IV.5. INFLUENCE OF EDTA ON THE FORMATION OF γ-FeOOH (Rongguang Lin and Burtron H. Davis).

IV.5.1. INTRODUCTION

In recent years, the influence of various organic molecules on the formation of ferrihydrite has been investigated (IV.5.1-IV.5.8). Ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) is a poorly ordered compound which is believed to transform into more crystalline compounds via two competing pathways: (1) dissolution/reprecipitation leading to α-FeOOH, and (2) internal aggregation and rearrangement leading to α-Fe_2O_3 (IV.5.9). The ability of ligands to effect the transformation of the ferrihydrite depends on the pH of the system and on the nature of the ligand. The pH range where a ligand absorbs on ferrihydrite is governed by the acid/base properties of the ligand. The extent of absorption is related to the stereochemistry of the ligand and the number of the potential coordinating groups. In general, polydentate species that form chelates adsorb more strongly than unidentate ligands.

The ability of EDTA (ethylenediamine tetraacetic acid) to bind to metal ions to form stable complexes over a broad pH range has resulted in a wide variety of chemical and industrial applications for EDTA. These include water softening, scale removal, and preservative action through the suppression of the catalytic effects of metal ion impurities. The adsorption of EDTA on various forms of iron hydroxide has been studied (IV.5.10-IV.5.15). It has been shown that EDTA adsorbs through deprotonated carboxyl groups.

Recently EDTA was shown to promote the formation of γ-FeOOH from $FeSO_4$, and it has been shown that EDTA alters Green Rust (II) intermediates produced

during the oxidation of $Fe(OH)_2$ (IV.5.16). The coordination of EDTA and its role on the formation of γ-FeOOH is not known. In this study, the effects of adding varying amounts of EDTA on the formation of γ-FeOOH and/or α-FeOOH during the oxidation of an aqueous suspension of $Fe(OH)_2$ were investigated. The aim of the present investigation is to define the role of EDTA on the formation of γ-FeOOH and to understand more about the mechanism by which EDTA operates during the crystallization.

IV.5.2. EXPERIMENTAL

IV.5.2.a. Materials

$FeSO_4 \bullet 7H_2O$ was purchased from Aldrich Chemical Co. NaOH solution (5.0 N) were prepared by dissolving NaOH (Mallinckrodt reagent grade) in distilled water free from O_2 and CO_2. The EDTA was Aldrich reagent grade.

IV.5.2.b. Preparation

The FeOOH was produced from a $FeSO_4$ solution (500 mL, 0.4M) at room temperature. Solid EDTA was added to the solution to give the desired concentration. EDTA was completely dissolved in the Fe^{2+} solution after stirring for 30 minutes. Nitrogen was bubbled through the solution to remove oxygen from the solution. NaOH solution (5.0M) was then added to produce a suspension of $Fe(OH)_2$. The nitrogen flow was stopped and oxygen was then bubbled through the suspension at a rate of 18 mL/min. at room temperature. Reaction time was measured from the start of the flow of oxygen. During the reaction, the pH was recorded every minute. After about 1 hour of oxygen flow, the pH of the suspension was below 4, and the iron hydroxide in the suspension was completely to FeOOH. The precipitate was washed

with deionized water several times until SO_4^{2-} was not detected in the wash water and then dried for 48 hours at 110°C in vacuum. The precipitate collected from this oxidation procedure is designated as the first oxidation product (W-1) and the filtrate as F-1.

The yellow filtrate (F-1) collected from the filtration was placed in a 1L beaker. NaOH solution (5.0M) was added to the filtrate to adjust the pH to 8.0, and a green precipitate formed. Oxygen flow at 18 mL/min. was passed through the suspension. During the oxidation, the pH of the suspension would decrease unless more base was added to the suspension. Thus, NaOH solution was added during the oxidation (5.0M) so that the pH was held constant at 8.0. After about 60 min., the pH of the suspension remained constant without adding base and the green-colored precipitate had become yellow-orange. The solid was collected by filtration, washed and dried using the procedure described above. The solid was designated as the second oxidation product (W-2). This filtrate was colorless, indicating that a significant amount of iron was not present in the solution, and this was verified by chemical analysis.

Three series of experiments have been performed using EDTA. The first series was carried out by adding EDTA to produce a molar ratio of EDTA/Fe^{2+} that ranged from 0 to 0.225 with a constant molar ratio of Fe^{2+}/NaOH, R, of 0.583. The second series was the same as the first except R = 2.0. The third series was conducted with a mixture that consisted of 0.2 mole of $FeSO_4$, 0.1 mole of NaOH and 0.002 mole of EDTA with varying amounts of water.

X-ray diffraction patterns of the products were obtained using a Philips X-ray diffractometer with $CuK\alpha$ (1.5418 Å) radiation (40 kV and 20 mA). The identification of the product was accomplished by matching the diffraction peak position and intensity

with standards contained in the ASTM data files. The proportion of α-FeOOH and γ-FeOOH in the product was estimated by comparing the area of the (110) peak of α-FeOOH with that of the (020) peak of γ-FeOOH. The particle size was calculated from the linewidth of these two peaks using the Debeye-Scherrer equation (IV.5.5).

The surface area of the products was measured by the BET method, using nitrogen as the adsorbate.

