EFFECT OF pH ON THE FORMATION OF GOETHITE AND HEMATITE FROM FERRIHYDRITE

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Abstract—Storage of ferrihydrite in aqueous suspensions at 24°C and pHs between 2.5 and 12 for as long as three years resulted in the formation of goethite and hematite. The proportions and crystallinity of these products varied widely with the pH. Maximum hematite was formed between pH 7 and 8, and maximum goethite at pH 4 and at pH 12. The crystallinity of both products, as indicated by X-ray powder diffraction line broadening and magnetic hyperfine field values and distribution widths, was poorer, the lower the proportion of the corresponding product in the mixture. The existence of two competitive formation processes is suggested: goethite is formed via solution, preferably from monovalent Fe(III) ions [Fe(OH)$_2$$^+$ and Fe(OH)$_4$$^-$], and hematite by internal rearrangement and dehydration within the ferrihydrite aggregates. This concept relates the proportions of goethite and hematite to the activity of the Fe(III) ion species in solution, and implies that conditions favorable for the formation of goethite are unfavorable for that of hematite and vice versa.

Key Words—Ferrihydrite, Goethite, Hematite, Mössbauer spectroscopy, pH, X-ray powder diffraction.

INTRODUCTION

Böhm (1925) first showed that freshly precipitated, so-called "amorphous Fe(III) hydroxide" turns rapidly into pure goethite if kept for 2 hr under 2 M KOH at 150°C, whereas hematite is the dominant end-product if the material is heated under water. A strong pH influence on the transformation products of what is now known as ferrihydrite is obvious from these early results. Whether or not pH is important in soils where goethite and hematite are commonly associated is not known; however, Kämpf and Schwertmann (1983) found the goethite/hematite ratios in soils of southern Brazil to increase with decreasing pH within the soil pH range of 4.0–5.6.

To obtain more information on the influence of pH on the formation of Fe-oxides under pedogenic conditions, a long-term experiment was conducted in which freshly prepared ferrihydrite was stored in aqueous suspensions at 24°C and pH 2.5–12.0 for almost three years. In this paper the results are described, and a pH-dependent mechanism for the formation of goethite and hematite is suggested.

MATERIALS AND METHODS

Several 100-ml batches of freshly prepared 0.1 M Fe(NO$_3$)$_3$ solution were precipitated with ammonia at pH 7.5–8.0. The precipitate is a very poorly ordered ferrihydrite, which gives only 2 broad X-ray powder diffraction (XRD) peaks at 2.5 and 1.5 Å. The precipitates were thoroughly washed with water between pH 7 and 8 and resuspended with 250 ml of water. The suspensions were adjusted to pH values of 2.5, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, and 12.0 with HNO$_3$ or NaOH and kept in a constant-temperature room at 24°C. The

pH was readjusted at first at weekly intervals, later once every several months.

Subsamples were taken at certain intervals, and the proportion of oxalate-soluble Fe (Fe$_o$; Schwertmann, 1959, 1964) in these samples was used as an indicator of the degree of transformation of ferrihydrite to goethite and/or hematite. After 441 days the samples were investigated by X-ray powder diffraction (XRD) (CoKα radiation, Philips PW 1130 diffractometer, graphite diffracted-beam monochromator), Mössbauer spectroscopy, and transmission electron microscopy (TEM) (Zeiss EM 10; 80 kV). Samples were also investigated by XRD after 970 days.

Mössbauer spectra were taken at room temperature on samples having an average Fe density of 10 mg/cm². Instrumentation included a ^{57}Co/Rh source mounted on a loudspeaker-type drive system, a Kr proportional counter, and a 1024-channel analyzer. The hematite components of the spectra were fitted with one quadrupole split sextet; those of goethite, which shows distributions of magnetic hyperfine fields, were fitted with series of up to 15 sextets of different intensities.

For quantitative determination of hematite (Hm) and goethite (Gt) by XRD the integrated intensity (maximum intensity times width at half height) of the 012 line of hematite multiplied by 3.5 (empirical factor for the 104/012-intensity ratio) and the integrated intensity of the 110 line of goethite were used.

