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The Transformation of γ-FeO(OH) to Fe_3O_4 and Green Rust II in an Aqueous Solution

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A mechanism of the transformation of γ-FeO(OH) to Fe_3O_4 and/or green rust II in an aqueous solution containing Fe^{II} ion in the presence or absence of the SO_4^{2-} ion at 298 K is described. γ-FeO(OH) is dissolved by two mols of Fe^{II} ions adsorbed on the surface of γ-FeO(OH), and a dissolved species (DS) is formed, which is then transformed to Fe_3O_4 or green rust II. The equilibrium of the formation of green rust II from γ-FeO(OH) is represented by:

$$K = [H^+]^2/(K_h^2[Fe^{2+}]^2[SO_4^{2-}]) \qquad K = 2.14 \times 10^8,$$

where K_h is the hydrolysis constant of Fe^{2+}. This equation shows that, for a given proton concentration (pH), higher concentrations of Fe^{2+} and SO_4^{2-} ions facilitate the formation of green rust II from γ-FeO(OH). When little green rust II is formed, the DS is transformed to Fe_3O_4.

The Fe^{II} ions dissolved from the steel surface in the course of the atmospheric rusting are oxidized by oxygen, and eventually the surface is covered with rusting products of iron oxides and hydroxide oxides. Studies of the formation of iron oxides and hydroxide oxides by the air oxidation of Fe^{II} ions in an aqueous solution give useful knowledge for an understanding of the atmospheric rusting of mild steel or low-alloy steel, as reported by Kiyama,[1] Bernal *et al.*,[2] and Misawa *et al.*[3] This oxidation reaction has also been studied in relation to the formation of ferrites in aqueous solutions; ferrites are formed by the air oxidation of an $Fe(OH)_2$ suspension containing other metal ions.[4—10] In these oxidation reactions, some intermediates are formed; greenish precipitates called "green rusts" are formed in the course of the oxidation reaction.[1—3] They are transformed to γ-FeO(OH) or Fe_3O_4 by further oxidation.

Recently we have ourselves reported that a green rust (green rust II) is spontaneously transformed into Fe_3O_4 without being oxidized[11] and that γ-FeO(OH) is transformed into Fe_3O_4 by Fe^{II} ions at pH 7—11 without any oxidation reaction.[12,13] Furthermore, ferrites are formed from a suspension containing γ-FeO(OH) and Fe^{II} and other metal ions without any oxidation reaction.[14,15] These findings suggest that there are two steps in the oxidation reaction where Fe_3O_4 or ferrites are formed: 1) The oxidation step of the Fe^{II} ion, where such intermediates as green rusts and γ-FeO(OH) are formed, and 2) the transformation step of the intermediates into Fe_3O_4 or ferrites without any oxidation reaction.

In the present paper, we have studied the transformation of γ-FeO(OH) into Fe_3O_4 and/or green rust II in the presence of Fe^{II} and SO_4^{2-} ions without any oxidation reaction. The reaction mechanism of the transformation will be discussed.

Experimental

Chemicals. All the chemicals were of an analytical grade, and distilled water was used for the preparation of the chemical solutions. The NaOH solution was prepared by dissolving NaOH in distilled water through which nitrogen gas had been passed to remove the dissolved oxygen. The γ-FeO(OH) was prepared according to the method described in a previous paper.[13]

Apparatus. The reaction vessel used in a previous paper was adopted.[13] The reaction vessel was immersed in a water bath, and the reaction temperature was kept at 298±0.5 K.

