The Formation of Mg-bearing Ferrite by the Air Oxidation of Aqueous Suspensions

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When the Mg^{2+}/Fe_{total} molar ratio in the initial aqueous suspension is below 0.1 at pH 9.0 and 65 °C, almost all Mg^{2+} is incorporated into the spinel type ferrite by the air oxidation of $Fe(OH)_2$. The chemical composition of the Mg-bearing ferrite thus obtained is not stoichiometric, and is expressed as the $MgFe_2O_4$–Fe_3O_4–γ-Fe_2O_3 system. When the Mg^{2+}/Fe_{total} ratio exceeds 0.1, the excess Mg^{2+} produces a basic magnesium sulfate which has a composition of $[Mg^{2+}_{1.00}, Na^{+}_{0.64}]\ [OH^{-}_{1.36}, (SO_4^{2-})_{0.64}]$. At pH 8.0, a small amount of the Mg^{2+} is incorporated into the ferrite, between pH 9.0 and 10.0 only the Mg-bearing ferrite is formed, and at pH 11.0, the α-FeOOH type compound is formed together with the Mg-bearing ferrite.

Recently, the formation of the spinel type ferrites from aqueous suspensions have been extensively studied.[1–5] Mn and Co ferrites have been synthesized by the air oxidation of the $Fe(OH)_2$ aqueous suspensions containing these metal ions by Kiyama.[5]

Feitknecht[6] studied in detail the formation of the iron oxides and presented the optimum conditions to form magnetite (Fe_3O_4) from the aqueous suspension of $Fe(OH)_2$. Kiyama[7] clarified the temperature dependence of the formation of Fe_3O_4 and pointed out that higher temperatures are more favorable. Recently, more favorable reaction conditions for the formation of Fe_3O_4 have been studied using some weak dispersing reagents.[8] The optimum conditions for the formation of the spinel type ferrites containing various heavy elements from aqueous suspensions appears to differ from those of Fe_3O_4, and are dependent on the pH value, temperature and the concentration of the metal ions in the $Fe(OH)_2$ aqueous suspension.

The complete removal of the heavy metal ions by means of the ferrite formation process is important not only for the basic study but also for the treatment of the concentrated waste water by the "Ferrite Process."[9]

In this study, the formation of the Mg-bearing ferrite from the aqueous suspension of $Fe(OH)_2$ by air oxidation has been investigated in the presence of various concentrations of magnesium at pH values ranging from 8 to 11 at 65 °C. On the basis of these results, the most favorable conditions for the formation of the Mg-bearing ferrite are presented.

Experimental

Reagents. Chemical reagents of analytical grades were used. A 2 mol/dm³-NaOH solution was prepared by dissolving NaOH in distilled water free from CO_2 and O_2. A 0.863 mol/dm³ of $MgSO_4$ solution was prepared using $MgSO_4\cdot 7H_2O$.

Apparatus. The Dewar reaction vessel used is shown in Fig. 1. The temperature of the vessel was kept constant at 65 °C by circulating warm water at just 65 °C through the outer jacket. The inner flask with a semi-spherical bottom (300 cm³) was closed with a silicone-rubber stopper incorporating a stirring apparatus(A), a N_2- or air-introducing tube (B), a condenser(C), a platinum electrode(D), a glass electrode (E), a calomel electrode with double junction(F) and a buret(G).

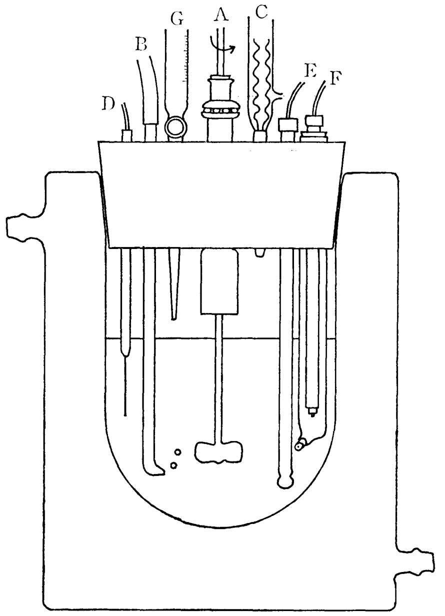

Fig. 1. The reaction vessel with a silicone stopper. A : Stirring apparatus, B : N_2- or air-introducing tube, C : reflux condenser, D : platinum electrode, E : glass electrode, F : calomel electrode(double junction type), G : buret.