For the determination of Hm/(Hm + Gt) ratios by Mössbauer spectroscopy, the hematite subspectra were fitted with one sextet. The goethite subspectra, which showed asymmetrically broadened lines typical for this mineral, were each fitted with sets of three sextets of identical isomer shift and quadrupole splitting (a sim-
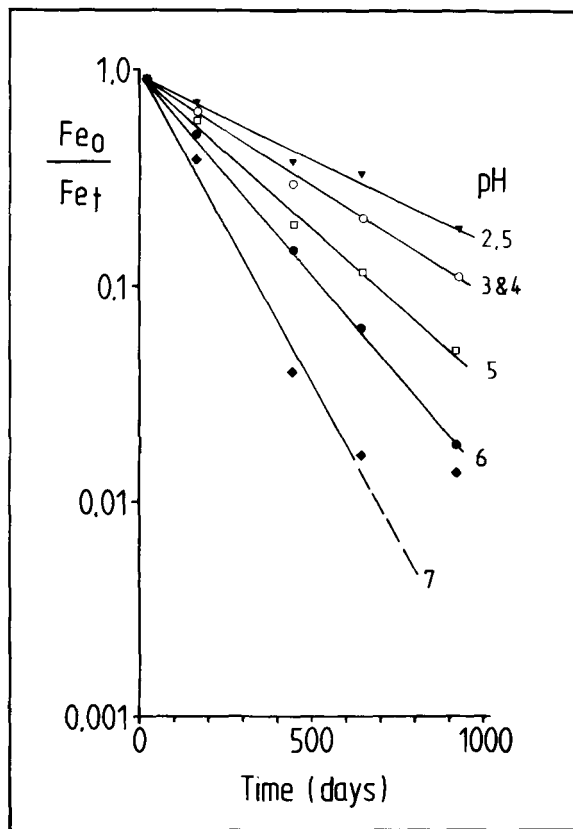
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Figure 1. First-order reaction plot for the transformation of ferrihydrite at various pH values.

Figure 2. Length of time for half conversion of ferrihydrite to goethite and hematite vs. pH.

plified version of the hyperfine field distribution model used to characterize this mineral by Murad, 1982).

RESULTS

Rate of transformation

The ratio Fe_0/Fe_t (Fe_t = total Fe) has proven useful to characterize the stage of transformation from ferrihydrite to goethite and/or hematite (Schwertmann and Fischer, 1966; Landa and Gast, 1973). A linear or nearly linear relationship for a semi-log plot (Figure 1) indicates a first-order type of reaction; the rate of transformation at any time is proportional to the amount of ferrihydrite left for transformation. The rate slows down as the pH decreases (Figure 1). A plot of half-conversion time against pH (Figure 2) shows a slightly curved relationship. The deviation of the pH 3 sample from this relation cannot be explained.

Products of transformation

Residual ferrihydrite in the system decreased with increasing pH. At or below pH 6 the proportion of ferrihydrite after 441 days was between 15 and 38%. This component was removed by oxalate treatment before further analysis. After 970 days the ferrihydrite con-
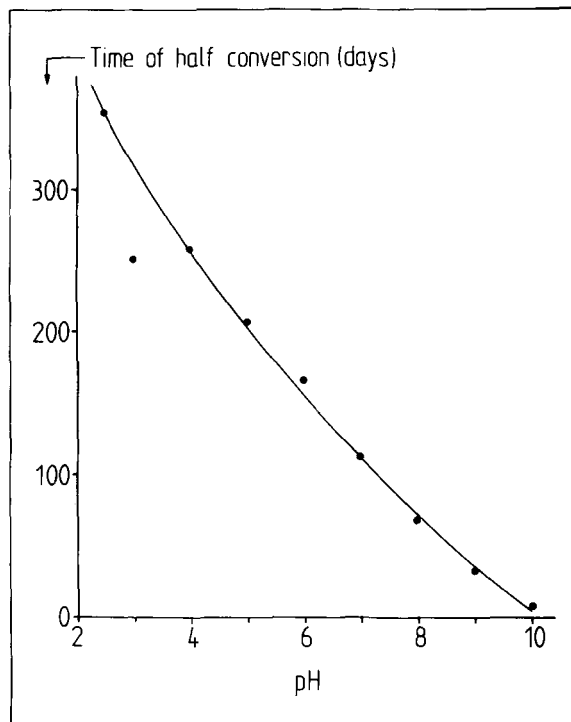
tents in the samples stored at pH $\leq$ 6 had decreased to between 2 and 19%, indicating further transformation. Less than 4% ferrihydrite was present in the samples stored at pH $\geq$ 7 after 441 days, and less than 2% after 970 days.