Procedures. Throughout the experiments, we tried to avoid leakage of oxygen into the reaction suspension. After passing nitrogen gas through a suspension of γ-FeO(OH) (0.7 dm^3, 0.002 kmol m^{-3}) of the desired pH (8.5 or 10.0), and $Fe(OH)_2$ suspension (0.02 dm^3, 0.40 kmol m^{-3}) of that pH was added. The suspension thus obtained will be referred to as "the reaction suspension." The reaction was initiated when the $Fe(OH)_2$ suspension was added. The reaction pH was maintained at 8.5 or 10.0±0.03 by adding a sulfuric-acid solution. The amount of released OH^- was estimated from the volume of the sulfuric-acid solution consumed. The time from the addition of the $Fe(OH)_2$ suspension is referred to as "the reaction time." In the course of the reaction, 0.005-dm^3 portions of the reaction suspension were taken out at constant time intervals using a syringe and transferred to a tartaric-acid solution (10 w/v%, pH 6.0, 0.04 dm^3). After allowing the suspension thus obtained to stand for 60 min, the suspension was centrifuged at 4000 r.p.m. The precipitate was washed with the tartaric-acid solution. The Fe_3O_4 formed and the γ-FeO(OH) left unreacted do not dissolve in the tartaric-acid solution, but the intermediate green rust II (GR-II) does. The precipitate thus obtained was dissolved in a 0.002-dm^3 HCl solution (1:1). The Fe^{II} and Fe_{total} in the solution were determined. The amount of Fe_3O_4 was evaluated from the Fe^{II} concentration by assuming the stoichiometric chemical composition of Fe_3O_4. The amount of γ-FeO(OH) left unreacted was evaluated from the difference between the amount of Fe^{III} in the precipitate and Fe_3O_4. The amount of the intermediate dissolved in the tartaric-acid solution was evaluated from the difference between the amount of Fe^{III} in the initial reaction suspension and the sum of the Fe^{III} in the Fe_3O_4 and γ-FeO(OH) found in the suspension. The intermediate dissolved in the tartaric-acid solution will henceforth be referred to as "the TA-soluble intermediate."

The sample for X-ray diffractometry was prepared as follows: The precipitate obtained through the centrifugation of the reaction suspension was mounted on a glass plate under a nitrogen atomosphere and sealed with cellophane tape to prevent oxidation. For the IR spectroscopy, the precipitate was washed with oxygen-free acetone to remove as much water as possible and then dried under a nitrogen atmosphere. The IR spectra of the dried product were obtained as Nujol mulls.

Chemical Analysis. The Fe^{II} and Fe_{total} concentrations were determined by the 2,2′-bipyridyl method.[16] The Fe_{total} concentration was determined after reducing the Fe^{III} to Fe^{II} with hydroxylamine.

Results and Discussion

Dissolved Species (DS) and the TA-soluble Intermediate. As reported previously,[13] when the Fe^{II} ion was added to the γ-FeO(OH) suspension (pH 8.5) in the absence of SO_4^{2-} (Curve A in Fig. 1), γ-FeO(OH) was transformed to Fe_3O_4 (Curve C). In this reaction, γ-FeO(OH) adsorbs the Fe^{II} ion, dissolves, and it transformed to Fe_3O_4.[13] The adsorption reaction is written as:

$$\gamma\text{-FeO(OH)}(s\text{-}) + \text{FeOH}^+ \rightleftharpoons \underset{\text{(ADInt)}}{\gamma\text{-FeO(OH)}(s\text{-FeOH}^+)}, \quad (1)$$

where *s*- is the adsorption site of γ-FeO(OH) and where ADInt is the Fe^{2+}-adsorbed intermediate.[13,17] The dissolved species formed in the dissolution step will be composed of Fe^{II} and Fe^{III} ions. The dissolution step will be given by:

$$\text{ADInt} \longrightarrow \underset{\text{(DS)}}{(\text{Fe}^{2+})_x(\text{Fe}^{3+})_y \text{ complex}}, \quad (2)$$

where DS means the dissolved species.

As can be seen in Fig. 2, when the SO_4^{2-} ion was present in the reaction suspension, γ-FeO(OH) (Curve A) was not transformed to Fe_3O_4 (Curve C), but to a TA-soluble intermediate (Curve B); almost all of the γ-FeO(OH) was transformed to the TA-soluble intermediate in 60 min. The X-ray diffraction pattern of the TA-soluble intermediate precipitate formed within 60 min corresponded to that of green rust II. In the IR spectrum of the precipitate, strong bands due to SO_4^{2-} appeared at 1100 and 630 cm^{-1}. These results suggest that the DS formed in the dissolution step combines with the SO_4^{2-} ion and is transformed to green rust II (GR-II).