Procedure. After addition of the distilled water and the solutions of $MgSO_4$ and Na_2SO_4, nitrogen gas was bubbled into the solution with stirring at 1000 r.p.m. for 1 h to remove the dissolved gases of carbon dioxide and oxygen. Then, $FeSO_4\cdot 7H_2O$ (12 g) was added to the solution and dissolved completely. The resultant volume of the solution was 200 cm³, and the total concentration of $SO_4{}^{2-}$ was fixed at 65 mmol/200 cm³ (this solution is termed the initial solution). The pH was adjusted using 2 mol/dm³ NaOH solution. After standing for 1 h with stirring under nitrogen 65 °C, the oxidation of the ferrous ion was initiated by passing air into the suspension instead of nitrogen at the rate of 0.20 dm³/min. During the oxidation, the pH value was kept constant by the addition of 2 mol/dm³ NaOH or 0.5 mol/dm³ H_2SO_4 solution, and the oxidation potential(ORP) was measured. At the end of the oxidation reaction, the ORP value increased rapidly from about −800 mV to nearly 0 mV (measured by Pt-calomel electrodes). Figure 2 illustrates the relationship between the Fe^{2+}/Fe_{total} value and the oxidation time (min). As seen the rapid increase of the ORP indicates an abrupt change in the oxidation rate. The detailed study of the ORP change will be reported in the near future. In

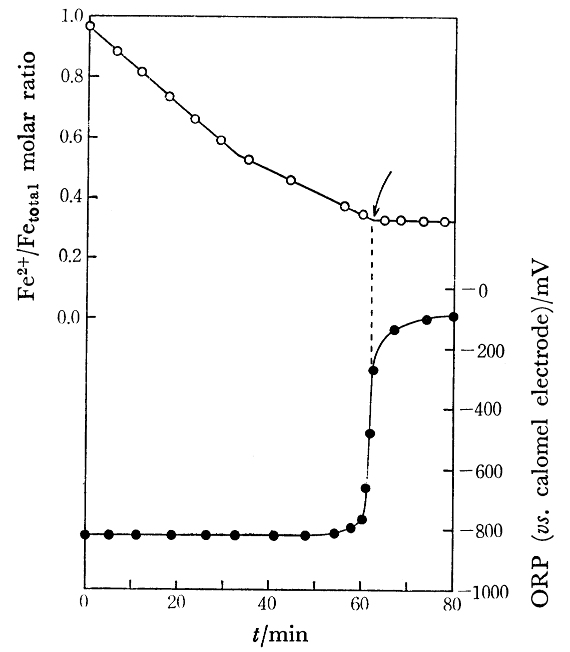

Fig. 2. The relationship between the Fe^{2+}/Fe_{total} molar ratio in suspension (the initial solution contains $Fe(OH)_2$ alone). An arrow means the end point of the formation of ferrite.

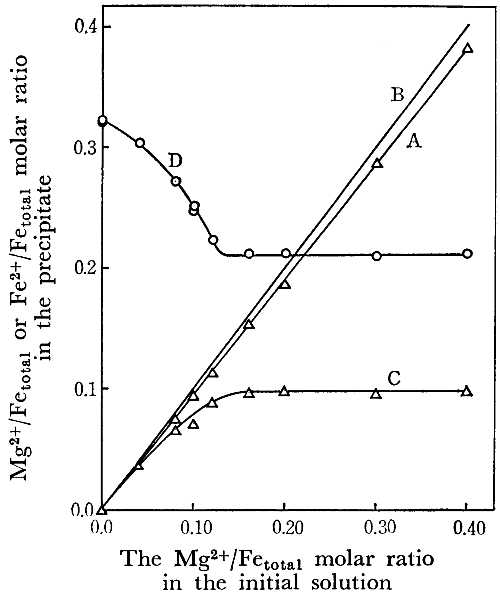

Fig. 3. The relationship between the Mg^{2+}/Fe_{total} molar ratio in the initial solution and the Mg^{2+}/Fe_{total} or Fe^{2+}/Fe_{total} molar ratio in the Precipitates A and B. Curve A: The Mg^{2+}/Fe_{total} molar ratio in the Precipitate A, Curve B: the Mg^{2+}/Fe_{total} molar ratio in the initial solution, Curve C: the Mg^{2+}/Fe_{total} molar ratio in the Precipitate B, Curve D: the Fe^{2+}/Fe_{total} molar ratio in the Precipitate B.

the present study, the air oxidation was stopped 10 min after the abrupt change in the ORP value and then nitrogen gas was passed through the suspension in place of the air. An aliquot of the suspension was removed and immediately centrifuged (3000 r.p.m.). The precipitate thus obtained is referred to as Precipitate A in this paper. The suspension containing Precipitate A was treated with 0.5 mol/dm^3-H_2SO_4 solution to lower the pH value of the suspension to 5.0. At this time, 0.5 mol/dm^3 H_2SO_4 solution was added very slowly at the rate of 0.1—1.0 cm^3/15 min. The obtained suspension was then centrifuged (3000 r.p.m.). The precipitate thus obtained is referred to as Precipitate B. Precipitates A and B were dried *in vacuo* at room temperature.

Chemical Analysis. The Fe^{2+} and Fe^{3+} contents in the Precipitates A and B were determined by the method described by Katsura.[10] When necessary, the spectrophotometric method using 2,2′-bipyridyl[11] or the gravimetric method was applied. The magnesium content was determined by EDTA titration after removal of iron from solution as tris(8-quinolinolato)iron(III) or iron(III) hydroxide. Sodium and sulfate ions were determined by flamephotometry and gravimetry(as $BaSO_4$), respectively.