IV.5.3. RESULTS

IV.5.3.a. Experimental Curves of pH with Time

The shapes of the pH/time curves for the oxidation of suspensions of $Fe(OH)_2$ with R {R = Fe^{2+}/OH$^-$} equal to 0.583 and 2.0 (Figures IV.5.1 and IV.5.2, respectively) are similar. During the conversion of Fe^{2+} with gaseous oxygen, two periods of nearly constant pH are generally observed. Following the second abrupt decrease in pH, oxygen consumption becomes very slow and the pH remains at about 4. The presence of EDTA does not alter the shape of the pH/time curves. However, for each of the two values of R, there was a decrease in the time required for the pH to drop below 4 as the molar ratio of EDTA/Fe^{2+} was increased. From Figures IV.5.1 and IV.5.2, it can be seen that the oxidation time required to reach a pH $\leq$ 4 was shorter for R = 2 than for R = 0.583. Also, since the same amount of iron was present in each run, the decrease in time to obtain a pH $\leq$ 4 as the EDTA/Fe^{2+} ratio increases indicates that the presence of EDTA causes the oxidation to terminate prior to complete oxidation of the Fe^{2+} corresponding to the amount when EDTA was not present.

IV.5.3.b. The Effect of Molar Ratio of Fe^{2+}/NaOH and EDTA/Fe^{2+} on the Yield of

Product

The yields of the products obtained from the first and second oxidations with

various molar ratio of EDTA/Fe^{2+} for R = 0.583 and 2.0 are collected in Tables IV.5.1

and IV.5.2, respectively. For R = 0.583, the yield of the first oxidation product (W1)

was higher than the corresponding second oxidation product (W2). For R = 2.0, the

trend was reversed. The data in Tables IV.5.1 and IV.5.2 show that as the molar ratio

of EDTA/Fe^{2+} increases, the yield of the first oxidation product decreases and the

yield of second oxidation product increases. However, in both instances the yield of

the two precipitates (W-1 + W-2) corresponds to a recovery of 99.2% or greater of the

theoretical amount of FeOOH. For R = 0.5833, it requires about 5 EDTA molecules

for each iron ion that is not precipitated (Table IV.5.3). For the suspension with R =

0.5833 there is sufficient base to precipitate 85.7% of the Fe^{2+} as $Fe(OH)_2$, and 86.4%

of the Fe^{2+} is oxidized before the pH is decreased to about 4. However, as the EDTA

concentration is increased there is nearly a linear decrease in the amount of the first

oxidation product, W-1. Thus, the limiting factor for iron oxidation is the amount of

base that is present. Likewise, for the R = 2 suspension 25% of the Fe^{2+} can be

present as $Fe(OH)_2$ and in the absence of EDTA 27.6% of the iron is oxidized. The

amount of base that is present therefore limits the amount of FeOOH that is produced

as the first oxidation product, W-1.

IV.5.3.c. Effect of EDTA/Fe^{2+} Ratio on the Phase Composition

(a) First Oxidation Product. The X-ray diffraction patterns of the products

obtained with various molar ratios of EDTA/Fe^{2+} and R = 0.583 show that γ-FeOOH

with some α-FeOOH is formed if EDTA is not present or is present in small amounts (Figure IV.5.3). The X-ray data (quantitative measurements were made on an expanded version of the patterns in Figure IV.5.3) in Figure IV.5.4 show that in the absence of EDTA the oxidation product for R = 0.583 was a mixture of α-FeOOH and γ-FeOOH with about 90% of the product being γ-FeOOH. The percentage of γ-FeOOH increases as the EDTA/Fe^{2+} ratio increases; when EDTA/Fe^{2+} $\geq$ 0.010 pure γ-FeOOH is obtained. These data indicate that the addition of EDTA enhances the formation of γ-FeOOH. In addition to altering the proportion of the α-FeOOH and γ-FeOOH that was formed, both the XRD peak intensity and width also varied. As the ratio of EDTA/Fe^{2+} increased, the XRD peak intensity decreased and the XRD lines became broader.

The X-ray diffraction patterns of the oxidation products produced with various molar ratios of EDTA/Fe^{2+} for R = 2.0 are shown in Figure IV.5.5. In the absence of EDTA, only α-FeOOH is formed (Figure IV.5.4). A mixture of α-FeOOH and γ-FeOOH is formed as EDTA is added at low concentrations, and the γ-FeOOH content increases as the EDTA/Fe^{2+} ratio increases. For EDTA/Fe^{2+} ratios $\geq$ 0.025, pure γ-FeOOH is obtained (Figures IV.5.4 and IV.5.5). The trend with respect to the XRD line intensity and width is the same for the series with R = 0.583 and 2.0.

(b) Second Oxidation Product. The X-ray diffraction patterns of the second oxidation products with increasing molar ratios of EDTA/Fe^{2+} for R = 2.0 are shown in Figure IV.5.6. All of the solids are γ-FeOOH except for the one product that is obtained in the absence of EDTA which is a mixture of α-FeOOH and γ-FeOOH.

Thus, oxidation with the addition of base to maintain a pH of about 8 produces only the γ-FeOOH phase.

IV.5.3.d. Effect of EDTA Concentration on the Phase Compositions

Four precipitates were obtained by oxidation of $Fe(OH)_2$ suspensions formed when a mixture containing 0.2 mole of $FeSO_4$, 0.1 mole of NaOH and 0.002 mole of EDTA was added to 500 mL, 750 mL, 1000 mL and 1250 mL of deionized water, respectively. The X-ray diffraction patterns of these products (Figure IV.5.7) show that the α-FeOOH content of the product increases with increasing amounts of H_2O. This indicates that even though the molar ratio of EDTA/Fe^{2+} is fixed, a decrease in concentration of EDTA and Fe^{2+} results in a decrease in the amount of γ-FeOOH in the final product.

