

# INFLUENCE OF $Mn^{2+}$ AND pH ON THE FORMATION OF IRON OXIDES FROM FERROUS CHLORIDE AND FERROUS SULFATE SOLUTIONS<sup>1</sup>

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**Abstract**—The influence of  $Mn^{2+}$  on the formation of Fe oxides at pHs of 6.0 and 8.0 and varying Mn/Fe molar ratios (0, 0.1, 1.0, and 10.0) in the  $FeCl_2-NH_4OH$  and  $FeSO_4-NH_4OH$  systems was studied by X-ray powder diffraction (XRD), infrared absorption, transmission electron microscopic, and chemical analyses. In the absence of  $Mn^{2+}$ , lepidocrocite ( $\gamma-FeOOH$ ) and maghemite ( $\gamma-Fe_2O_3$ ) were the crystalline species formed at pHs of 6.0 and 8.0, respectively, in the  $FeCl_2$  system, whereas lepidocrocite and goethite ( $\alpha-FeOOH$ ) and lepidocrocite were the crystalline species formed at pHs of 6.0 and 8.0, respectively, in the  $FeSO_4$  system. The amount of Mn coprecipitated with Fe (as much as 8.1 mole % in the  $FeCl_2$  system and 15.0 mole % in the  $FeSO_4$  system) increased as the initial solution Mn/Fe molar ratio increased from 0 to 10.0, resulting in the perturbation of the crystallization processes of the hydrolytic products of Fe formed. At pH 6.0, the perturbation led to the formation of poorly ordered lepidocrocite, as reflected in the increasing broadening of its characteristic peaks in the XRD patterns. At pH 8.0, poorly ordered lepidocrocite and a honessite-like mineral ( $Mn-Fe-SO_4-H_2O$ ) formed in the  $FeCl_2$  and  $FeSO_4$  systems, respectively.

**Key Words**—Goethite, Infrared spectroscopy, Iron oxides, Lepidocrocite, Maghemite, Manganese, Synthesis, X-ray powder diffraction.

## INTRODUCTION

The presence of inorganic (phosphate, silicate) and organic (citrate, tartrate, malate) anions even in small amounts has been shown to retard the crystallization of Fe oxides (Schwertmann, 1985; Schwertmann *et al.*, 1986). Studies of the effect of foreign ions have contributed to an understanding of the mechanisms of the transformation of ferrihydrite to goethite and hematite (Fisher and Schwertmann, 1975; Cornell and Schwertmann, 1979; Cornell, 1985). The only cationic species that has been considered in detail in affecting the formation of Fe oxides is Al although recently, Cornell and Giovanoli (1987, 1988) studied the influence of Mn and Cu in the transformation of ferrihydrite. In addition to modifying the kinetics and products of transformation, Al may be incorporated in the crystal structure of both goethite and hematite (e.g., Schwertmann, 1985). Another cation that might be expected to influence the formation and transformation of Fe oxides is Mn. The close chemical similarity between Mn and Fe is reflected geologically in their coexistence in rocks of all kinds formed in both marine and terrestrial environments. Mn has recently been shown to replace 15 mole % of Fe in goethite (Stiers and Schwertmann, 1985). Krishnamurti and Huang (1987, 1988) recently reported the effect of Mn oxides (birnessite, pyrolusite, cryptomelane, and hausmannite) on the formation of various hydrolytic products of Fe, including

lepidocrocite, akaganeite, magnetite, ferroxhyte, and X-ray-noncrystalline Fe oxides. The nature of the product was attributed to the influence of the widely different surface properties of the Mn oxide present in the system during the oxidation of  $Fe^{2+}$  and the subsequent crystallization of its precipitation products.

During the oxidation of  $Fe^{2+}$  to  $Fe^{3+}$ ,  $Mn^{4+}$  and  $Mn^{3+}$  in the Mn oxides is partly reduced to  $Mn^{2+}$ .  $Mn^{2+}$  in solution may significantly influence the formation and transformation of iron oxides. In studying the influence of temperature and foreign ions on the formation of goethite in the  $FeSO_4-NaOH$  system, Detourney *et al.* (1975) reported that  $Mn^{2+}$  impeded the formation and growth of goethite crystals, with lepidocrocite formed as an additional phase, at Mn/Fe molar ratio of 0.1–0.2. No attempt was made to maintain the pH of synthesis in their system. Recently, Cornell and Giovanoli (1987) reported that ferrihydrite, in the presence of  $Mn^{2+}$  at pH 11–13, transformed to Mn-goethite and/or jacobsonite with as much as 15 mole % Mn replacing Fe in the goethite structure in the  $Fe^{3+}-Mn^{2+}$  nitrate system. To date, no work has been carried out to evaluate the influence of  $Mn^{2+}$  on the formation of Fe oxides from  $Fe^{2+}$  in pH range of 6.0–8.0, typical of hydromorphic soils, in which  $Fe^{2+}$  and  $Mn^{2+}$  coexist in solution. Chloride and sulfate ions are common inorganic anions in natural systems. Chloride and sulfate ions are common inorganic anions in natural systems. The present paper reports the results of an investigation of the influence of  $Mn^{2+}$  on the crystallization of Fe oxides in the ferrous chloride and ferrous sulfate systems in the pH range 6–8.