Precipitates A and B were examined by the X-ray powder diffraction method using Fe $K\alpha$ radiation. The Curie point of Precipitate B was measured *in vacuo*, and the saturation magnetization was measured at room temperature in comparison with Ni as standard.

Results and Discussion

The Oxidation Products at pH *9.0.* Mg-bearing ferrites were prepared at pH 9.0 and at 65 °C by varying the Mg^{2+}/Fe_{total} molar ratio, the results of which are shown in Fig. 3. As shown by Curve A in Fig. 3, the Mg^{2+} content in Precipitate A increases linearly with increasing concentration of Mg^{2+} in the initial solution. The initial concentration of Mg^{2+} before the air oxidation is also given by Curve B in Fig. 3, and Curve B is very similar to Curve A, indicating that almost all the Mg^{2+} added to the initial solution was incorporated into Precipitate A. The Mg^{2+}/Fe_{total} ratio in Precipitate B is also given by Curve C in Fig. 3. As seen in Curve C, the concentration of Mg^{2+} in Precipitate B increases with increasing concentration of Mg^{2+} in the initial solution when the Mg^{2+}/Fe_{total} ratio in the initial solution is sufficiently low. However, when the Mg^{2+}/Fe_{total} ratio is higher than 0.1, the ratio in Precipitate B gives a constant value of about 0.1, suggesting that Precipitate A is composed of a heterogeneous mixture of a soluble and an insoluble Mg compound at pH 5.0.

The X-ray diffraction patterns of Precipitates A and B at conditions below the Mg^{2+}/Fe_{total} ratio of 0.15 were almost identical and all peaks corresponded to those of the spinel type structure. An example is given by A in Fig. 4. In the patterns of Precipitate A which has a Mg^{2+}/Fe_{total} ratio of 0.3, there are two distinct additional peaks other than those of the Mg-bearing ferrite. An example is given by B in Fig. 4. These small and broadened peaks could not assigned, but in the patterns of Precipitate B having the same Mg^{2+}/Fe_{total} ratio, these two peaks disappeared as shown by C in Fig. 4. This suggests that Precipitate A contains some Mg-bearing compound which is soluble at pH 5.0. In addition, the amount of iron dissolved from Precipitate A was negligibly small at pH 5.0, indicating the absence of iron-bearing compounds in Precipitate A other than Mg-bearing ferrite. The chemical composition of the soluble Mg-bearing compound was determined to be $[Mg^{2+}_{1.00}, Na^{+}_{0.64}][OH^{-}_{1.36}, (SO_4^{2-})_{0.64}]$ on the basis of the differences between the

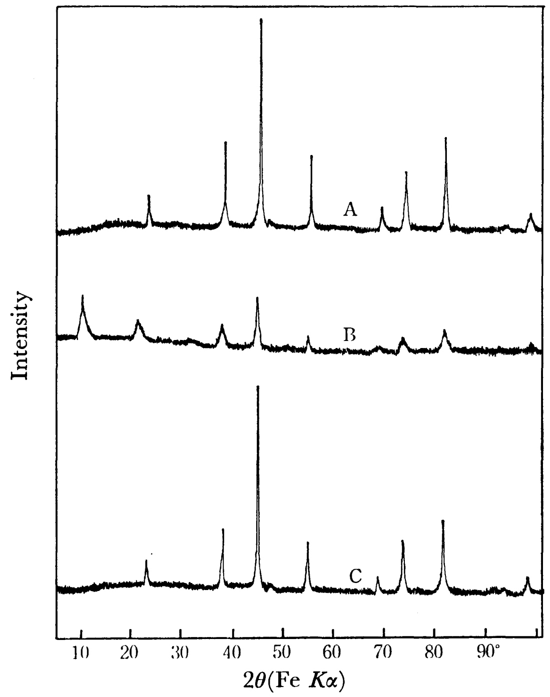

Fig. 4. The X-ray powder diffraction patterns of the Precipitates A and B. Pattern A : For the Precipitate A obtained at the Mg^{2+}/Fe_{total} molar ratio of 0.1, Pattern B : for the Precipitate A at the ratio of 0.3, Pattern C : for the Precipitate B obtained at the ratio of 0.3.

chemical compositions of Precipitates A and B. Here the number of hydroxy entities has been estimated based on the electrical neutrality. This estimation will be discussed in a later section of this paper.