Besides residual ferrihydrite, hematite and goethite were the only oxides present. The quantitative determination of hematite and goethite by XRD and Mössbauer spectroscopy agreed reasonably well (Table 1). As shown in Figure 3, the hematite : goethite ratio Hm/(Hm + Gt) varied strongly with pH. Whereas at pH 12 only goethite was formed, mixtures of goethite and hematite were formed at all other pHs. Maximum hematite formation occurred at pH 7 and 8. Below this pH the Hm/(Hm + Gt) ratio decreased drastically, reaching a minimum at about pH 4, below which the ratio again increased. After 970 days the Hm/(Hm + Gt) ratio was essentially the same as after 441 days except at pH 2.5, where the proportion of hematite had increased relative to that of goethite at the expense of residual ferrihydrite.

Besides the proportion of the two iron oxides, their crystallinity also varied with pH. The XRD width at half height (WHH) of the 110 line of goethite and the 012 line of hematite varied reciprocally (Figure 4). Similar conclusions with regard to crystallinity can be drawn from their Mössbauer spectra (Figure 5). As the XRD lines narrowed, both the widths of the hyperfine field
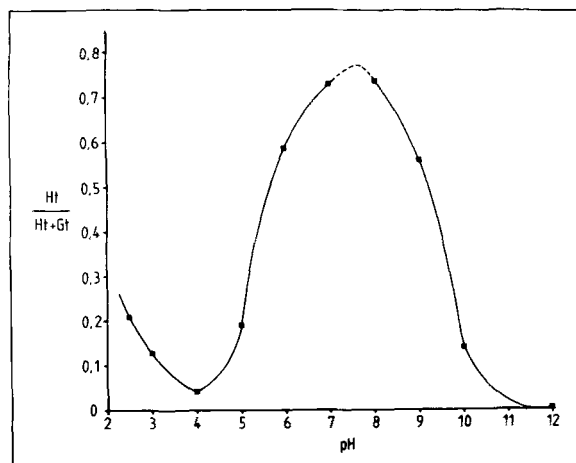
Figure 3. Hematite/(hematite + goethite) ratios vs. pH after 441 days of storage.

Figure 4. Widths at half height (WHH) of goethite 110 and hematite 012 and magnetic hyperfine field (H_i) of goethite vs. pH. CoKα radiation.

distributions and the magnitudes of the hyperfine fields of maximum absorption (Hi_{max}) decreased. The parallel nature of these trends is demonstrated by the corresponding curves in Figure 4, and is in agreement with observations by Murad (1982) that the hyperfine fields of maximum absorption of pure goethites decrease and the widths of hyperfine field distributions increase as crystallinity becomes poorer. A similar trend with respect to the hyperfine field of hematite is also evident; the highest field occurred where most hematite was formed and where its XRD lines were sharpest, i.e., where the conditions of hematite formation relative to those of goethite were most favorable.

Both the proportions of the two minerals and their crystallinity clearly indicate that conditions favorable for the formation of goethite are unfavorable for the for-
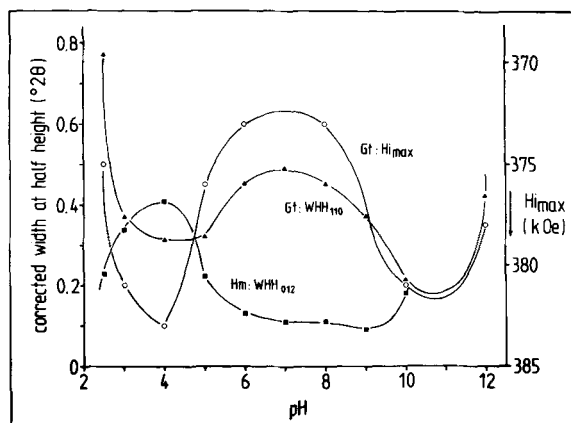
mation of hematite and vice versa. Goethite and hematite must therefore be formed through a pair of competitive reactions as postulated earlier (Schwertmann and Fischer, 1966). The lower crystallinity of the goethite formed at pH 12, as indicated by both WHH and Hi_{max}, seems to contradict this statement, because no hematite was formed at this pH. An explanation for this is given below.

