the carboxyl groups of this compound, experiments similar to those described were conducted with other dicarboxylic acids. The results (Table 2) show that only malonic

Table 2. The influence of various dicarboxylic acids (10^{-2} M) on the nature of the product formed by ageing amorphous Fe(III)hydroxide for 7 hr, at 80°C and pH 6 (G = goethite, H = hematite, A = amorphous hydroxide)

Acid	Formula	Product
no	—	(G)(H)*
oxalic	$\text{HOOC}-\text{COOH}$	H(A)
malonic	$\text{HOOC}-\text{CH}_2-\text{COOH}$	(H)A
maleinic	$\text{HOOC}-\text{CHN}=\text{CH}-\text{COOH}$	A
succinic	$\text{HOOC}-(\text{CH}_2)_2-\text{COOH}$	A
adipic	$\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$	A
phthalic	$\text{o}-\text{C}_6\text{H}_4-(\text{COOH})_2$	A

* () — indicates small amounts

acid had an effect similar to but much weaker than that of oxalic acid. The other acids all inhibited crystallization (compare Schwertmann, 1969/70).

DISCUSSION

Feitknecht and Michaelis (1962) have proposed that the mechanism of hematite formation from amorphous Fe(III)hydroxide is fundamentally different from that of goethite. Goethite is formed by dissolution and reprecipitation (reconstructive transformation, Mackey, 1960), and similarly, lepidocrocite is converted to goethite by the same mechanism (Schwertmann and Taylor, 1972). However, hematite is formed by 'internal dehydration' of the aggregated amorphous hydroxide. This conclusion is supported by the structure of the amorphous hydroxide. It has the same oxygen arrangement as hematite with partial replacement of O by OH and OH_2 but with random distribution and deficiency of Fe atoms. The strongest hematite diffraction lines are therefore lacking (Towe and Bradley 1969, Chukhrov *et al.*, 1972). The amorphous mineral has been called ferrihydrite and occurs in nature (Chukhrov *et al.*, 1972, Schwertmann and Fischer 1973).

The results reported here support the proposal of Feitknecht and Michaelis, and supply further details. Aggregation of the small hydroxide particles followed by nucleation and crystallization of hematite appear to be the essential steps of the process. If nucleation is rate-determining (zero or low oxalate concentration) then aggregation precedes nucleation. Aggregation obviously facilitates nucleation and the subsequent crystal growth of hematite within the aggregate at the expense of the hydroxide. From time curves the nucleation phase is clearly indicated by the slowly increasing rate of transformation at the beginning of the reaction. During the main transformation the rate is determined by the concentration of hydroxide remaining and thus follows first-order kinetics. At the end of this process the aggregates approach hexagonal morpho-

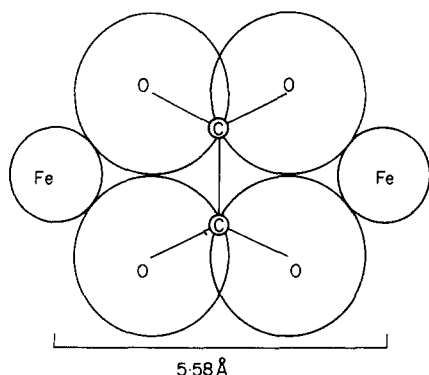


Fig. 9. Schematic presentation of the iron oxalate molecule. Interatomic distances according to Garavelli (1957); Size of atoms from the Goldschmidt radii.

logy and seem to consist of single crystals, but the aggregate construction is still clearly visible.

If this assumption is correct, then conditions which enhance aggregation of the hydroxide should favor hematite formation. This is in accordance with Feitknecht and Michaelis (1962). Our earlier experiments have shown that hematite is favored by increasing temperature, increasing suspension concentration, pre-heating of the hydroxide (Schwertmann and Fischer 1966) and ageing in the neighborhood of the isoelectric pH of the hydroxide (Schwertmann 1969). All of these factors enhance aggregation.

In the presence of higher oxalate concentrations the single hydroxide particles seemed to be nucleated much earlier, i.e. *before* or simultaneously with aggregation. The final aggregates do not show hexagonal morphology and consist of collections of small individual hexagonal hematite crystals similar in size to those of the original hydroxide. The time curves show a much shorter nucleation phase which decreases with increasing oxalate concentration indicating oxalate is able to induce nucleation of hematite. As seen from the behavior of other but similar organic acids the distance between the two COOH groups seems to have an important effect. Since the oxalate molecule is taken up by the hydroxide, it may act as a template for the nucleation of hematite. The structure of iron oxalate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) has been determined by Garavelli, 1957 (see also *Structure Reports* **21**, 505–506) and from this the distance Fe–Fe (Fig. 9) can be calculated to be 5.58 Å. This is very similar to the lattice parameter $a = 5.42$ Å of hematite. Since the Fe is associated with O atoms of different carboxyl groups (Fig. 9) it is probable that the Fe–Fe distance is different in dicarboxylic

acids with 1 or more C atoms between the functional groups. This may explain why only oxalate has such a strong template effect.

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