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Table 1. Chemical analysis of the precipitates formed in the absence and presence of Mn<sup>2+</sup>.

pH of formation	Solution Mn/Fe molar ratio	Products <sup>1</sup>	$\frac{Mn_1 - Mn_0}{(Mn_1 - Mn_0) + (Fe_1 - Fe_0)}$ (mole %)	Fe <sub>0</sub> <sup>3</sup> (mole %)
FeCl <sub>2</sub> -NH <sub>4</sub> OH system				
6.0	0	L	0	24.0
6.0	0.1	L	0.3	17.5
6.0	1.0	POL	1.3	40.1
6.0	10.0	POL	3.2	40.2
8.0	0	M	0	16.0
8.0	0.1	M	0.3	11.1
8.0	1.0	POL	2.0	38.5
8.0	10.0	NC	8.1	41.8
FeSO <sub>4</sub> -NH <sub>4</sub> OH system				
6.0	0	L, G	0	18.5
6.0	0.1	L	0.6	9.0
6.0	1.0	POL	1.6	37.6
6.0	10.0	POL	3.0	40.0
8.0	0	L	0	15.5
8.0	0.1	L	0.7	13.0
8.0	1.0	POL	2.1	33.2
8.0	10.0	HLM	15.0	24.4

<sup>1</sup> Dominant precipitation products identified by X-ray powder diffraction: L = lepidocrocite; POL = poorly ordered lepidocrocite; M = maghemite; NC = noncrystalline; G = goethite; HLM = honessite-like mineral.

<sup>2</sup> Mn<sub>1</sub> and Fe<sub>1</sub> = total manganese and iron; Mn<sub>0</sub> and Fe<sub>0</sub> = Mn and Fe extractable by hydroxylamine hydrochloride.

<sup>3</sup> Average of duplicates: ±0.2%.

## EXPERIMENTAL

Suitable quantities of MnCl<sub>2</sub> or MnSO<sub>4</sub> were added to 50 ml of freshly prepared aqueous solution of 0.01 M FeCl<sub>2</sub> or FeSO<sub>4</sub> in 150-ml beakers to obtain desired Mn/Fe molar ratios of 0, 0.1, 1.0, and 10. The Mn/Fe molar ratio of this study refers to the molar ratio of the solution Fe and Mn initially present in the system. A 0.1 M NH<sub>4</sub>OH or 0.5 M NH<sub>4</sub>OH solution was then added dropwise (flow rate of ~0.375 ml/min) with constant stirring using a magnetic stirrer on a Metrohm 672 Titroprocessor to maintain the final pH of the suspension for 1 hr at 6.0 or 8.0, respectively. Air had free access to the system during the reaction period. No attempt to protect the systems from possible oxidation by the air was made during the reaction. The reaction carried out at 23.5°C did not reach equilibrium, and not all the Fe<sup>2+</sup> was oxidized at the end of the reaction period. The precipitates were washed free of electrolytes by centrifugation at 1750 g for 10 min and ultrafiltration (nitrocellulose filter of 0.025-μm pore size) and then air dried under vacuum.

The total Fe and Mn contents of the precipitates were determined by atomic absorption spectrophotometry, after complete dissolution of the precipitate by slow boiling in 6 M HCl. The hydroxylamine hydrochloride method (Chao and Zhou, 1983) was used to remove the free Mn oxides and noncrystalline Fe compounds

that were present as admixtures in the crystalline Fe oxides.

X-ray powder diffraction (XRD) patterns of the precipitates were obtained using Mn-filtered FeKα radiation on a Philips X-ray diffractometer (Model PW 1310). Infrared (IR) spectra were obtained in the range 1900–300 cm<sup>-1</sup> on a Perkin Elmer 983 infrared spectrophotometer using the KBr pellet technique (1 mg of sample mixed with 300 mg of KBr). For the transmission electron microscopic (TEM) examination, a drop of sample suspension was deposited on carbon-coated Formvar film on a copper grid. TEMs of the precipitates were obtained using a Philips EM 400 transmission electron microscope.

## RESULTS AND DISCUSSION

The amount of Mn coprecipitated with the Fe oxides increased with increasing Mn/Fe molar ratios. The increase was 20.9 to 67.8 times at pH 8.0 and 6.2 to 11 times at pH 6.0, as the initial Mn/Fe molar ratio increased from 0.1 to 10.0 (Table 1). The Fe and Mn extractable in hydroxylamine hydrochloride reflected the free Mn oxides and X-ray-noncrystalline Fe compounds present in the precipitation products as admixtures with the crystalline Fe oxides formed. The difference between the amounts of total Mn (Mn<sub>1</sub>) and those of Mn extractable in hydroxylamine hydrochloride (Mn<sub>0</sub>) was possibly due to Mn substituting for Fe in the structure of the crystalline Fe oxides formed. The amount of Fe extractable in hydroxylamine hydrochloride (Fe<sub>0</sub>) generally increased with increasing Mn/Fe molar ratio from 0.1 to 10.0 (Table 1), indicating increased amounts of poorly ordered Fe oxides formed in the products. The amounts of Mn<sub>1</sub> and Mn<sub>0</sub> in the precipitates consistently increased with the increase in the initial Mn/Fe molar ratio of the solution. The increasing amounts of nonextractable Mn (Mn<sub>1</sub> - Mn<sub>0</sub>) in the precipitates formed at increasing Mn/Fe molar ratios (Table 1) indicate an increase in the amount of Mn substituting for Fe in the structure. The values of (Mn<sub>1</sub> - Mn<sub>0</sub>)/[(Fe<sub>1</sub> - Fe<sub>0</sub>) + (Mn<sub>1</sub> - Mn<sub>0</sub>)] in Table 1 represent the mole % Mn substituting in the Fe oxides formed. The crystallization processes of the Fe oxides were perturbed apparently by the increasing amounts of Mn<sup>2+</sup> present in the system during the oxidation of Fe<sup>2+</sup> and the subsequent hydrolysis and precipitation of Fe, resulting in the formation of various crystalline and noncrystalline Fe oxides.