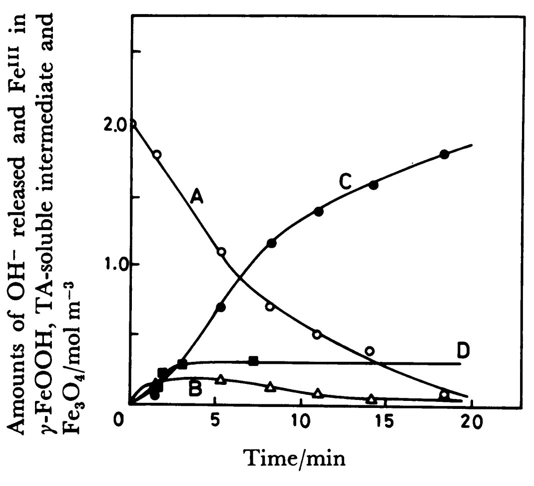

Fig. 1. The transformation of γ-FeOOH to Fe_3O_4 at pH 8.5. Fe^{2+}/γ-FeOOH=3.60, SO_4^{2-}=0 mol m^{-3}. Curve A; γ-FeOOH, B; TA-soluble intermediate, C; Fe_3O_4, D; OH^-.

Curves D in Figs. 1 and 2 show the release of OH^- during the formation of GR-II. These results suggest that no OH^- is released in the formation of Fe_3O_4, but only in that of GR-II. This OH^--releasing will be discussed later.

Here, we studied the effect of the Fe^{II} concentration on the formation of GR-II from γ-FeO(OH). The results are given in Figs. 3a and 3b, where the reaction pH and the concentrations of γ-FeO(OH) and SO_4^{2-} are the same as those of Fig. 2, but where the Fe^{II} concentrations in the reaction suspensions are lower than that of Fig. 2. As the Fe^{II} concentration in the reaction suspension decreased from 7.40 mol m^{-3} (Fig. 2) to 1.63 mol m^{-3} (Fig. 3b), the consumption of γ-FeO(OH) (Curve A) decreased. The relationship between the

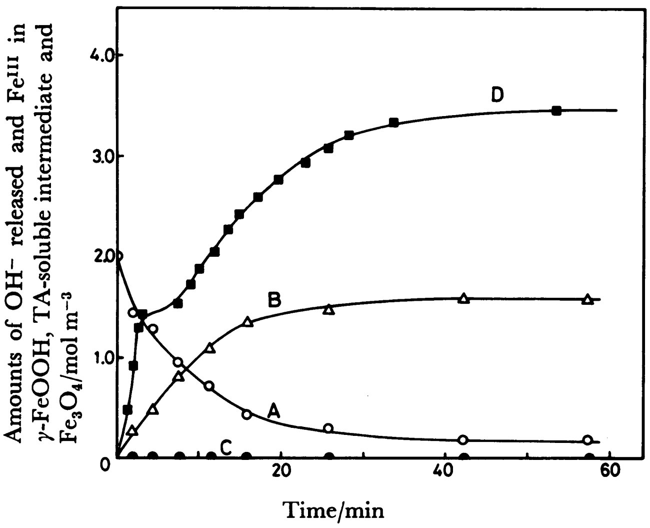

Fig. 2. The transformation of γ-FeOOH to green rust II at pH 8.5. Fe^{2+}/γ-FeOOH=3.60, SO_4^{2-}=10.0 mol m^{-3}. Curve A; γ-FeOOH, B; green rust II (TA-soluble intermediate), C; Fe_3O_4, D; OH^-.

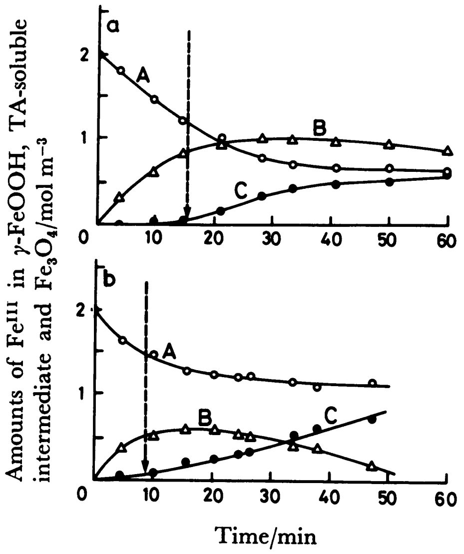

Fig. 3. Effect of Fe^{2+} concentration on the transformation of γ-FeOOH at pH 8.5 and at 10.0 mol m^{-3} of SO_4^{2-}. Fe^{2+}/γ-FeOOH=1.50(a), and 0.81(b). Curve A; γ-FeOOH, B; green rust II, C; Fe_3O_4.