The relationship between the Fe^{2+}/Fe_{total} molar ratio in Precipitate B and the Mg^{2+}/Fe_{total} ratio in the initial solution is given by Curve D in Fig. 3. As seen the amount of Fe^{2+} relative to the total concentration of iron in Precipitate B decreases with increasing concentration of Mg^{2+} in the initial solution becoming constant at approximately 0.21 of the Fe^{2+}/Fe_{total} ratio. Thus, Curves C and D are in good agreement with each other. Moreover, the fall in concentration of Fe^{2+} is approximately equal to the rise in concentration of Mg^{2+}. These results indicate the high possibility that the Mg-bearing ferrite is formed during the course of the air oxidation and that the Mg^{2+} replaces the Fe^{2+} in the crystal lattice of the spinel structure. The formation of the solid solution between Fe_3O_4 and $MgFe_2O_4$ is narrowly limited to below 0.1 measured by the Mg^{2+}/Fe_{total} ratio. It is easy however to synthesize the complete solid solution at high temperatures above 1000 °C.[12] In addition, the composition of Fe_3O_4 (magnetite), formed from the $Fe(OH)_2$ suspended solution by air oxidation, is usually non-stoichiometric, tending to form the γ-Fe_2O_3 component with a spinel structure. Thus, it is necessary to analyze Fe^{2+}, Fe^{3+}, and Mg^{2+} in solid solution to obtain the composition as a ternary system. In the present work, the maximum solid solubility of the component $MgFe_2O_4$ has been caluculated to be 0.249 $MgFe_2O_4 \cdot 0.541\ Fe_3O_4 \cdot 0.210\ \gamma$-$Fe_2O_3$ implying that the solid solution is appreciably non-stoichiometric in composition.

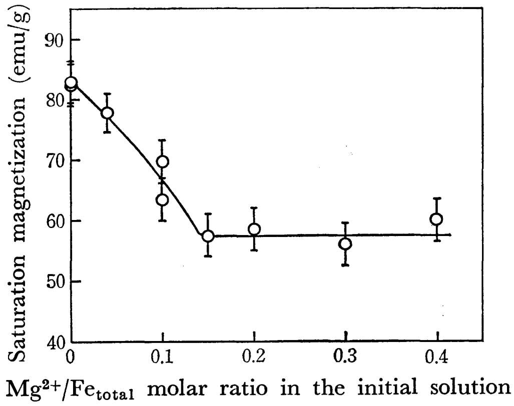

Fig. 5. The magnetization of the Precipitate B with various amounts of Mg^{2+} (at room temperature).

Saturation Magnetization. Precipitate B is a ferromagnet at room temperature. The temperature dependence of the magnetization of Precipitate B obtained at the Mg^{2+}/Fe_{total} ratio of 0.3 was measured under 4000 Oe of the external magnetic field(1 Oe$=(1000/4\pi)$A/m) and *in vacuo*. The Curie temperature was found to be approximately 568 °C. The magnetization of Precipitate B formed from the initial solution with varying Mg^{2+}/Fe_{total} ratios was also measured at room temperature, the results of which are shown in Fig. 5. As seen the magnetization at room temperature decreases with increasing concentration of Mg^{2+} in the initial solution, but in the range of Mg^{2+}/Fe_{total} ratio from 0.1 to 0.4, the magnetization becomes constant at about 60 emu/g(1 emu/g$=10^{-7}$ Tm^3/kg). This value is intermediate between those of $MgFe_2O_4$ (27 emu/g at 20 °C), Fe_3O_4(92 emu/g at 20 °C), and γ-Fe_2O_3(82.5 emu/g at 0 K). The results obtained from the magnetic properties are in good agreement with those obtained from chemical analysis and the X-ray analysis previously described. It may thus be concluded that at the Mg^{2+}/Fe_{total} ratio below 0.1, almost all Mg^{2+} in the initial solution is incorporated into the spinel type structure by replacement of Fe^{2+}. Above 0.1, the excess Mg^{2+} does not replace the Fe^{2+} which is constructing the spinel type structure.

Non-stoichiometry in the Mg-bearing Ferrite Composition. It is convenient to illustrate the non-stoichiometry in the Mg-bearing ferrite using three components as the Fe_3O_4–Fe_2O_3–$MgFe_2O_4$ system. The results are shown in Fig. 6. The letter at each point in Fig. 6 corresponds to the Mg^{2+}/Fe_{total} in the initial solution, and the broken line indicates an oxygen reaction lines as an example. When the stoichiometric composition of the Fe_3O_4–$MgFe_2O_4$ solid solution was obtained, the composition of the product must be on the Fe_3O_4–$MgFe_2O_4$ line. As clearly seen in Fig. 6, the Mg-bearing ferrite is appreciably oxidized while maintaining a spinel type structure, and the degree of oxidation increases with increasing $MgFe_2O_4$ component.

pH *Change during Reaction.* In general, as indicated by Katsura *et al.*,[9] the pH of the suspension decreases with air oxidation. However, when the initial solution contains Mg^{2+}, the pH increases gradually in the early stages of the air oxidation and then falls.

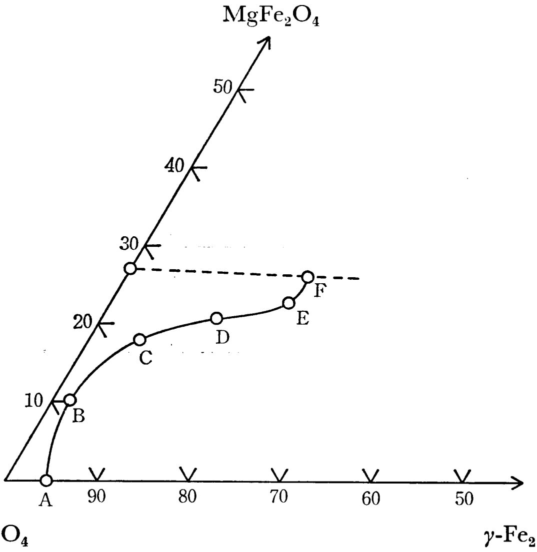

Fig. 6. The chemical compositions of the Precipitates B expressed as the Fe_3O_4–Fe_2O_3–$MgFe_2O_4$ system. Points A, B, C, D, E, and F were obtained at the Mg^{2+}/Fe_{total} molar ratios of 0.00, 0.04, 0.08, 0.10, 0.12, and above 0.15, respectively. The broken line shows *the oxygen reaction line.*