The influence of Mn<sup>2+</sup> on the nature of the Fe oxides formed from Fe<sup>2+</sup> in both the chloride and sulfate systems is elucidated by the data obtained from XRD, IR, and TEM, as stated below.

### FeCl<sub>2</sub>-NH<sub>4</sub>OH system

In the absence of Mn, lepidocrocite and maghemite were the precipitation products formed at pHs of 6.0 and 8.0, respectively. The XRD pattern of the Fe oxide precipitate formed at pH 6.0 was characterized by

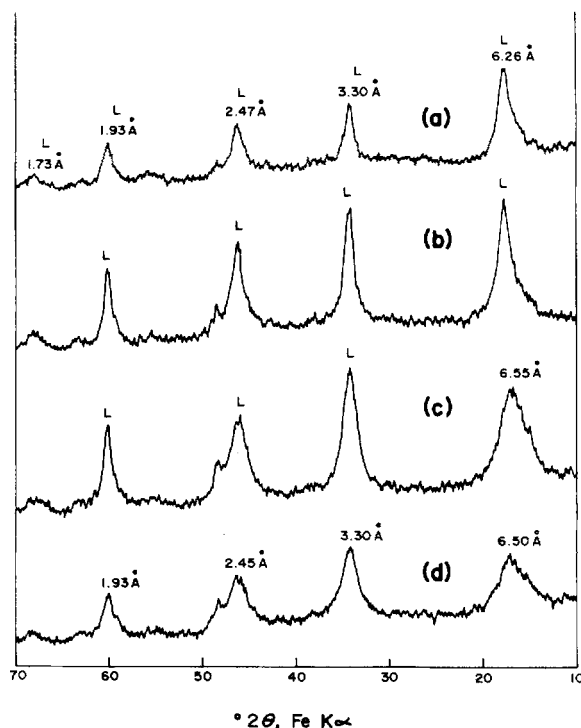


Figure 1. X-ray powder diffractograms of the precipitation products of Fe in the  $FeCl_2-NH_4OH$  system at pH 6.0 and at initial solution Mn/Fe molar ratios of (a) 0, (b) 0.1, (c) 1.0, and (d) 10.0. L = lepidocrocite.

d-values of 6.26, 3.30, 2.47, 1.93, and 1.73 Å (Figure 1a), matching well the XRD data of lepidocrocite (JCPDS 8-98). The XRD pattern of the precipitate formed at pH 8.0 was characterized by d-values of 4.83, 2.96, 2.53, 2.10, and 1.71 Å (Figure 2a), matching well the XRD data of magnetite (JCPDS 19-629) and maghemite (JCPDS 25-1402). Magnetite was virtually impossible to distinguish from maghemite from XRD evidence alone. The IR spectrum of the precipitate formed at pH 6.0 contained absorption bands at 1634, 1020, 743, 476, and 353  $cm^{-1}$  (spectrum a, Figure 3A), characteristic of lepidocrocite (Gadsden, 1975), whereas that of the precipitate formed at pH 8.0 contained well-defined absorption bands at 1634, 632, 559, and 397  $cm^{-1}$  (spectrum a, Figure 3B), matching reasonably well with maghemite (Farrell, 1972; Taylor and Schwertmann, 1974). The bands could not be assigned to magnetite, which has been reported to have an ill-defined IR spectrum containing two broad bands at about 400 and 590  $cm^{-1}$  (Farrell, 1972; Gadsden, 1975).

At pH 6.0, the XRD reflections of lepidocrocite were sharper for the Mn/Fe molar ratio of 0.1, indicating a greater degree of crystallinity compared with the reflections of lepidocrocite formed in the absence of Mn (Figures 1a and 1b). The chemical analysis of the precipitate formed at a Mn/Fe molar ratio of 0.1 also showed less  $Fe_0$  representing the poorly crystalline Fe

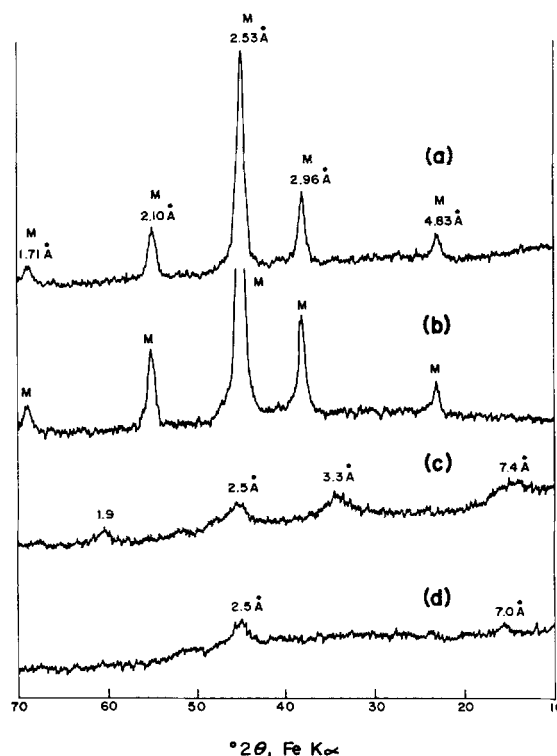


Figure 2. X-ray powder diffractograms of the precipitation products of Fe in the  $FeCl_2-NH_4OH$  system at pH 8.0 and at initial solution Mn/Fe molar ratios of (a) 0, (b) 0.1, (c) 1.0, and (d) 10.0. M = maghemite.