TABLE 1. THE EFFECT OF THE Fe(II) CONCENTRATION ON THE TRANSFORMATION OF γ-FeOOH

Figure No.	$Fe^{2+}_{initial}$ (mol m^{-3})	γ-$FeOOH_{initial}$ (mol m^{-3})	$Fe^{2+}_{initial}$ / γ-$FeOOH_{initial}$ (mol m^{-3})	γ-$FeOOH_{reacted}$ (mol m^{-3})	$Fe^{2+}_{initial}$ / γ-$FeOOH_{reacted}$ (mol m^{-3})
2	7.40	2.06	3.60	1.92	3.70
3a	3.08	2.06	1.50	1.38	2.23
3b	1.67	2.06	0.81	0.68	2.46

amount of reacted γ-FeO(OH) and that of the Fe^{II} ions initially present in the reaction suspension is given in Table 1. The amount of Fe^{II} in the initial suspension is higher than the amount of γ-$FeO(OH)_{initial}$ in Figs. 2 and 3a, but lower than that in Fig. 3b (Column 4 in Table 1). The amount of γ-$FeO(OH)_{reacted}$ (Column 5) decreased as the initial amount of Fe^{II} decreased (Column 2). However, the mol ratios of $Fe^{2+}_{initial}/\gamma$-$FeO(OH)_{reacted}$ (Column 6) are approximately 2 at a $Fe^{2+}_{initial}/\gamma$-$FeO(OH)_{initial}$ ratio below 2 (column 4). This suggests that at least two mols of the Fe^{II} ions are needed to dissolve one mol of γ-FeO(OH). These results suggest that the dissolved species (DS) are composed of one Fe^{III} and two Fe^{II} ions.

Three Stages of γ-FeO(OH)-transformation Reaction. At lower Fe^{II} concentrations (Fe^{2+}/γ-$FeO(OH)_{initial}$ ratio below 2; Figs. 3a and 3b), the amount of GR-II increased, attaining its maximum as the reaction proceeded (Curve B). When the amount of GR-II became near the maximum in Figs. 3a and 3b (indicated by arrows), the Fe_3O_4 formation (Curve C) became prominent. The amount of Fe_3O_4 increased with time, accompanied by the consumption of γ-FeO(OH) (Curve A). However, as the reaction proceeded further (*cf.* Figs. 3a and 3b), the amount of GR-II decreased (slightly in Fig. 3a, but prominently in Fig. 3b). This decrease resulted in the Fe_3O_4-formation (Curve C) without any consumption of γ-FeO(OH), indicating that GR-II is transformed to Fe_3O_4.

Thus, at lower Fe^{II} concentrations (the $Fe^{2+}_{initial}/\gamma$-$FeO(OH)_{initial}$ ratio below 2), the DS is transformed to GR-II in the initial stage, and then to Fe_3O_4 in the second stage, where no further GR-II is formed. In the third stage, the transformation of GR-II to Fe_3O_4 mainly occurs.

On the other hand, at a high Fe^{II} concentration ($Fe^{2+}_{initial}/\gamma$-$FeO(OH)_{initial}$ ratio=3.60, Fig. 2), only the first-stage reaction is seen. In this case, an excess of Fe^{II} ions is present, since $Fe(OH)_2$ precipitates coexist throughout the reaction. This means that the suspension contains dissolved Fe^{II} ions, whose concentration is estimated to be about 10^{-4} kmol m^{-3} from the solubility product of $Fe(OH)_2$. On the other hand, in the case shown in Figs. 3a and 3b, since most of the Fe^{II} ions are consumed in the formation of GR-II, the concentration of the dissolved Fe^{II} ions seems to become lower than 10^{-4} kmol m^{-3} as the reaction proceeded. This lowering of the Fe^{II} concentration seems to cause the second-stage reaction. That is, in the second stage (Figs. 3a and 3b), the GR-II-formation reaction seems to attain an equilibrium as a result of the lowering of the concentration of the dissolved Fe^{II} ions.