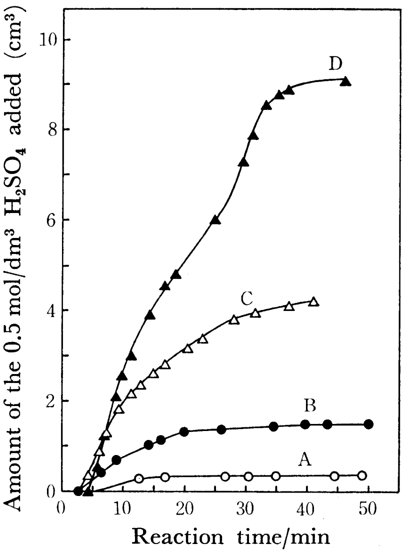

Fig. 7. The relationship between the reaction time and the amount of 0.5 mol/dm^3 H_2SO_4 solution added to the suspension to keep the pH value of the initial solution constant at pH 9.0. Curves A, B, C, and D were obtained at the Mg^{2+}/Fe_{total} molar ratios of 0.1, 0.2, 0.3, and 0.4, respectively.

In this study, a 0.5 mol/dm^3 H_2SO_4 solution was added at an early stage in the reaction to maintain the pH at 9.0. Figure 7 illustrates the relationship between the reaction time and the amount of 0.5 mol/dm^3 H_2SO_4 solution necessary to maintain the pH at 9.0. The amount of 0.5 mol/dm^3 H_2SO_4 solution in Fig. 7 indicates the total amount of solution added at each reaction time. The curves A, B, C, and D show the results corresponding to varying the Mg^{2+}/Fe_{total} ratios; 0.1, 0.2, 0.3, and 0.4, respectively. As seen in Fig. 7, the pH did not change for about 4 min from the starting time irrespective of the Mg^{2+}/Fe_{total} ratio. However, when the Mg^{2+}/Fe_{total} ratio exceeded 0.1, rapid increases in the 0.5 mol/dm^3 H_2SO_4 solution were necessary to maintain the pH at 9.0, and the amount of 0.5 mol/dm^3 H_2SO_4 solution added depended on the Mg^{2+}/Fe_{total} ratio in the initial solution. In the case of A, the amount of the H_2SO_4 solution added was very small (0.36 cm^3), and the addition of H_2SO_4 solution ceased at about 15 min after the reaction was initiated. In a previous section, it was suggested that Precipitate A contains a basic Mg-bearing sulfate with the composition of $[Mg^{2+}_{1.00}, Na^{+}_{0.64}][OH^{-}_{1.36}, (SO_4^{2-})_{0.64}]$ (hereafter compound A). On the basis of these experimental results, the following schematic equation has been postulated for the change in pH of the suspension in the early stages of oxidation,

$$\begin{aligned}&3Fe(OH)_2 + 3x\cdot Mg(OH)_2 + 1.92(x-y)\cdot Na_2SO_4\\&\quad + \frac{1+y}{2}\cdot O_2 \rightarrow (1+y)\cdot[Mg^{2+}_{3y/(1+y)}Fe^{2+}_{(1-2y)/(1+y)}Fe^{3+}_2O_4]\\&\quad + 3(1-y)\cdot A + 1.92(x-y)\cdot NaOH + 3(1+x-0.64)\cdot H_2O\\&\quad (x>0.1), \qquad (1)\end{aligned}$$

where x and y are the Mg^{2+}/Fe_{total} ratios in the initial solution and the spinel type Mg-bearing solid solution, respectively. It is evident from Eq. 1 that some amount of Na_2SO_4 in the initial solution should be consumed to form compound A. The calculated amount of 0.5 mol/dm^3 H_2SO_4 solution was obtained on the basis of Eq. 1 at the molar ratios of 0.2, 0.3, and 0.4 and the values obtained are summarized in Table 1. As seen in Table 1, the calculated values are in reasonable agreement with the experimental values within experimental error strongly supporting the validity of Eq. 1 in representing the oxidation process occurring in the suspension at the early stage when the Mg^{2+}/Fe_{total} ratio in the solution exceeds 0.1.