IV.5.3.e. Effect of EDTA on Surface Area and Particle Size of Products

The EDTA/Fe^{2+} ratio impacts the specific surface area and the particle size of the product. The specific surface area increases with increasing EDTA/Fe^{2+} ratio (Figure IV.5.8). The molar ratio of EDTA/Fe^{2+} alters the particle sizes in the crystal orientations corresponding to the 020, 110, 031, 200, and 231 planes of γ-FeOOH (Figure IV.5.9). The particle size in each of these directions decreases as the EDTA/Fe^{2+} ratio increases. This decrease in crystal size parallels the increase for the specific surface area.

IV.5.4. DISCUSSION

From stoichiometry considerations, 0.2 mole of Fe^{2+} in the absence of EDTA should produce 0.2 mole (17.8g) of FeOOH according to the reaction

$$Fe^{2+} + 1/4\ O_2 + 2OH^- \rightarrow FeOOH + 1/2\ H_2O \qquad\text{(IV.5.1)}$$

When R = 0.582, only 6/7 of Fe^{2+} precipitates as $Fe(OH)_2$ and 1/7 of the added Fe^{2+} remains in solution. According to our previous study (IV.5.18), the oxidation·of Fe^{2+} ions in solution at pH $\leq$ 4 is very slow. Thus, only 0.17 mole (15.1g) of FeOOH forms during the first oxidation reaction and 0.03 mole of Fe^{2+} remains in the filtrate. Similarly, 0.05 mole (4.5g) of FeOOH precipitates during the first oxidation reaction when R = 2.0, and 0.15 mole of Fe^{2+} remains unoxidized in the solution. The data in Tables IV.5.1 and IV.5.2 are consistent with this. Thus, the oxidation time, with a constant gas flow, required to reach a pH $\leq$ 4 was much shorter for R = 2 than for R = 0.583.

The formation of α-FeOOH and γ-FeOOH in aqueous solutions has been studied by Bernal *et al.* (IV.5.19), Kiyama (IV.5.20), Misawa *et al.* (IV.5.21,IV.5.22), and other workers (IV.5.23,IV.5.24). The transformation of γ-FeOOH to α-FeOOH has been investigated by Oosterhout (IV.5.25), Schwertmann and Taylor (IV.5.26), and Inoue *et al.* (IV.5.27). These latter authors consider green rust to be an intermediate during the course of oxidation of $Fe(OH)_2$ in a slightly basic medium. They suggest that γ-FeOOH is topotactically formed by the surface oxidation of green rust. α-FeOOH formation involves the dissolution of γ-FeOOH into small, probably monomeric units which undergo polymerization and precipitation to form α-FeOOH. In short, γ-FeOOH was proposed to form topotactically in the solid state while α-FeOOH formation involved a dissolution/reprecipitation process. On the other hand, Oosterhout (IV.5.25) found that γ-FeOOH transformed easily to α-FeOOH in a $FeSO_4$ solution or in an alkaline solution. He suggested that this was not a solid state transformation but was produced by dissolution and crystallization. He argued that

the transformation from γ-FeOOH, having a cubic close-packed structure of oxygen, to the hexagonal close-packed α-FeOOH by solid state reaction was difficult. The acceleration of the transformation by the Fe^{2+} and OH^- ions is because of the increase in the dissolution of γ-FeOOH (IV.5.28,IV.5.29). From this viewpoint, it therefore seems likely that the composition of the oxidation products of Fe^{2+} is related to the concentration of the Fe^{2+} ion and the pH. As is seen from Figure IV.5.4, the oxidation of Fe^{2+} hydroxide with R = 0.583 in the absence of EDTA leads to a γ-FeOOH-rich product, whereas the product with R = 2.0 is α-FeOOH. The amount of Fe^{2+} in solution for R = 2.0 is much higher than that for R = 0.583, and this presumably favors the more stable α-FeOOH.

The EDTA effect on the promotion of the formation of γ-FeOOH might be attributed to its excellent ability of complexation and adsorption. In other words, EDTA can effectively reduce or eliminate the Fe^{2+} effect and protect γ-FeOOH by: (1) adsorption on γ-FeOOH produced during the course of oxidation of Fe^{2+} hydroxide, thereby preventing its dissolution to form α-FeOOH, (2) complexing with Fe^{2+} ions in solution to suppress the dissolution of γ-FeOOH; and (3) binding at the surface of α-FeOOH nuclei, thus retarding and inhibiting α-FeOOH crystal growth. Although there are no experimental data for the adsorption of EDTA on γ-FeOOH in this study, strong adsorption of EDTA on various iron(II) hydroxide or hydrous oxides have been reported by several workers (IV.5.10-IV.5.15).

The EDTA was added to the Fe^{2+} solution prior to adding the sodium hydroxide. EDTA contains four equivalents of acid and could potentially neutralize four equivalents of base; however, it is a weak acid compared to sulfuric acid. The

experimental value of the change of moles of iron oxidized to the moles of EDTA added (ΔFe^{2+}/EDTA) should be four if the carboxylic acid reacted completely with the added base; however, the experimental value is only about 0.2 for each of the ratios of R (0.5833 and 2.0). On the other hand, if the anion of EDTA formed upon addition is subsequently neutralized by the acid generated during the oxidation, EDTA should not impact the total amount of iron oxidized. This is not observed so that it is presumed that some of the EDTA remains as the anion at a pH at about 4.