Crystal morphology and size of goethite and hematite

In transmission electron micrographs (Figure 6), goethite and hematite can be easily distinguished by their crystal shapes. Hematite typically forms irregular hexagonal crystals whose diameters are about 3 times as large (~900 Å) in the pH range 7–9 (where maximum amounts of hematite were formed) as at pH ≤4 (where

Table 1. Amounts and properties of goethite (Gt) and hematite (Hm) formed at various pH after 441 days.

pH	HCT[1] (days)	Composition Hm/(Hm + Gt)			Properties of goethite			Properties of hematite	
		XRD[2]	MS[3]	XRD[4]	WHH$_{110}$[5] (°2θ)	Hi_{max}[6] (kOe)	HWHD[7] (kOe)	WHH$_{012}$[5] (°2θ)	Hi[6] (kOe)
2.5	354	0.20	0.25	0.37	0.77	375	43	0.23	497
3.0	250	0.12	0.13	0.14	0.37	381	22	0.34	504
4.0	258	0.04	0.05	0.04	0.31	383	22	0.41	504
5.0	206	0.19	0.25	0.23	0.32	377	22	0.22	508
6.0	166	0.58	0.58	0.60	0.45	373	24	0.13	508
7.0	112	0.70		0.69	0.49			0.11	
8.0	68	0.72	0.65	0.70	0.45	373	33	0.11	510
9.0	32	0.52		0.54	0.37			0.09	
10.0	8	0.14	0.17	0.14	0.21	381	24	0.18	507
12.0	<4	0	0	0	0.42	378	27	—	—

[1] Half conversion time.
[2] X-ray powder diffraction, CoKα radiation.
[3] Mössbauer spectroscopy.
[4] After 970 days.
[5] Corrected width at half height of XRD peak.
[6] Maximum internal magnetic field.
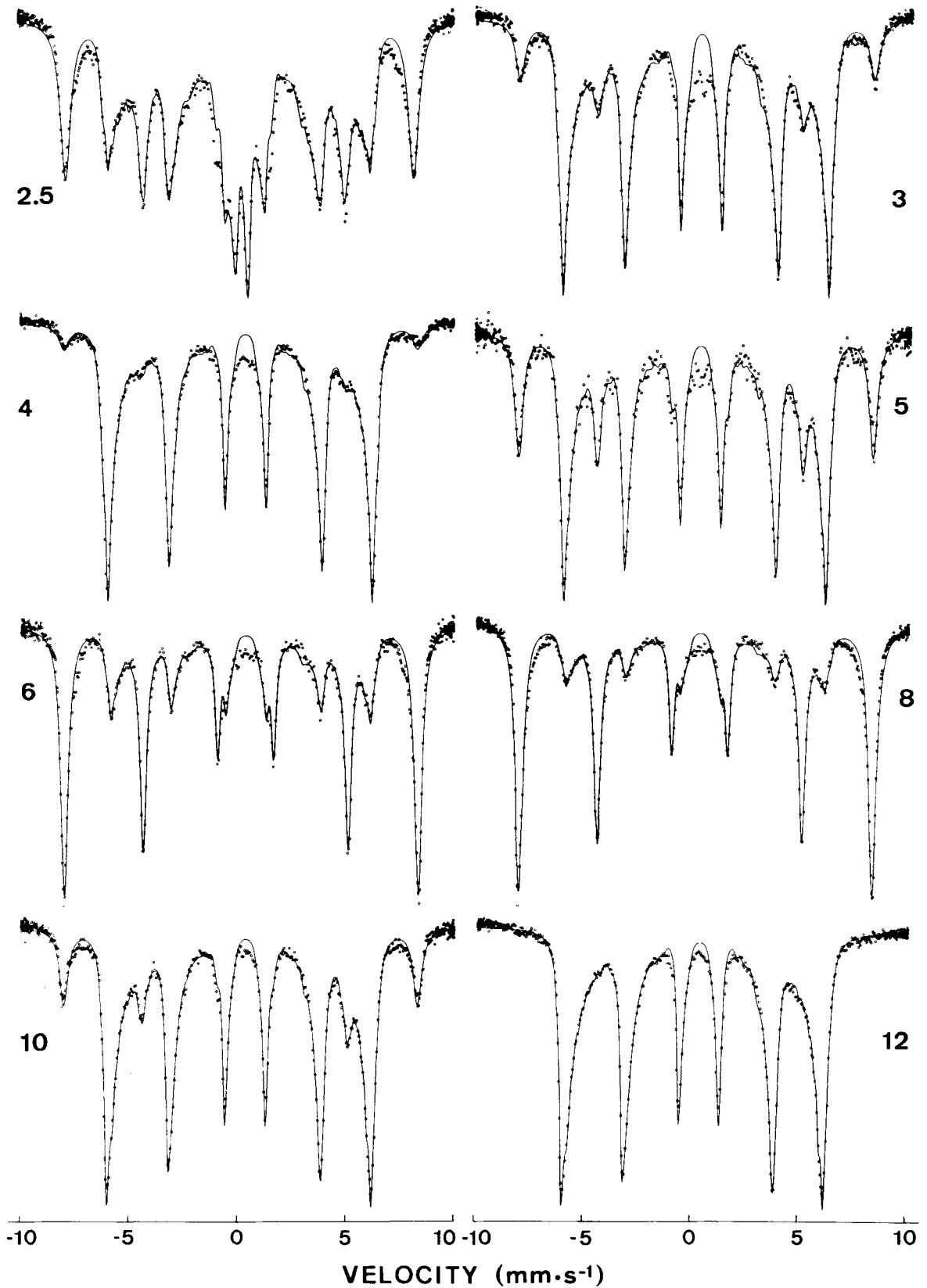[7] Half width of magnetic field distribution.