TABLE 1. TOTAL AMOUNTS OF THE 0.5 mol/dm^3 H_2SO_4 SOLUTION CONSUMED TO KEEP THE pH CONSTANT IN THE COURSE OF THE OXIDATION REACTION

Amount of Mg^{2+} in the initial solution (Mg^{2+}/Fe_{total})	Experimental value (cm^3)	Theoretical value evaluated from Eq. 1 (cm^3)
0.20	1.5	2.42
0.30	4.15	5.33
0.40	9.10	7.89

As previously reported when the Mg^{2+}/Fe_{total} ratio in the initial solution is below 0.1, all the Mg^{2+} is completely incorporated into the spinel type structure to form Mg-bearing ferrite solid solution. Consequently there is no need to consume H_2SO_4 solution to maintain the pH in the suspension, and no magnesium basic sulfate A is formed. Thus, the oxidation reaction may be represented as the following when the Mg^{2+}/Fe_{total} ratio in the initial solution is below 0.1.

$$\begin{aligned}&3Fe(OH)_2 + 3x\cdot Mg(OH)_2 + \frac{(x+1)}{2}\cdot O_2 \rightarrow\\&\quad (x+1)\cdot[Mg^{2+}_{3x/(x+1)}Fe^{2+}_{(1-2x)/(x+1)}Fe^{3+}_2O_4] + 3(x+1)\cdot H_2O\\&\quad (x<0.1). \qquad (2)\end{aligned}$$

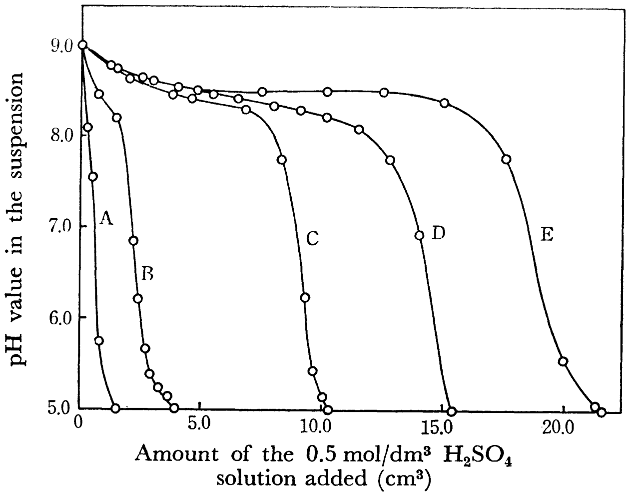

Fig. 8. The relationship between the pH changes of the suspensions containing the Precipitate A and the amount of 0.5 mol/dm^3 H_2SO_4 solution. Curves A, B, C, D, and E were obtained at the Mg^{2+}/Fe_{total} molar ratios of 0.04, 0.1, 0.2, 0.3, and 0.4, respectively.

Dissolution of Compound A. Figure 8 demonstrates the relationship between the change in pH of the suspended solution containing Precipitate A and the added amount of 0.5 mol/dm^3 H_2SO_4 solution. The curves A, B, C, D, and E show the pH change curves at Mg^{2+}/Fe_{total} ratios of 0.04, 0.1, 0.2, 0.3 and 0.4 at pH 9.0, respectively. As seen in Fig. 8, a smooth plateau exists in the pH range from 8.0 to 8.5 when the Mg^{2+}/Fe_{total} ratios are above 0.2. These results may indicate that compound A is formed at higher concentrations of Mg^{2+} and that compound A appears to consist of one phase considering the smooth plateau at pH 8.5. It is reasonable to assume that the amounts of 0.5 mol/dm^3 H_2SO_4 solution consumed to lower the pH of the suspension to 5.0 correspond to the amounts of OH^- of compound A. Consequently the OH^-/Mg^{2+} ratio has been determined in each suspension for Mg^{2+}/Fe_{total} ratios of 0.2, 0.3, and 0.4, and 1.30 obtained as an average value. This ratio is in good agreement with that estimated by chemical analysis, $[Mg^{2+}_{1.00}, Na^{+}_{0.64}][OH^{-}_{1.36}, (SO_4^{2-})_{0.64}]$.

The pH *Dependence of Precipitate A.* In the preceding sections, the properties of Precipitate A formed at pH 9.0 and 65 °C have been discussed. In subsequent experiments the pH was changed from 8.0 to 11.0 at constant temperature. The Mg^{2+}/Fe_{total} ratio in the initial solution was fixed at 0.1. Curve A in Fig. 9 illustrates the relationship between the Mg^{2+}/Fe_{total} ratio in Precipitate A and the pH value of the suspension, and Curve B that for Precipitate B. As seen in Curves A and B in Fig. 9, the Mg^{2+}/Fe_{total} ratio in Precipitates A and B is almost constant (0.1 to 0.095) in the pH range 9.0 to 11.0, but at pH 8.0 the ratio was lowered to 0.02 and 0.01 in Precipitates A and B, respectively. The implication is that the incorporation of Mg^{2+} into Precipitate B having a spinel type structure is strongly influenced by a lowering of the pH. Some appreciable but small differences in composition are seen between Precipitates A and B, even in the high pH range 9.0 to 11.0. This small difference may be attributed to the presence of small amounts of compound A included in Precipitate A.