The total moles of Fe^{2+} that oxidize, based on the amount of oxygen that reacts, decreases as the amount of added EDTA increases. However, the ratio of the decrease in the moles oxidized to the moles of EDTA added remains rather constant at a value of about 0.45 to 0.47 (Table IV.5.3). This value is higher than the one based on the FeOOH collected and is most likely due to the incomplete conversion of oxygen during the period of the second step in the pH versus time curve. In fact, the fraction of oxygen that passes through the reactor unconverted increases almost linearly from 0 to 1 during the period of the second step. Thus, it is considered that the value of 0.2 obtained from the weight of the FeOOH collected is a more accurate value for the decrease in the moles of Fe^{2+} oxidized per mole of EDTA added. This incomplete conversion of oxygen during the second step will also impact the ratio of iron oxidized up to the completion of the first step to that oxidized to the completion of oxidation to produce a pH of 4; however, this should only cause a slight impact upon the ratio.

In the absence of EDTA the ratio of the amount of oxygen converted at the end of the first step of the pH versus time curve (O_1) to the total at the end of the second step (O_2) is about 0.45 to 0.47; this ratio is essentially the same for the values of R =

IV.5.10

0.5833 and 2.0. In this study the iron concentration was 0.4 M; in a previous study with a 0.2M Fe^{2+} solution the ratio iron converted in the first step to the total iron converted (O_1/O_2) was 0.31 (IV.5.18). This suggests that the composition ($Fe^{2+}:Fe^{3+}$) of the green rust that is formed depends upon the total concentration of the iron in the suspension (Figure IV.5.10); however, the composition does not depend upon the ratio R (Fe^{2+}/OH^-).

When EDTA is added to the suspension there is a gradual decrease in the amount of oxygen converted in the first step (O_1), and the corresponding amount of Fe^{3+} produced, to that of the total oxygen converted (O_2) (Figure IV.5.11). For the two lower concentrations of added EDTA in the experiments with R = 0.5833, the decrease in the moles of iron oxidized (equal to four times the moles of oxygen converted) to that of the moles of EDTA added is approximately 1 (Table IV.5.3). This is a greater change in the amount of iron oxidized per mole of added EDTA than occurs for the total iron (1 and 0.45, respectively). Thus, it is considered that some of the added EDTA is incorporated into the green rust, substituting for the Fe^{3+} and thereby decreasing the amount of Fe^{3+} that must be formed to reach the maximum amount of the green rust intermediate.

In summary, it appears that the major impact of EDTA during the oxidation of Fe^{2+} is during the period of the oxidation that produces the green rust intermediate. From the decrease in the amount of Fe^{2+} oxidized as the ratio EDTA/Fe_{total} is increased, it appears that the EDTA is being incorporated into the green rust and does this by substituting for Fe^{3+}. This view is consistent with the observations of Barton et al. (IV.5.16,IV.5.30) who reported that the EDTA must be added before the

maximum amount of Fe^{2+} is oxidized to produce green rust if it is to have an impact upon the fraction of γ-FeOOH in the final product. When the suspension is kept at a constant pH of about 8 during the total oxidation, the product is essentially pure γ-FeOOH. Thus, it does not appear that the EDTA makes an impact upon the oxidation during the second step of the oxidation whether this oxidation is carried out at a pH of about 8 or 6.5. Furthermore, it has been shown that the large hexagonal green rust crystals that are formed as the intermediate during the early portion of the oxidation gradually disappear to be replaced by smaller needle-shaped γ-FeOOH crystals as the oxidation is completed (IV.5.31). It therefore appears that the seed that leads to the production of γ-FeOOH is included in the green rust structure, and that this seed remains intact as the green rust dissolves at the intermediate pH level. If the EDTA functions by forming a complex with Fe^{3+} in solution, it should be possible to add the EDTA after the formation of green rust and have it effect the formation of γ-FeOOH.

IV.5.5. ACKNOWLEDGMENT

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Table IV.5.1
Yield of Oxidation Products for Various Molar Ratio of EDTa/Fe^{2+} with Reaction Conditions: $[Fe^{2+}]$ = 0.4M, R = 0.5833 The time of First Oxidation Reaction: 60 min.

Ratio of EDTA/Fe^{2+} of the First Oxidation Reaction	Yield of the first Oxidation Product (g) (W-1)	Yield of the Second Oxidation Product (G) (W-2)		Total Yield of Oxidation Product (g) (W-1 + W-2)	
0.000	15.30	2.26	0.0255	17.56	(99.2)[a]
0.019	15.00	2.56	0.0289	17.56	(99.2)[a]
0.038	14.63	3.04	0.0344	17.64	(99.7)[a]
0.075	14.07	3.59	0.0406	17.66	(99.8)[a]
0.113	13.32	4.35	0.0492	17.67	(99.8)[a]
a. Percent of total iron recovered.					

<table>
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Table IV.5.2

Yields of Oxidation Products for Various Molar Ratio
of EDTA/Fe^{2+} with Reaction Conditions:
$[Fe^{2+}]$ = 0.2M, R = 2.0,
The Time of First Oxidation Reaction: 30 min.