oxides (Table 1). The greater degree of crystallinity indicates that a certain degree of replacement of Mn for Fe improved crystallinity, as has been observed for the substitution of Mn for Fe in goethite (Stiers and Schwertmann, 1985), and of Al for Fe in goethite (Schulze and Schwertmann, 1984) and hematite (Schwertmann *et al.*, 1979). The presence of small amounts of Mn might have slowed the kinetics of  $Fe^{2+}$  oxidation, resulting in better crystallinity of the products of hydrolysis. The broadening of the characteristic XRD peaks of lepidocrocite at Mn/Fe molar ratios of 1.0 and 10.0 (Figures 1c and 1d) may have been due to a decrease in particle size and crystallinity. The increase in the  $d(020)$  value of lepidocrocite (from 6.26 to 6.55 Å) may have been due to increased incorporation of Mn in the structure. As the Mn/Fe molar ratio increased from 0 to 10, the characteristic absorption bands of lepidocrocite at 1020, 743, 476, and 353  $cm^{-1}$  (Mn/Fe molar ratio = 0, spectrum a, Figure 3A) became broader and shifted to 1019, 750, 481, and 360  $cm^{-1}$  (Mn/Fe molar ratio = 10, spectrum d, Figure 3A), possibly due to incorporation of Mn in the structure. The TEM of the precipitation product formed at a Mn/Fe molar ratio of 10 shows laths, and aggregates of irregularly shaped (probably laths?) particles (Figure 4b). The particle size of the laths is smaller than those observed for the precipitate formed at a Mn/Fe molar

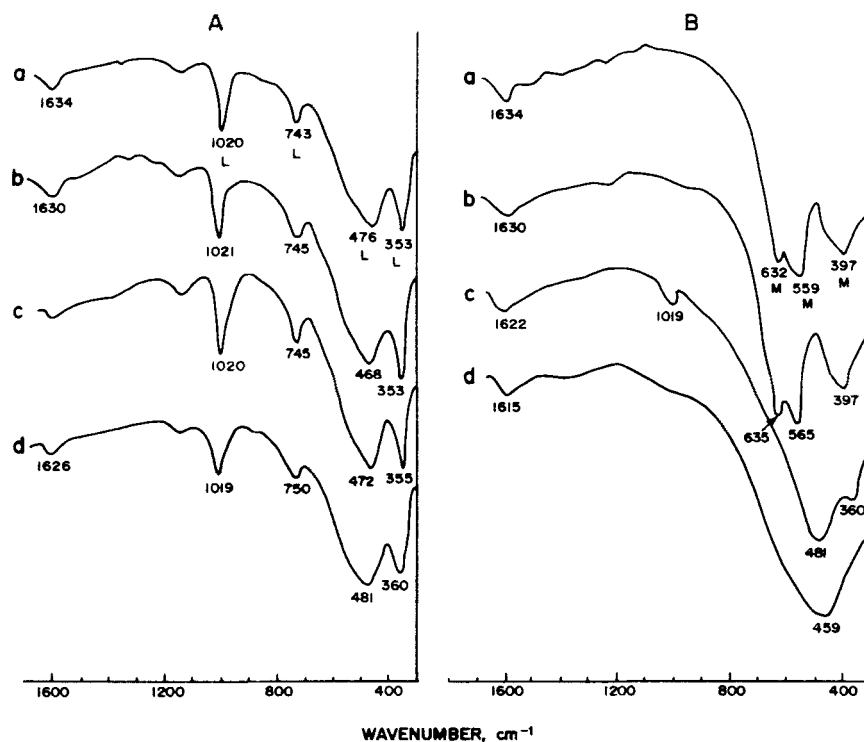


Figure 3. Infrared absorption spectra of the precipitation products of Fe formed at different initial solution Mn/Fe molar ratios of (a) 0, (b) 0.1, (c) 1.0, and (d) 10.0 in the  $\text{FeCl}_2\text{-NH}_4\text{OH}$  system at (A) pH 6.0 and (B) pH 8.0.

ratio = 0 (Figure 4a). Schwertmann and Taylor (1977) showed lepidocrocite to occur in laths by TEM.

At pH 8.0, the XRD pattern of the precipitate formed at a Mn/Fe molar ratio of 0.1 (Figure 2b) was characterized by sharp XRD reflections at 4.83, 2.96, 2.53, 2.10, and 1.71 Å, characteristic of maghemite (JCPDS 25-1402), indicating a higher degree of crystallinity than the maghemite formed in the absence of Mn (Figure 2a). The chemical analysis of the precipitate showed lower amounts of  $\text{Fe}_0$  representing the poorly crystalline Fe oxides, compared with that of the precipitate formed at a Mn/Fe molar ratio of 0 (Table 1). The XRD pattern of the precipitate formed at Mn/Fe molar ratio of 1.0 (Figure 2c) was characterized by broad peaks at 7.4, 3.3, 2.5, and 1.9 Å, presumably due to poorly ordered lepidocrocite, whereas that of the precipitate formed at a Mn/Fe molar ratio of 10.0 showed only two weak peaks at about 7.0 and 2.5 Å (Figure 2d), illustrating the influence of  $\text{Mn}^{2+}$  on the crystallization of the precipitation products of Fe. The TEMs of the precipitation products formed at a Mn/Fe molar ratio of 0 (Figure 4c) and 10 (Figure 4d) show cubes of maghemite, and sharp needles and anhedral particles, respectively. The IR spectrum of the precipitate formed at a Mn/Fe molar ratio of 0.1 (spectrum b, Figure 3B) has bands at 635, 565, and 397  $\text{cm}^{-1}$ , indicating maghemite, as observed also by XRD analysis (Figure 2b). The IR spectrum of the precipitate formed at a Mn/Fe molar ratio of 1.0 (spectrum c, Figure 3B)

has broad bands at 1622, 1019, 481, and 360  $\text{cm}^{-1}$ . The broadening and slight shift of the characteristic bands of lepidocrocite may be due to the substitution of Mn for Fe in the structure and the resulting perturbation in the crystallinity, as observed by XRD. The IR spectrum of the precipitate formed at a Mn/Fe molar ratio = 10 (spectrum d, Figure 3B) shows a weak band at 1615  $\text{cm}^{-1}$  and a strong band at 459  $\text{cm}^{-1}$ , which can be attributed to the HOH-deformation in the adsorbed water and ( $\text{Fe-O}_6$ ) octahedral vibrations (Brady *et al.*, 1986), respectively, of the poorly crystalline Fe oxide formed.