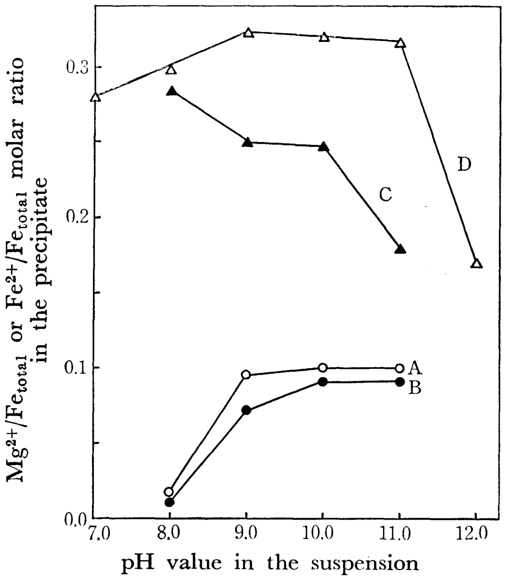

Fig. 9. The relationship between the pH value of the suspension and the chemical composition of the Precipitates A and B. The Mg^{2+}/Fe_{total} molar ratio in the initial solution is fixed to 0.1. Curve A : The ratio in the Precipitate A, Curve B : the ratio in the Precipitate B, Curve C : the Fe^{2+}/Fe_{total} molar ratio in the Precipitate B, Curve D : the Fe^{2+}/Fe_{total} molar ratio in the precipitate formed by the air oxidation of the $Fe(OH)_2$ suspension without Mg^{2+}.

Curve C in Fig. 9 illustrates the relationship between the Fe^{2+}/Fe_{total} ratio in Precipitate B and the pH value in the suspension. At pH 8.0 the Fe^{2+}/Fe_{total} ratio was 0.285. This means that the $(Mg^{2+}+Fe^{2+})/(Mg^{2+}+Fe_{total})$ ratio for this sample is 0.292 which is close to that for the Fe_3O_4 compound. In the case of pH 11.0, the Mg^{2+}/Fe_{total} ratio was 0.1 and the Fe^{2+}/Fe_{total} ratio 0.180, and so the $(Mg^{2+}+Fe^{2+})/(Mg^{2+}+Fe_{total})$ ratio becomes 0.254. This decrease in value is caused by the oxidation of Precipitate B with or without change in crystal structure. Thus, it is evident from Curve C in Fig. 9 that Precipitate B, prepared at relatively high pH is oxidized.

According to the powder X-ray diffraction patterns, the peaks were all of the spinel type when Precipitate B was prepared in the pH range 8.0 to 10.0. Precipitate B prepared at pH 11.0 however contained the α-FeOOH type together with the spinel type compound. Thus it is evident that when Precipitate A is prepared at relatively high pH, such as 11 or greater, then the Fe^{2+} in the Precipitate A is oxidized to form the α-FeOOH type but not the γ-Fe_2O_3 type compound.

As a comparison, the results shown in Curve C in Fig. 9, the Fe^{2+} content in the precipitate formed by the air oxidation of the $Fe(OH)_2$ suspension without magnesium at various values of pH(7 to 12) and at 65 °C were determined, the results of which are shown by Curve D in Fig. 9. As seen the Fe^{2+}/Fe_{total} ratio in the precipitates gradually increased with increasing pH of the suspension (from 7 to 9), after which the ratio remained constant (0.323) in the pH interval

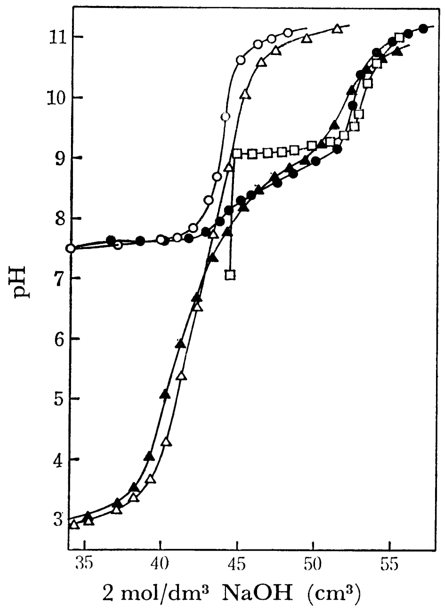

Fig. 10. Titration curves of Fe(II), Fe(II)+Mg(II), Fe(III), Fe(III)+Mg(II) and Mg(II) solutions by the 2 mol/dm^3-NaOH solution. Open circle: 4.31×10^{-2} mol of Fe(II), Closed circle : 4.31×10^{-2} mol Fe(II)+ 8.63×10^{-3} mol Mg(II), Open triangle : 2.88×10^{-2} mol Fe(III), Closed triangle : 2.88×10^{-2} mol Fe(III) + 8.63×10^{-3} mol Mg(II) and Open square : 8.63×10^{-3} mol Mg(II). The titration curve of Mg(II) solution is shown from the titer of 44.3 cm^3 to compare with the others. The initial volume of the solutions was fixed to 200 cm^3.

from 9 to 11. At pH 12.0 however the ratio sharply decreased to 0.170. From a comparison of Curve C and Curve D, it may be concluded that the α-FeOOH type compound is liable to form in the presence of Mg^{2+}.