Figure 5.   Room temperature Mössbauer spectra of goethite-hematite (Gt-Hm) mixtures synthesized at various pH values.
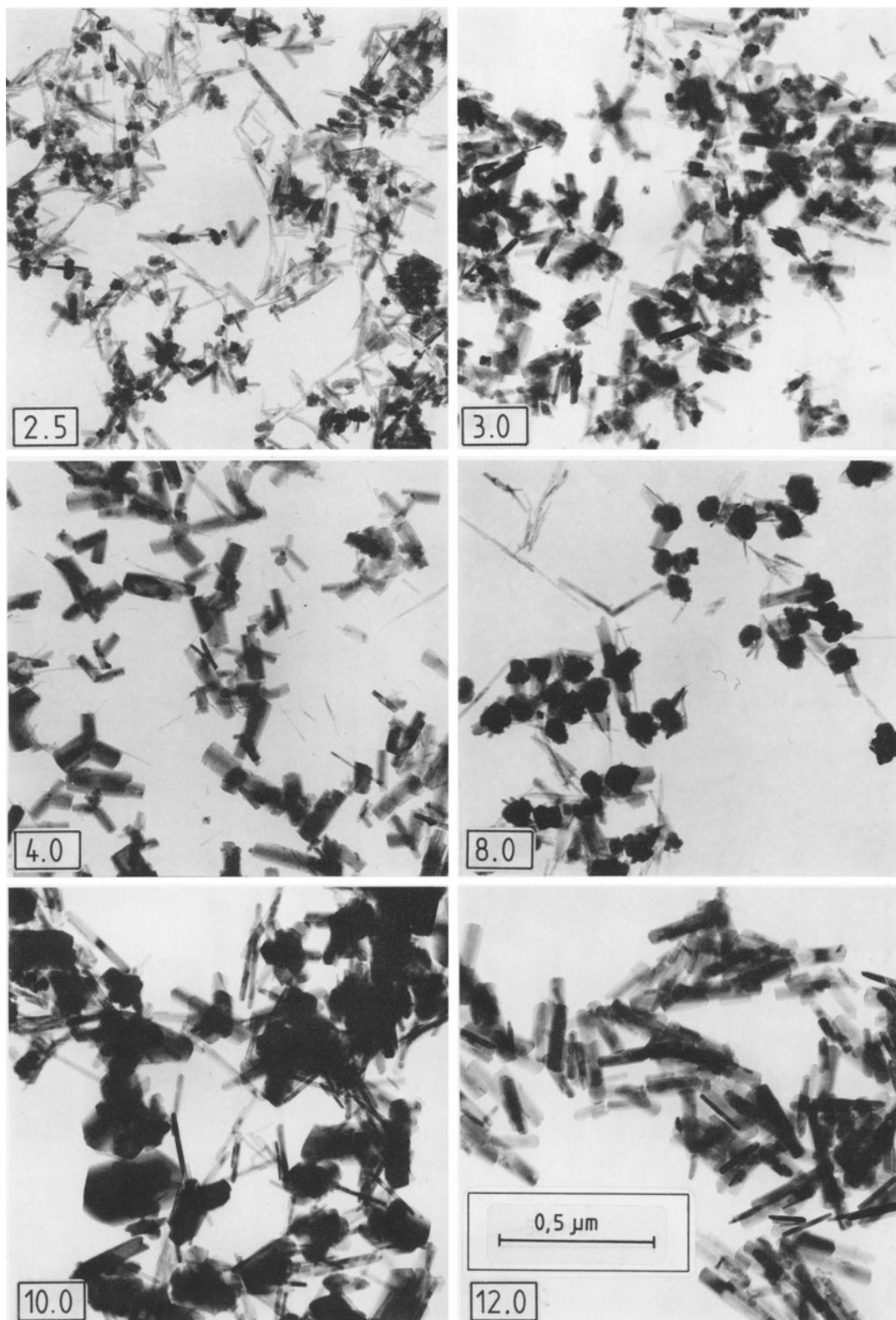
Figure 6.   Electron micrographs of goethites and goethite-hematite mixtures produced from ferrihydrite at various pH-values (inserted figure).
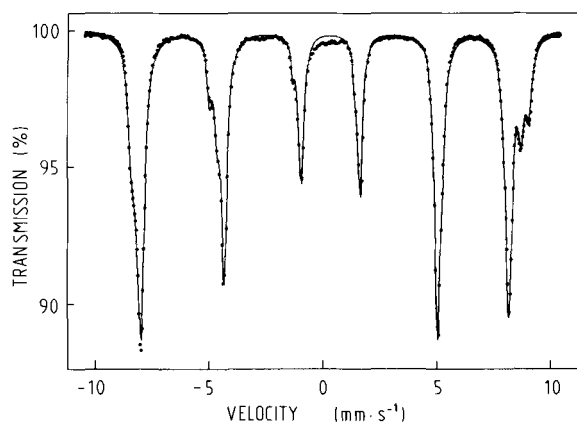
Figure 7. Mössbauer spectrum at 4°K of hematite-goethite mixture synthesized at pH 2.5.