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Ratio of EDTA/Fe^{2+} of the First Oxidation Reaction	Yield of the first Oxidation Product (g) (W-1)	Yield of the Second Oxidation Product (G) (W-2)		Total Yield of Oxidation Product (g) (W-1 + W-2)
0.0000	4.88	12.77		17.65
0.0010	4.78	12.84	0.070	17.62
0.0075	4.67	12.90	0.13	17.57
0.0100	4.57	13.03	0.26	17.60
0.0250	4.45	13.22	0.45	17.67

		$\Delta Fe_t{}^a$/EDTA		
$\dfrac{moles\ EDTA}{moles\ Fe^{2+}}$	R	Table 1[b]	Figure 1[c]	$-\Delta Fe_1{}^d$/EDTA
0.019	0.583	0.18	0.41	0.95
0.039	0.583	0.20	0.53	1.0
0.075	0.583	0.18	0.45	0.67
0.113	0.583	0.20	0.26	0.35
0.001	2.0	11.0	2.4	0.79
0.0075	2.0	0.32	0.85	0.37
0.01	2.0	0.35	0.87	0.59
0.025	2.0	0.19	0.36	0.35

Table IV.5.3

Changes in the Amount of Fe^{2+} Oxidized by the Addition of EDTA

a. ΔFe_t = Fe^{2+} oxidized at pH = 4.
b. ΔFe_t = difference in moles Fe^{2+} oxidized without and with indicated amount of EDTA based on W-1 in Table 1 or Table 2.
c. ΔFe_t based on completion of second break in Figure 1 or 2.
d. ΔFe_1 = difference in moles Fe^{2+} oxidized without and with indicated amount of EDTA based on moles of oxygen (= moles Fe^{2+}) converted at end of first break in Figures 1 or 2.
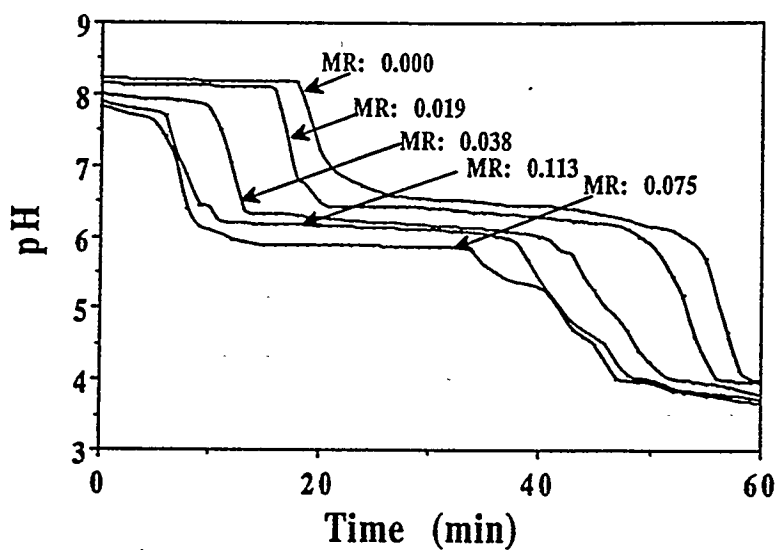
Figure IV.5.1.   Variation of the pH of the suspension with increasing oxidation time as the mole ratio of EDTA/Fe^{2+} (MR) is varied (Fe^{2+}/OH$^-$ = R = 0.583).
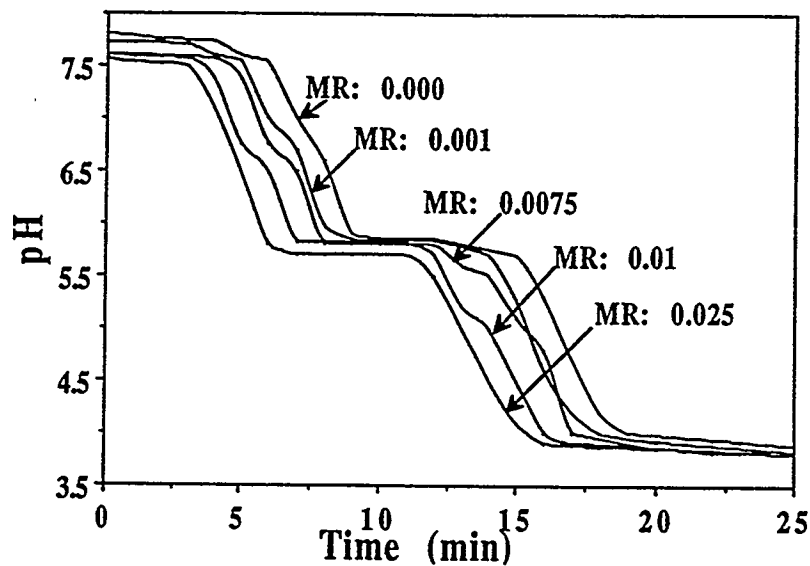
Figure IV.5.2.   Variation of the pH of the suspension with increasing oxidation time as the mole ratio of EDTA/Fe^{2+} (MR) is varied (Fe^{2+}/OH$^-$ = R = 2.0).