#### $\text{FeSO}_4\text{-NH}_4\text{OH}$ system

The XRD pattern of the precipitate formed at pH 6.0 in the absence of Mn (Figure 5a) was characterized by sharp XRD maxima at 6.26, 4.18, 3.30, 2.69, 2.47, 1.94, and 1.73 Å, indicating a highly crystalline lepidocrocite (JCPDS 8-98) and goethite (JCPDS 29-713), whereas that of the precipitate formed at pH 8.0 (Figure 6a) is characterized by d-values of 6.26, 3.30, 2.47, 1.94, and 1.73 Å, matching well with the standard data of lepidocrocite (JCPDS 8-98). Brady *et al.* (1986) observed that specific adsorption of the sulfate anion on the surface of hydrous iron oxide caused destabilization of colloidal sols produced by  $\text{Fe}^{3+}$  hydrolysis. Possibly, at pH 6.0, the destabilization introduced by the sulfate anion during the crystallization resulted in the formation of goethite. Instead of maghemite, which formed

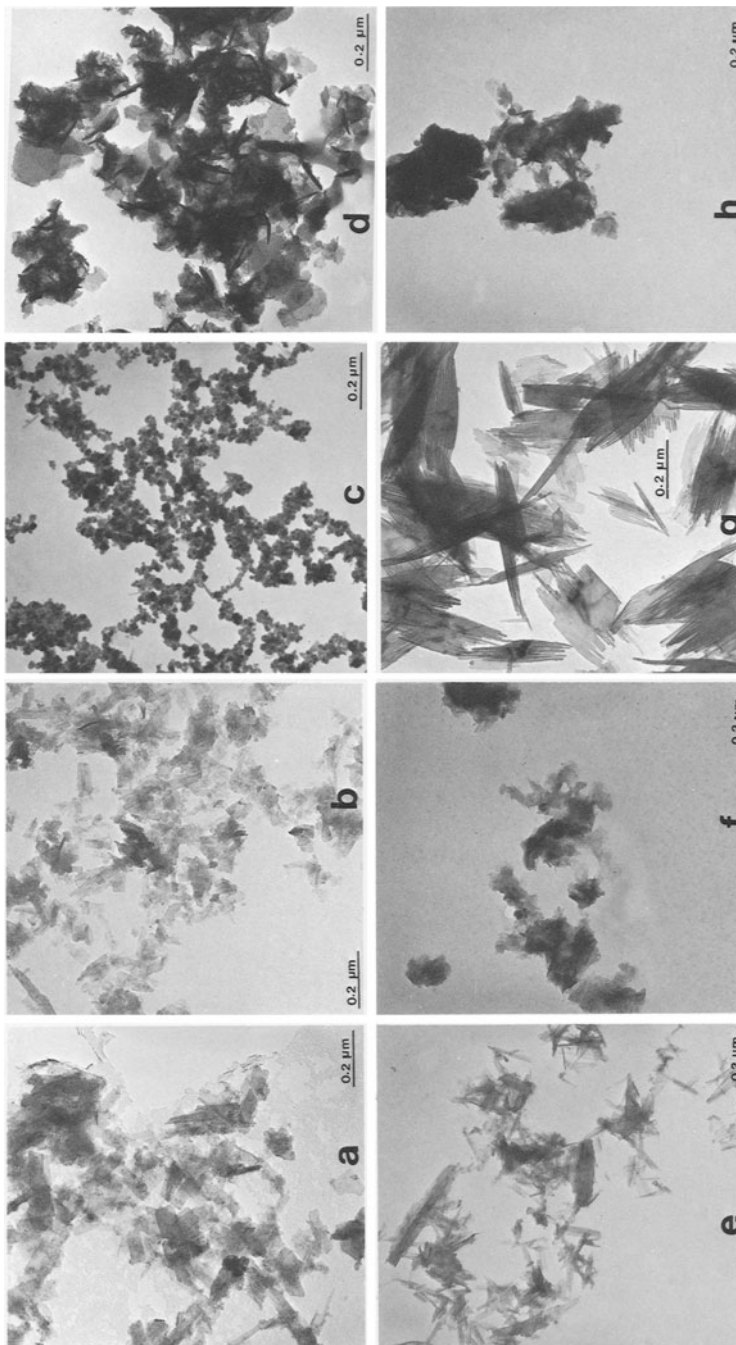


Figure 4. Transmission electron micrographs of the precipitation products of Fe formed in the  $FeCl_2-NH_4OH$  system at pH 6.0 and initial solution Mn/Fe molar ratio of (a) 0, and (b) 10.0; in the  $FeCl_2-NH_4OH$  system at pH 8.0 and initial solution Mn/Fe molar ratio of (c) 0, and (d) 10.0; in the  $FeSO_4-NH_4OH$  system at pH 6.0 and initial solution Mn/Fe molar ratio of (e) 0, and (f) 10.0; and in the  $FeSO_4-NH_4OH$  system at pH 8.0 and initial solution Mn/Fe molar ratio of (g) 0, and (h) 10.0.