Figure 8. Fe(III) ion species as a function of pH using reaction constants given by Lindsay (1979).

only minor amounts of hematite were present). The average diameter of the hematite platelets formed at pH 9 (calculated from the width at half height of the 110 and 300 lines[1]) is 880 and 890 Å, which agrees well with the TEM observations.

The room temperature Mössbauer spectrum of the sample stored at pH 2.5 showed, even after oxalate treatment, a superparamagnetic component (Figure 5). At 111° and 4.2°K Mössbauer spectra of this sample consisted of three sextets. The strongest sextet results from goethite, which the spectra indicate to make up about 75% the sample. The other two components can be attributed to hematite which has, and hematite which has not passed through a Morin transition; at 4.2°K (Figure 7) these latter components have approximately equal areas. According to Nininger and Schroeer (1978), this would indicate that about half of the hematite particles have sizes below 200 Å, i.e., a median particle size of about 200 Å. This value is in good agreement with the mean crystal dimension parallel to the c-axis of 220 ± 40 Å calculated from the widths at half height of six XRD lines with $l \neq 0$.

The goethite crystals show the usual acicular shape, but vary in size and morphology. At pH 12 rather uniform needles 500–1500 Å long and 150–500 Å wide were formed. At pH 10 broad crystals, commonly twinned and with terminal crystal faces—probably (012) and (0$\bar{1}$2)—dominate, and the needles are somewhat thinner than those at pH 12. At pH 8, where much less goethite was formed, twins are rare and the needles are extremely thin.