IV.5.18

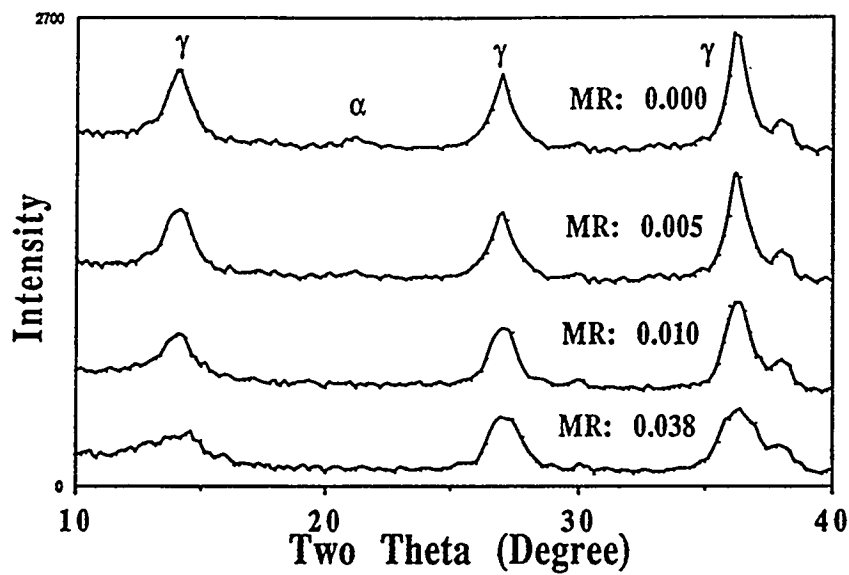Figure IV.5.3.   The dependence of the X-ray diffraction patterns of the first oxidation product upon the EDTA/Fe^{2+} ratio (Fe^{2+}/OH^- = 0.583) (MR = EDTA/Fe^{2+}).
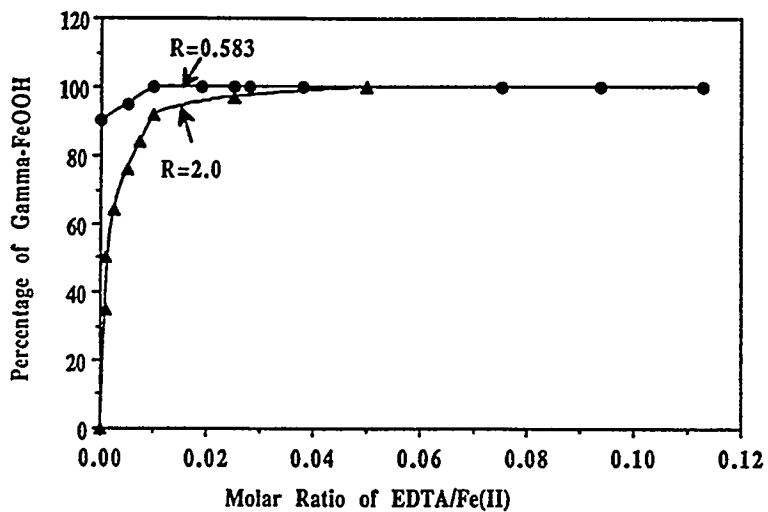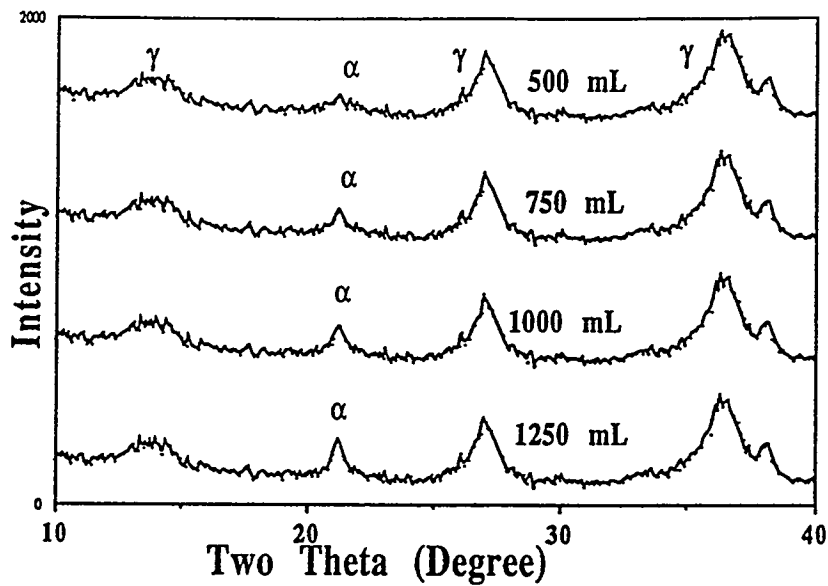