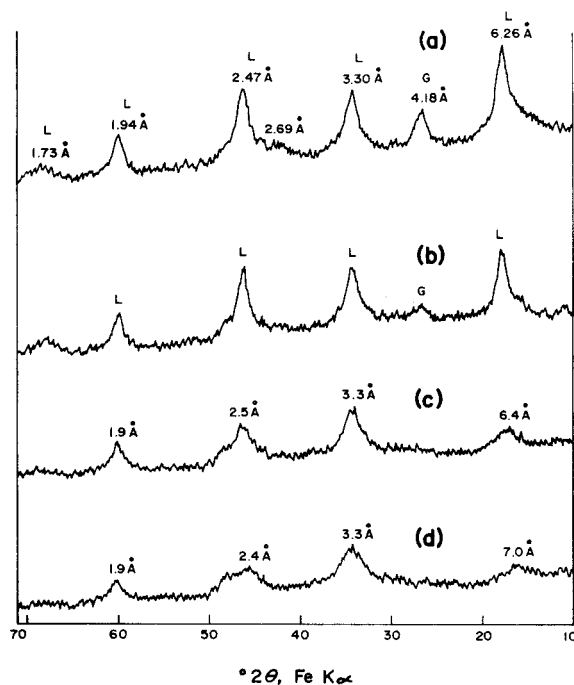


Figure 5. X-ray powder diffractograms of the precipitation products of Fe in the  $\text{FeSO}_4\text{-NH}_4\text{OH}$  system at pH 6.0 and at initial solution Mn/Fe molar ratios of (a) 0, (b) 0.1, (c) 1.0, and (d) 10.0. L = lepidocrocite, G = goethite.

in the  $\text{FeCl}_2$  system at pH 8.0, lepidocrocite formed in the  $\text{FeSO}_4$  system at the same pH.

The IR absorption spectrum of the precipitate formed at pH 6.0 and a Mn/Fe molar ratio of 0 (spectrum a, Figure 7A) shows bands at 1136, 1020, and  $355\text{ cm}^{-1}$ , characteristic of lepidocrocite and at 886, 792, 580, and  $405\text{ cm}^{-1}$ , characteristic of goethite. The IR spectrum of the precipitate formed at pH 8.0 and a Mn/Fe molar ratio of 0 shows bands at 1155, 1020, 749, 472, and  $354\text{ cm}^{-1}$ , characteristic of lepidocrocite (spectrum a, Figure 7B). Goethite has been reported to give IR bands at 880, 780, and  $400\text{ cm}^{-1}$  (Gadsden, 1975). The band observed at about  $1615\text{--}1635\text{ cm}^{-1}$  in all the spectra can be assigned to the HOH-deformation vibration of adsorbed water (Brady *et al.*, 1986) of the significant amounts of X-ray-noncrystalline Fe oxides in the precipitation products (Table 1).

The precipitation products of Fe formed at pH 6.0 and a Mn/Fe molar ratio of 0 occur as laths (lepidocrocite, Figure 4e), together with acicular needles (goethite, Figure 4e). Those formed at pH 8.0 occur as well-defined laths (lepidocrocite, Figure 4g), corroborating the XRD (Figure 6a) and IR data (spectrum a, Figure 7B). The crystalline Fe oxides are morphologically similar to the Fe oxides reported by Schwertmann and Taylor (1977).

At pH 6.0 and a Mn/Fe molar ratio of 0.1 and in the presence of sulfate (Figure 5b), the characteristic XRD peaks of goethite (4.18 and  $2.69\text{ \AA}$ ) were weaker

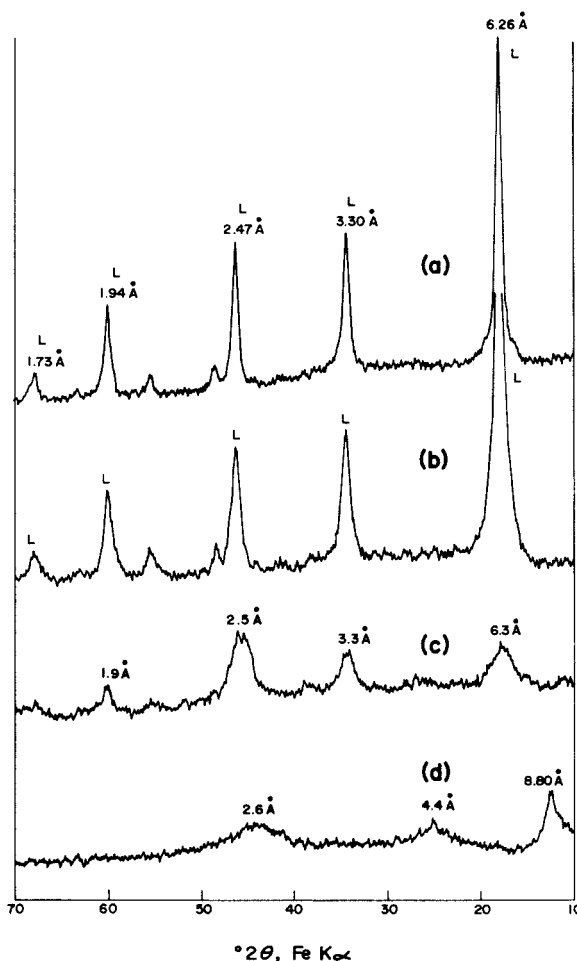


Figure 6. X-ray powder diffractograms of the precipitation products of Fe in the  $\text{FeSO}_4\text{-NH}_4\text{OH}$  system at pH 8.0 and at initial solution Mn/Fe molar ratios of (a) 0, (b) 0.1, (c) 1.0, and (d) 10.0. L = lepidocrocite.