These observations support the conclusion of the previous section: whenever the conditions for goethite crystallization are favorable, thick needles and twins

develop, indicating that the crystals grow well not only in the crystallographic c-direction (parallel to the needle axis) but also in the a- and b-directions. As conditions becomes less favorable (indicated by the formation of less goethite and more hematite) the a- and b-direction growth is retarded relative to the growth in the c-direction. This leads to growth of acicular crystals of smaller width. The width of the 110 line, which is rather sensitive to crystal development in the a- and b-direction, clearly reflects this situation by showing minima between pH 3 and 5 and at pH 10, where twins dominate, and broader lines at pH 2.5, 6–9, and 12 (Table 1), where needles dominate. Correspondingly, larger hematite crystals were formed when the proportion of hematite in the mixture was high and vice versa.

DISCUSSION

The results support and refine a concept developed earlier, according to which goethite and hematite form from ferrihydrite by two different and competitive mechanisms: goethite crystals form in solution from dissolved Fe(III) ions produced by the dissolution of ferrihydrite, whereas hematite forms through an internal dehydration and rearrangement within the ferrihydrite aggregates (Schwertmann, 1959; Schwertmann and Fischer, 1966; Fischer and Schwertmann, 1975). Therefore, goethite should be favored as the concentration of Fe(III) ions in equilibrium with ferrihydrite increases, and hematite should be favored as the concentration decreases.

The concentration and form of Fe(III) ions in equilibrium with ferrihydrite depend strongly on pH. Using the appropriate equilibrium constants the diagram in Figure 8, which shows the pH-dependence of various monomeric Fe(III) ions, has been constructed. Comparison of this diagram with the distribution of goethite and hematite (Figure 3) suggests that goethite is strong-

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[1] Calculated from the Scherrer formula: $MCD = 0.9\lambda(54.7)/b \cos \theta$, where λ is the wavelength, b the width at half height after correction for instrumental line broadening, and θ the diffraction angle.
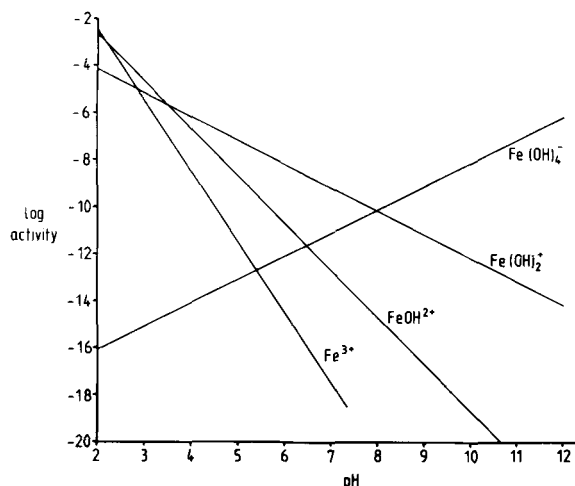
ly favored where the concentration of monovalent Fe(III) ions, either $Fe(OH)_2^+$ or $Fe(OH)_4^-$, is at a maximum. The maximum for $(Fe(OH)_2^+)$ [() denotes activity] is at pH ~4, and that for $(Fe(OH)_4^-)$—within the pH range tested—at pH 12. On the other hand, hematite shows maximum formation where these concentrations are at their minimum, i.e., around pH 8 (Figure 8), which is also the point of zero charge of ferrihydrite.

Below pH ~4, although $(Fe(OH)_2^+)$ increases further, it is overridden by the concentration of the divalent $Fe(OH)^{2+}$ ions which appear to be less favorable for goethite crystal growth than the monovalent form. This situation may retard the formation of goethite but not that of hematite, so that relatively more hematite is formed. The lower suitability of $Fe(OH)^{2+}$ compared to $Fe(OH)_2^+$ can be explained as follows: Fe(III) ions feeding the growing goethite crystal must be discharged at the crystal surface before being built into the crystal; this discharge is probably easier for monovalent than it is for divalent ions.

This concept is further supported by earlier results of Knight and Sylva (1974) who observed a positive relationship between $(Fe(OH)_2^+)$ and the rate of goethite formation. It is also in agreement with recent work by Hsu and Wang (1980), who found more hematite to form as acidity increased below pH 2.