Hydrolysis of Magnesium in Fe(OH)$_2$ Suspension. The hydrolysis of Mg^{2+} in the course of formation of Precipitate A, was studied using the titration curves of the solution containing only Mg^{2+} and Mg^{2+}+ Fe^{2+} at 65 °C. The hydrolysis may enable an interpretation of the low concentration of Mg^{2+} in the Precipitates A and B when the precipitates were prepared at relatively low pH, the results of which are shown in Fig. 10. As evident from Fig. 10, Mg^{2+} was titrated at pH 9.1 to 9.3, but when the solution contained Fe^{2+} together with Mg^{2+}, both ions were titrated at 8.0 to 9.0. This lowering of the pH value is due to the co-precipitation of Mg^{2+} with Fe^{2+}. In the presence of Fe^{2+}, the hydrolysis of Mg^{2+} is therefore completed at pH 9.0, but not at 8.0, suggesting that the unhydrolyzed Mg^{2+} is not incorporated into the spinel type ferrite structure.

Feitknecht[6] demonstrated that Fe_3O_4 is formed *via* the intermediate "green rust" in neutral solution, but in slightly alkaline solutions, Fe_3O_4 is formed directly from the Fe(OH)$_2$ suspension. In the present experiments, greenish precipitates were seen in the early stages of the oxidation in the presence of the Mg^{2+} at pH 8.0. No incorporation of Mg^{2+} into the ferrite structure at pH 8.0 may, therefore, account for the formation of the "green rust" in the course of reaction.

Conclusion

From the experimental results, several conditions concerning the formation of Mg-bearing ferrite by the air oxidation of the Fe(OH)$_2$ aqueous suspension may be drawn:

1. At pH 9.0 and at 65 °C, almost all Mg^{2+} is incorporated into the spinel type ferrite when the Mg^{2+}/Fe_{total} ratio in the initial solution is less than 0.1. The chemical composition thus obtained may be expressed as the $MgFe_2O_4$–Fe_3O_4–γ-Fe_2O_3 ternary system, implying that the Mg-bearing ferrite which is a ferromagnet is not stoichiometric in its composition. The degree of oxidation increases with increasing Mg^{2+}/Fe_{total} ratio while the spinel type structure is maintained.
2. When the Mg^{2+}/Fe_{total} ratio exceeds 0.1 at pH 9.0 and 65 °C, the excess Mg^{2+} produces a basic magnesium sulfate which readily dissolves at pH 5.0. The chemical composition of this compound has been estimated as $[Mg^{2+}_{1.00}, Na^{+}_{0.64}][OH^{-}_{1.36}, (SO_4^{2-})_{0.64}]$.
3. At pH 8.0, a small amount of Mg^{2+} is incorporated into the ferrite, attributed to the formation of "green rust" in the course of reaction, indicating an absence of interaction between Mg^{2+} and the "green rust." In connection with this, the Mg^{2+} incorporated must be hydrolyzed before producing the ferrite.
4. Between pH 9.0 and 10.0, only the Mg-bearing ferrite is formed, but at pH 11.0, the α-FeOOH type compound is formed together with the Mg-bearing ferrite. Thus, the pH interval for Mg-bearing ferrite formation is limited from 9.0 to 10.0.

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References

1) H. Yasuoka, A. Hirai, T. Shinjo, M. Kiyama, Y. Bando, and T. Takada, *J. Phys. Soc. Jpn.*, **22**, 174 (1967).

2) T. Akashi, I. Sugano, Y. Kenmoku, Y. Shimada, and T. Tsuji, "Proc. Intern. Conf. Ferrites," Univ. Tokyo Press, Japan (1971). p. 183.

3) H. Takei, T. Kanzaki, Y. Tamura, and T. Katsura, Meeting of the Chemical Society of Japan in Tohoku District, Akita, October 1977, Abstr. No. 1B02.

4) K. Kaneko, T. Kanzaki, Y. Tamaura, and T. Katsura, Meeting of the Chemical Society of Japan in Tohoku District, Akita, October 1977, Abstr. No. 1B03.

5) M. Kiyama, *Bull. Chem. Soc. Jpn.*, **51**, 134 (1978).

6) W. Feitknecht, *Z. Electrochem.*, **63**, 34(1959).

7) M. Kiyama, *Bull. Chem. Soc. Jpn.*, **47**, 1646(1974).

8) Y. Tamaura, G. S. Chyo, and T. Katsura, *Water Res.*, **13**, 21 (1979).

9) T. Katsura, Y. Tamaura, and H. Terada, *Kogyo Yosui*, **223**, 16 (1977).

10) T. Katsura, "Zikken Kagaku Koza," ed by the Chemical Society of Japan, Maruzen (1958), No. 15, pp. 272—275.

11) I. Iwasaki, T. Katsura, T. Ozawa, M. Mashima, H. Hamamura, and B. Iwasaki, *Bull. Volc. Soc. Jpn.*, *Ser. II*, **5**, 75 (1960).

12) T. Katsura and S. Kimura, *Bull. Chem. Soc. Jpn.*, **38**, 1664 (1965).