Derivation of Empirical Formula of the Dissolved Species (DS). Since the Fe^{II} ion is adsorbed in the hydrolyzed form, $FeOH^+$, and since two mols of Fe^{II} ions seem to react with one mol of γ-FeO(OH), the adsorption step may be written as:

$$\gamma\text{-FeO(OH)}[(OH)_s(O)_s] + 2Fe(OH)_2 \rightleftharpoons \gamma\text{-FeO(OH)}[(OH)_sFeOH^+(O)_sFeOH^+] + 2OH^- \quad (3)$$
$$(\text{ADInt*})$$

where the subscript s denotes the adsorption site. Here, it is assumed that one Fe^{II} ion is adsorbed on the OH group of γ-FeO(OH), and another, on the oxygen of the oxo-bridge of γ-FeO(OH). Since one OH^- ion takes part in the dissolution step,[13] the dissolution step may be given by:

$$\text{ADInt*} + OH^- \longrightarrow \text{DS}. \quad (4)$$

In the absence of SO_4^{2-}, the γ-FeO(OH) is transformed to Fe_3O_4 (Fig. 1). In this reaction, it is considered that the DS is directly transformed to Fe_3O_4. Since the DS contains one Fe^{III} and two Fe^{II} ions, the Fe_3O_4-formation reaction from DS may be given by:

$$\text{DS} \longrightarrow 1/2Fe_3O_4 + 3/2Fe^{2+} + x/2OH^- + y/2H_2O. \quad (5)$$

The overall reaction obtained from Eqs. 3, 4, and 5 for the Fe_3O_4 formation from γ-FeO(OH) is written as:

$$\gamma\text{-FeO(OH)} + 2Fe(OH)_2 \longrightarrow 1/2Fe_3O_4 + 3/2Fe(OH)_2 + (x/2-2)OH^- + y/2H_2O. \quad (6)$$

or:

$$\gamma\text{-FeO(OH)} + 1/2Fe(OH)_2 \longrightarrow 1/2Fe_3O_4 + (x/2-2)OH^- + y/2H_2O \quad (6')$$

As stated previously, no OH^- is released during the Fe_3O_4 formation from γ-FeO(OH) (Curve D in Fig. 1). Therefore, $x=4$ in Eq. 6 or 6′. With $x=4$, we get $y=2$. With these x and y values, the DS composition is estimated from Eq. 5 to be $[(Fe^{2+})_2(Fe^{3+})(OH^-)_4(O^{2-})]^{1+}$.

Green Rust-II Formation Reaction from γ-FeO(OH). We know the following: The ratio of Fe^{II}/Fe^{III} in GR-II is 2;[11] the formation of one mol GR-II from one mol of γ-FeO(OH) and 2 mol of $Fe(OH)_2$ forms 2 mol of OH^- (Curves B and D in Fig. 2); the formation of GR-II from γ-FeO(OH) and $Fe(OH)_2$ requires the presence of SO_4^{2-} in the reaction suspension. In addition, GR-II is composed not of ions but of electroneutral precipitates. These findings lead to:

$$\gamma\text{-FeO(OH)} + 2Fe(OH)_2 + SO_4^{2-} \rightleftharpoons [(Fe^{2+})_2(Fe^{3+})_1O_n(OH)_{5-2n}]^{2+}\cdot SO_4^{2-} + 2OH^- + (n-1)H_2O. \quad (7)$$

If the GR-II is formed from DS in SO_4^{2-}-containing suspensions, then the reaction is given by:

$$\underset{\text{(DS)}}{[(\mathrm{Fe^{2+}})_2(\mathrm{Fe^{3+}})(\mathrm{OH^-})_4(\mathrm{O^{2-}})]^+} + \mathrm{SO_4{}^{2-}} \rightleftarrows \underset{\text{(GR-II)}}{[(\mathrm{Fe^{2+}})_2(\mathrm{Fe^{3+}})_1\mathrm{O}_n(\mathrm{OH^-})_{5-2n}]^{2+}\cdot\mathrm{SO_4{}^{2-}}} + \mathrm{OH^-} + (n-1)\mathrm{H_2O}. \tag{8}$$