Figure IV.5.4.   The percentage of γ-FeOOH upon the EDTA/Fe^{2+} ratio for Fe^{2+}/OH^- = 0.583 (●) and 2.0 (▲).
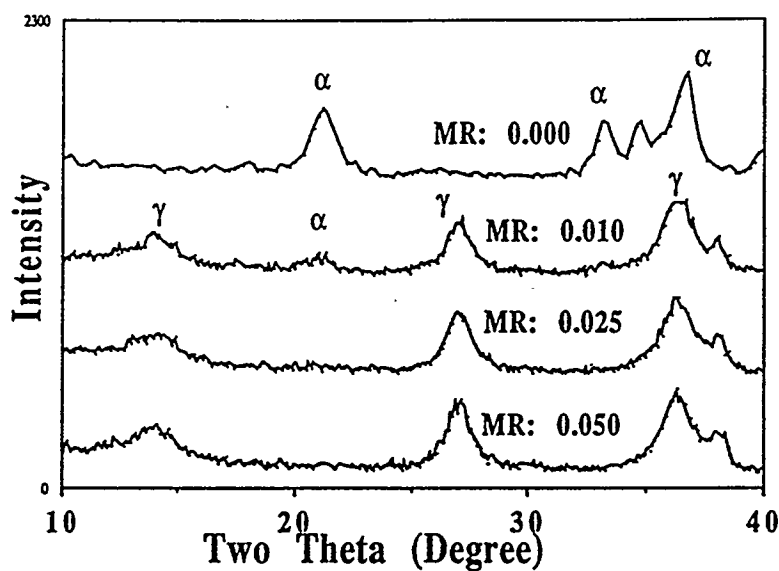
Figure IV.5.5.   The dependence of the X-ray diffraction patterns of the first oxidation product upon the EDTA/Fe^{2+} ratio (Fe^{2+}/OH^- = 2.0) (MR = EDTA/Fe^{2+}).
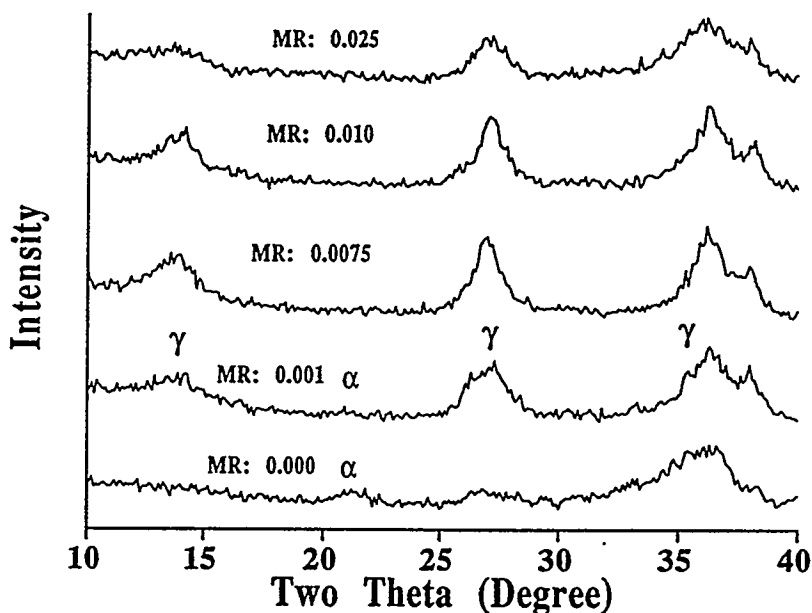
Figure IV.5.6.   The dependence of the X-ray diffraction patterns of the second oxidation product upon the EDTA/Fe^{2+} ratio (Fe^{2+}/OH^- = 2.0) (MR = EDTA/Fe^{2+}).