and/or broader and those of lepidocrocite were slightly broader than those observed for the precipitate formed at a Mn/Fe molar ratio = 0 (Figure 5a), indicating perturbation in the crystallinity resulting in poorly ordered species. The  $\text{Fe}_0$  value for this precipitation product (Table 1), however, was slightly lower than that formed at Mn/Fe molar ratio = 0, indicating the presence of increased amounts of crystalline species. At this low ratio, the  $\text{SO}_4^{2-}$  anion possibly hindered sterically precipitation and crystal growth and might have contributed to a decrease in crystal size, as suggested by the broadening of the XRD peaks. At a Mn/Fe molar ratio of 1.0, the XRD peaks of goethite were absent, and the XRD pattern of the precipitate had broad peaks at 6.4, 3.3, 2.5, and  $1.9\text{ \AA}$  (Figure 5c), indicating the presence of poorly ordered lepidocrocite. The perturbation in the crystallization processes was even more evident at the Mn/Fe molar ratio of 10.0. The XRD pattern (Figure 5d) had broad XRD peaks at 7.0, 3.3, 2.4, and  $1.9\text{ \AA}$ . About 3.0 mole % Mn (0.22 mole/

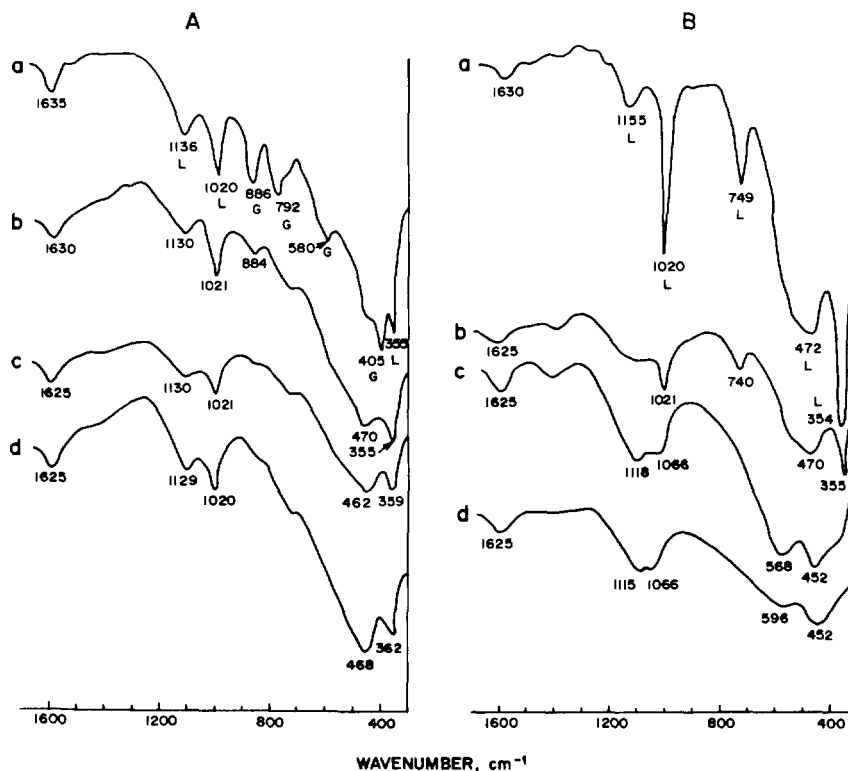


Figure 7. Infrared absorption spectra of the precipitation products of Fe formed at different initial solution Mn/Fe molar ratios of (a) 0, (b) 0.1, (c) 1.0, and (d) 10.0 in the  $FeSO_4-NH_4OH$  system at (A) pH 6.0 and (B) pH 8.0.

kg) was present in the precipitate formed at this high Mn/Fe molar ratio (Table 1). The increase of the  $d(020)$  value of lepidocrocite from 6.26 Å (Mn/Fe molar ratio = 0, Figure 5a) to 6.40 Å (Mn/Fe molar ratio = 1.0, Figure 5c) and 7.0 Å (Mn/Fe molar ratio = 10, Figure 5d) was possibly due to the substitution of  $Mn^{2+}$  (ionic radius = 0.80 Å) for Fe (ionic radius of  $Fe^{2+}$  = 0.76 Å and of  $Fe^{3+}$  = 0.64 Å) in the structure. The large increase in  $d(020)$  suggests that Mn was present in the structure as  $Mn^{2+}$  (ionic radius = 0.80 Å) rather than as  $Mn^{3+}$  (ionic radius = 0.66 Å). Further,  $Mn^{3+}$  in solution easily disproportionates to  $Mn^{2+}$  (Baes and Mesmer, 1976). Similar increase in the  $d$ -values of goethite formed in the presence of  $Mn^{2+}$  was attributed to the substitution of Mn for Fe in the structure by Stiers and Schwertmann (1985) and Cornell and Giovanoli (1987). The IR spectra of the precipitates formed at pH 6.0 and a Mn/Fe molar ratio of 1 (spectrum c, Figure 7A) and 10 (spectrum d, Figure 7A) show broad bands at about 1130, 1020, 465, and 360  $cm^{-1}$ . The broadening and shift of the band at 355  $cm^{-1}$  (Mn/Fe = 0, spectrum a, Figure 7A) to 359  $cm^{-1}$  (Mn/Fe = 1.0, spectrum c, Figure 7A) and 362  $cm^{-1}$  (Mn/Fe = 10, spectrum d, Figure 7A) may be due to the perturbation in the crystallinity caused by the substitution of Mn for Fe in the structure. The weak band at 884  $cm^{-1}$  and the shoulder at  $\sim 800$   $cm^{-1}$  in the precipitate formed at pH 6.0 and a Mn/Fe molar ratio of 0.1

(spectrum b, Figure 7A) are probably due to small amounts of goethite present. The TEMs of the precipitates formed at pH 6.0 and a Mn/Fe molar ratio of 10 show ill-defined laths, suggesting a poorly ordered lepidocrocite (Figure 4f).