At very high pHs (>1 M OH^-), where crystallization was very rapid and only goethite formed, the crystals consisted of very thin (~100 Å) and long (up to 5 μm) needles, indicating an increasingly strong retardation of crystal growth in the a- and b-directions and a rapid growth in the c-direction. In analogy to the strongly acid range this could indicate the formation of divalent $Fe(OH)_5^{2-}$ ions under the influence of an extremely high (OH^-) instead of monovalent $Fe(OH)_4^-$ ions at lower (OH^-), the former being less suitable for crystal growth than the latter. This could explain why the crystallinity of goethite formed at pH 12 was lower than that formed at pH 10 and below, although goethite was the only phase to form at pH 12.

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Резюме—Результатом хранения ферригидрита в водных суспензиях при 24°C и величинах pH от 2,5 до 12 в течение так длительного периода как три года было образование гетита и гематита. Пропорции и кристалличность этих продуктов изменялись значительно с величиной pH. Максимальное количество гематита образовывалось при pH от 7 до 8, а максимальное количество гетита при pH = 4 и pH = 12. Как показали расширение линий рентгеновской порошковой дифракции, величины магнетических сверхтонких полей и распределение ширин, кристалличность обоих продуктов была тем слабее, чем меньше была пропорция соответствующего продукта в смеси. Предложено существование двух конкурирующих обра- зовательных процессов: гетит образуется из раствора, преимущественно из моновалентных ионов [$Fe(OH)_2^+$ и $Fe(OH)_4^-$], содержащих Fe(III), а гематит—в результате внутренной перегруппировки и дегидратации внутри аггрегатов феррогидрита. Эта концепция связывает пропорции гетита и гематита с активностью ионов, содержащих Fe(III) в растворе, и подразумевает, что условия благоприятные для образования гетита являются неблагоприятными для образования гематита и наоборот. [E.G.]

Resümee—Aus Ferrihydrit wird bei 24°C und pH 2.5 bis 12 innerhalb von bis zu 3 Jahren Goethit und Hämatit. Ihr Mengenverhältnis und ihre Kristallinität variieren stark mit dem pH. Maximale Hämatitanteile traten zwischen pH 7 und 8 auf, maximale Goethitanteile bei pH 4 und bei pH 12. Die Kristallinität beider Fe-oxide, gemessen an der Röntgenlinienverbreiterung, dem magnetischen Hyperfeinfeld und dessen Verteilungsbreite, war umso geringer, je geringer ihr entsprechender Anteil an der Mischung war. Für die Bildung beider Fe-oxide wird ein kompetitiver Mechanismus vorgeschlagen: Goethit bildet sich über die Lösung und zwar bevorzugt aus einwertigen Fe(III)-Ionen ($Fe(OH)_2{}^+$ und $Fe(OH)_4{}^-$) und Hämatit durch interne Umstrukturierung und Entwässerung innerhalb der Ferrihydritaggregate. Dieses Konzept stellt eine Beziehung her zwischen dem Anteil an Goethit und Hämatit und der Aktivität der Fe(III)-Ionenspezies in der Lösung und begründet die Aussage, daß günstige Bedingungen für die Goethitbildung ungünstige für die des Hämatits sind und vice versa.

Résumé—La mise en réserve de ferrihydrite dans des suspensions aqueuses à 24°C et à des pH entre 2,5 et 12 pour une durée aussi longue que trois ans a resulté en la formation de goethite et d'hématite. Les proportions et la cristallinité de ces produits ont varié largement en fonction du pH. Un maximum d'hématite a été formé entre pH 7 et 8 et un maximum de goethite a été formé au pH 4 et 12. La cristallinité des deux produits s'est appauvrie proportionnellement à une diminution de la proportion du produit correspondant dans le mélange, comme l'ont indiqué l'élargissement des lignes de diffraction poudrée des rayons-X, et les valeurs de champs et la distribution de largeurs magnétiques hyperfins. L'existence de deux procédés compétitifs est suggeré: la goethite est formée via solution, préférablement à partir d'ions monovalents Fe(III) [$Fe(OH)_2{}^+$ et $Fe(OH)_4{}^-$], l'hématite par réarrangement interne et déshydration au sein des aggrégats ferrihydrite. Ce concept relie les proportions de goethite et d'hématite à l'activité de l'espèce d'ion Fe(III) en solution, et implique que les conditions favorables pour la formation de goethite sont défavorables à celle de l'hématite et vice versa. [D.J.]