Figure IV.5.7.   The X-ray diffraction patterns for the FeOOH produced as the concentration of the suspension is varied (R = 2 and EDTA/Fe^{2+} = 0.01).
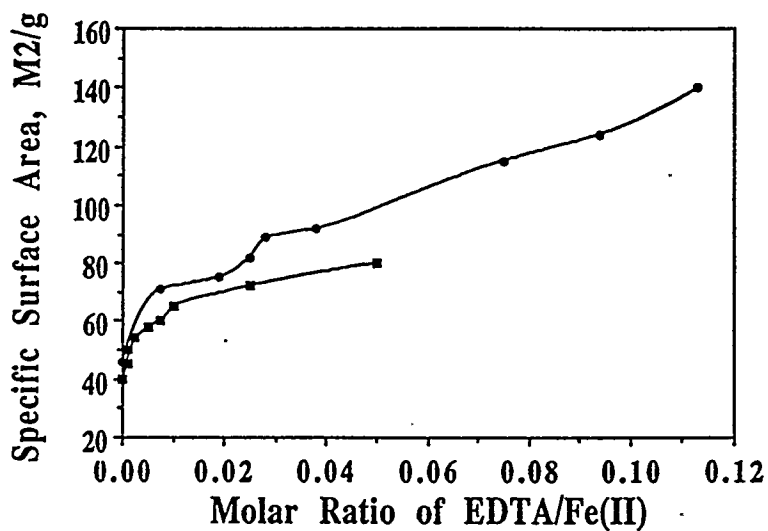
Figure IV.5.8.   The BET surface area of FeOOH produced for various EDTA/Fe^{2+} ratios (R = 0.5833 (■); 2.0 (●)).
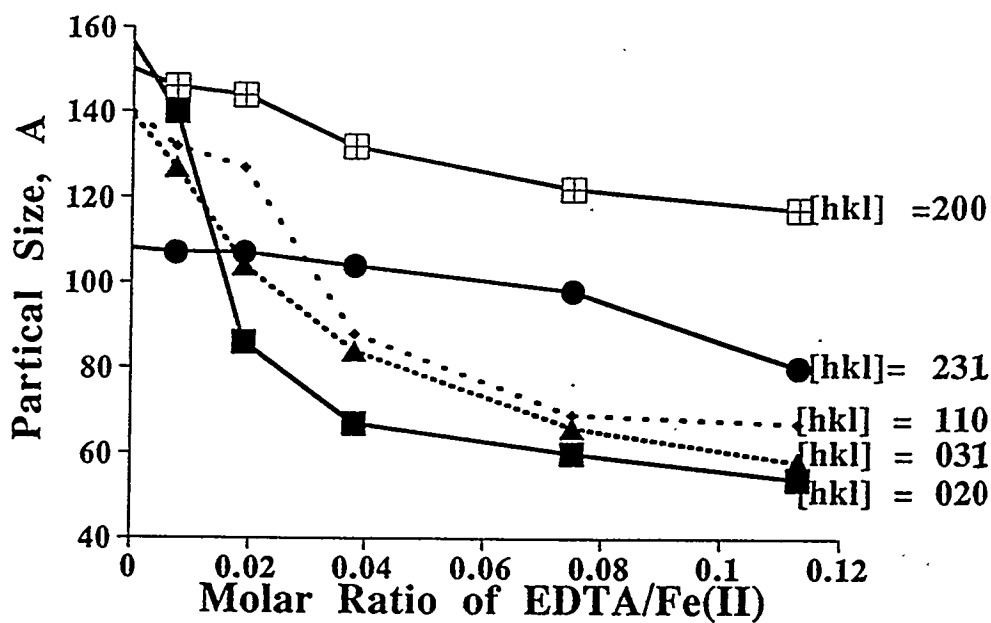
Figure IV.5.9.   Dependence of the particle size calculated for five planes for the FeOOH on the EDTA/Fe^{2+} ratio (R = 0.5833).
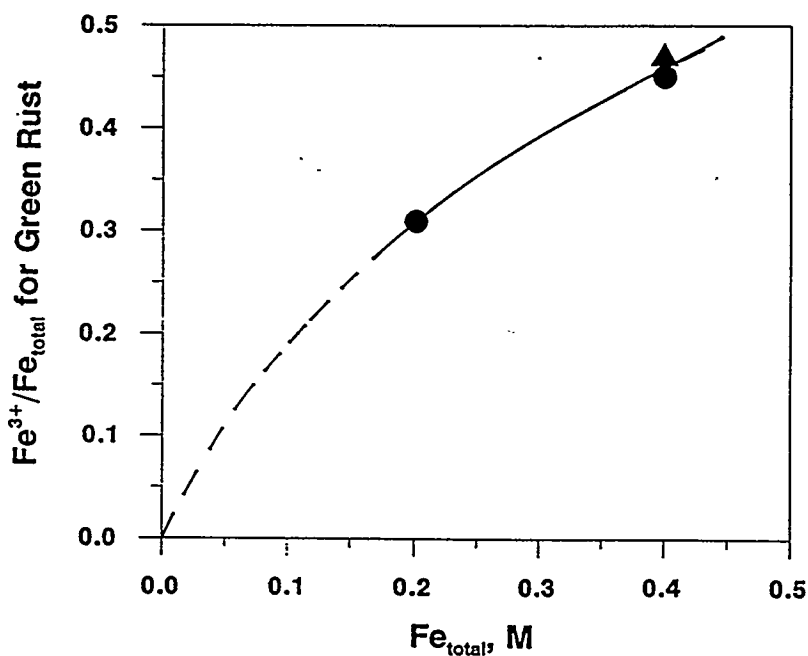

Figure IV.5.10.   The dependence of the ratio of Fe^{3+}/Fe_{total} on total iron concentration for the stoichiometry of the Green Rust ($\bullet$, R = 0.583; $\blacktriangle$, R = 2.0).
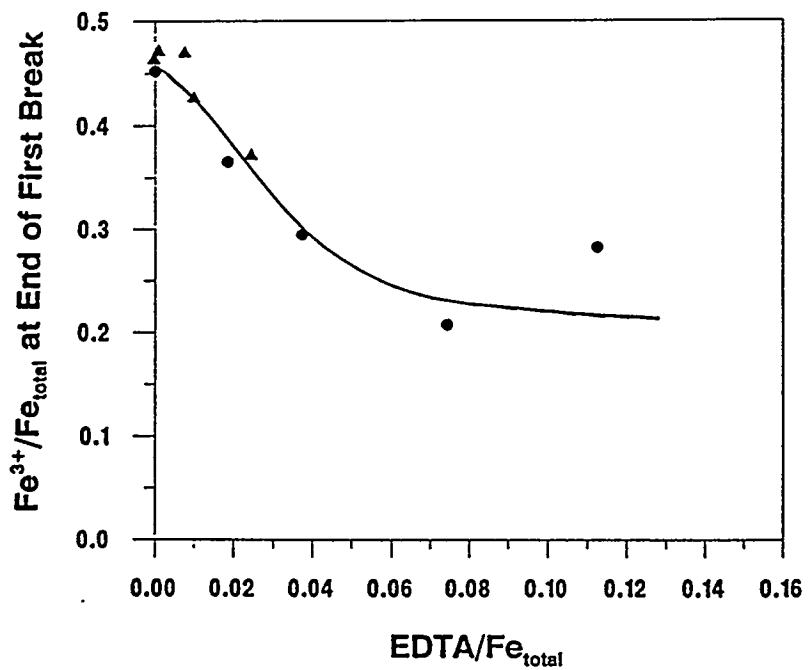
IV.5.22

Figure IV.5.11.   The fraction of iron oxidized in the first step (Figures 1 and 2) dependency upon the molar ratio of EDTA to total iron (●, R = 0.583; ▲, R = 2.0).