Equilibrium Consideration of the Green Rust-II Formation. A practical reaction for Eq. 7 is considered to be:

$$\gamma\text{-FeO(OH)} + 2\mathrm{FeOH^+} + \mathrm{SO_4{}^{2-}} \rightleftarrows \text{GR-II} + (n-1)\mathrm{H_2O}, \tag{9}$$

where it is assumed that a dissolved $\mathrm{FeOH^+}$ ion is a reacting species for Reaction (7). Equation 9 means that $\mathrm{FeOH^+}$ is adsorbed on γ-FeO(OH) and that GR-II is formed. The equilibrium constant, K, is given by:

$$K = 1/([\mathrm{FeOH^+}]^2[\mathrm{SO_4{}^{2-}}]) \tag{10}$$

or:

$$K = [\mathrm{H^+}]^2/(K_\mathrm{h}{}^2[\mathrm{Fe^{2+}}]^2[\mathrm{SO_4{}^{2-}}]), \tag{11}$$

where K_h is the hydrolysis constant of $\mathrm{Fe^{2+}}$. Equation 11 tells that the concentrations of the dissolved $\mathrm{Fe^{2+}}$ and $\mathrm{SO4^{2-}}$ ions and the proton (pH) affect the formation of GR-II from γ-FeO(OH). Here, we studied the effect of the $\mathrm{SO4^{2-}}$ concentration. Figure 4 shows the results at a low $\mathrm{SO4^{2-}}$ concentration (2.0 mol $\mathrm{m^{-3}}$). As may be seen here, only the first-stage reaction (GR-II formation from γ-FeO(OH)) took place, as in the case of Fig. 2 (high $\mathrm{SO4^{2-}}$ concentration; 10.0 mol $\mathrm{m^{-3}}$). However, in the case of Fig. 4 (low $\mathrm{SO4^{2-}}$ concentration; 2.0 mol $\mathrm{m^{-3}}$), about one fourth of the γ-FeO(OH) remained unreacted, and the formation of GR-II seems to have ceased. This indicates that the formation of GR-II attained an equilibrium at a low $\mathrm{SO4^{2-}}$ concentration. Since an excess of $\mathrm{Fe^{II}}$ ions was added, the $\mathrm{Fe(OH)2}$ precipitate coexisted with γ-FeO(OH) and GR-II, but the formation of GR-II did not proceed further because of a lack of dissolved $\mathrm{SO4^{2-}}$. The substitution of the solubility product of $\mathrm{Fe(OH)2}$ for $[\mathrm{Fe^{2+}}]$ in Eq. 11 results in:

$$K = \left(\frac{K_\mathrm{w}}{K_\mathrm{h}K_\mathrm{sol}}[\mathrm{OH^-}]\right)^2[\mathrm{SO_4{}^{2-}}]^{-1} \tag{12}$$

where K_w is the water-dissociation constant. The K value estimated from Eq. 12 is 2.14×10^8 for the values of $[\mathrm{OH^-}]=10^{-5.5}$, $[\mathrm{SO4^{2-}}]=6.6\times10^{-4}$ kmol $\mathrm{m^{-3}}$, $K_\mathrm{h}=10^{-9.5}$,[18] and $K_\mathrm{sol}=10^{-15.15}$.[18]

Table 2 summarizes the concentrations of the $\mathrm{Fe^{II}}$ ion calculated for various reaction conditions using Eq. 11 and the K value estimated above. The $\mathrm{Fe^{II}}$ concentrations evaluated at the points shown by arrows in Figs. 3a and 3b (Column 2 in Table 2) are lower than those estimated from the solubility product of $\mathrm{Fe(OH)2}$(Column 4). This supports the speculation that the lowering of the concentration of the dissolved $\mathrm{Fe^{II}}$ ion causes the cessation of the formation of GR-II from γ-FeO(OH). The $\mathrm{Fe^{II}}$ concentration calculated