At pH 8.0, the XRD pattern of the precipitate formed at a Mn/Fe molar ratio of 0.1 showed the characteristic XRD peaks of lepidocrocite (Figure 6b). With an increase in the Mn/Fe molar ratio, the amount of Mn coprecipitated along with the Fe oxide increased (Table 1) and the crystallization processes of the precipitation products of Fe were perturbed. At pH 8.0 and a Mn/Fe molar ratio of 1.0 (Figure 6c), the XRD pattern of the precipitate contained broad peaks at 6.3, 3.3, 2.5, and 1.9 Å, indicative of poorly ordered lepidocrocite. The XRD pattern of the precipitate formed at a Mn/Fe molar ratio of 10.0 contained a sharp peak at 8.80 and two broad peaks at about 4.4 and 2.6 Å (Figure 6d). This pattern was similar to that of honessite ( $Ni-Fe-SO_4-H_2O$ ), which is reported to have XRD reflections at 8.70, 4.33, 2.67, and 1.54 Å (JCPDS 25-407). At the high Mn/Fe molar ratio of 10.0, a crystallographically similar compound, viz.,  $Mn-Fe-SO_4-H_2O$ , may have formed. The larger ionic radius of  $Mn^{2+}$  (0.80 Å) compared with  $Ni^{2+}$  (0.69 Å) was apparently reflected in the  $d$ -values of 8.80 and 4.40 Å (Figure 6d) compared with 8.70 and 4.33 Å for honessite. The smaller  $Fe_0$  value (Table 1) indicates a higher degree

of crystallinity in the compound formed, probably due to the formation of a honessite-like mineral. The TEM of the precipitation product formed at pH 8.0 and a Mn/Fe molar ratio of 10.0 shows a mass of anhedral particles (Figure 4h), in contrast to the well-defined laths of lepidocrocite formed at a Mn/Fe molar ratio = 0 (Figure 4g). The IR spectrum of the precipitate formed at pH 8.0 and a Mn/Fe molar ratio of 0.1 (spectrum b, Figure 7B) contains bands at 1625, 1021, 740, 470, and 355  $\text{cm}^{-1}$ . The broadening and the slight shift of the characteristic bands of lepidocrocite indicate perturbation in the crystallinity due to Mn-for-Fe substitution in the structure. The IR spectra of the precipitates formed at Mn/Fe molar ratios of 1.0 (spectrum c, Figure 7B) and 10.0 (spectrum d, Figure 7B) show broad bands at 1625, 1118, 1066, 568, and 452  $\text{cm}^{-1}$  and 1625, 1115, 1066, 596, and 452  $\text{cm}^{-1}$ , respectively. The bands at about 1115 and 1060  $\text{cm}^{-1}$  can be attributed to the  $\nu_3$  fundamental of uncoordinated  $\text{SO}_4^{2-}$  of  $T_d$  symmetry (Nakamoto, 1970), and the band at 1625  $\text{cm}^{-1}$  may be due to the HOH-deformation vibration of the adsorbed water (Brady *et al.*, 1986). The bands observed at 596, 568, and 453  $\text{cm}^{-1}$  may be due to  $(\text{Fe}-\text{O}_6)_t$  octahedral vibration (Brady *et al.*, 1986).

#### SUMMARY AND CONCLUSIONS

In the absence of  $\text{Mn}^{2+}$ , lepidocrocite ( $\gamma\text{-FeOOH}$ ), and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) were the crystalline species formed at pHs of 6.0 and 8.0, respectively, in the  $\text{FeCl}_2\text{-NH}_4\text{OH}$  system, whereas lepidocrocite + goethite ( $\alpha\text{-FeOOH}$ ) and lepidocrocite alone were the crystalline species formed at pH 6.0 and 8.0, respectively, in the  $\text{FeSO}_4\text{-NH}_4\text{OH}$  system.

Chemical analyses of the precipitates indicated that the amounts of Mn coprecipitated with Fe oxides increased with the increasing initial solution Mn/Fe molar ratios. As the initial solution Mn/Fe molar ratio increased from 0.1 to 10.0, the amount of Mn coprecipitated with Fe increased from 0 to 3.2 mole % Mn (0 to 0.31 mole/kg) at pH 6.0 and from 0 to 8.1 mole % Mn (0 to 3.14 mole/kg) at pH 8.0 in the  $\text{FeCl}_2$  system, and from 0 to 3.0 mole % Mn (0 to 0.22 mole/kg) at pH 6.0 and from 0 to 15.0 mole % Mn (0 to 2.71 mole/kg) at pH 8.0 in the  $\text{FeSO}_4$  system (Table 1). The crystallization processes of the precipitation products of Fe were perturbed by increasing coprecipitation of Mn. At pH 6.0, the perturbation resulted in the formation of poorly ordered lepidocrocite in both systems (Figures 1 and 5). At pH 8.0, the perturbation resulted in the formation of poorly ordered lepidocrocite and a honessite-like species ( $\text{Mn-Fe-SO}_4\text{-H}_2\text{O}$ ) in the  $\text{FeCl}_2$  and  $\text{FeSO}_4$  systems, respectively (Figures 2 and 6).

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