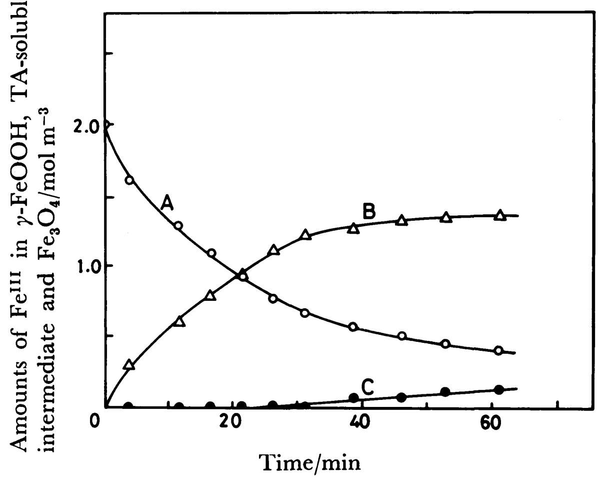

Fig. 4. Effect of $\mathrm{SO^{2-}}$ at a low concentration (2.0 mol $\mathrm{m^{-3}}$) on the transformation of γ-FeOOH. pH 8.5, $\mathrm{Fe^{2+}}$/γ-FeOOH=3.60. Curve A; γ-FeOOH, B; green rust II (TA-soluble intermediate), C; $\mathrm{Fe_3O_4}$.

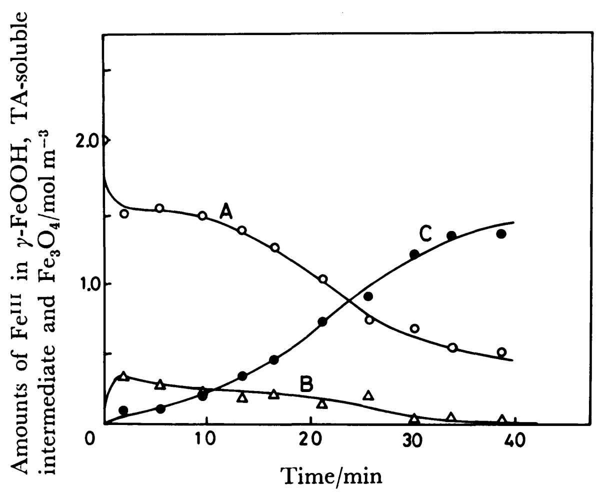

Fig. 5. The transformation of γ-FeOOH to $\mathrm{Fe_3O_4}$ at pH 10.0. $\mathrm{Fe^{2+}}$/γ-FeOOH=3.60, $\mathrm{SO_4^{2-}}$=10.0 mol $\mathrm{m^{-3}}$ Curve A; γ-FeOOH, B; green rust II, C; $\mathrm{Fe_3O_4}$.

TABLE 2. CONCENTRATIONS OF THE Fe(II) ION CALCULATED FOR VARIOUS REACTION CONDITIONS USING THE EQUATION $K=[\mathrm{H^+}]^2/(K_\mathrm{h}{}^2[\mathrm{Fe^{2+}}]^2[\mathrm{SO_4{}^{2-}}])$ AND $K=2.14\times10^8$

pH	$\mathrm{Fe^{2+}}$ Concentration Calcd (kmol $\mathrm{m^{-3}}$)	$\mathrm{SO_4{}^{2-}}$ Concentration (kmol $\mathrm{m^{-3}}$)	$\mathrm{Fe^{2+}}$ Concentration Evaluated from the Solubility Product of $\mathrm{Fe(OH)_2}$ (kmol $\mathrm{m^{-3}}$)
8.5 (Fig. 3a)	1.91×10^{-5}	9.13×10^{-3}	7.08×10^{-5}
8.5 (Fig. 3b)	1.87×10^{-5}	9.48×10^{-3}	7.08×10^{-5}
10.0	5.75×10^{-7}	1.00×10^{-2} *	7.08×10^{-8}

* The $\mathrm{Fe^{2+}}$ concentration was calculated assuming this value, which is near those at pH 8.5.

at pH 10.0 and at a high SO_4^{2-} concentration (10.0 mol m^{-3}) is 5.75×10^{-7} kmol m^{-3}. On the other hand, the Fe^{II} concentration evaluated from the solubility product of $Fe(OH)_2$ at the same pH(10.0) is 7.08×10^{-8} kmol m^{-3}. This suggests that little GR-II is formed at the pH value of 10.0, even at a high SO_4^{2-} concentration. Figure 5 shows the results under those conditions (pH 10.0, SO_4^{2-}; 10.0 mol m^{-3}). As predicted above, the amount of GR-II was very small, and Fe_3O_4 was mainly formed (Curve C in Fig. 5). These results suggest that the DS is transformed to Fe_3O_4 when little GR-II is formed from the DS.

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